ABSTRACT

LUISO, SALVATORE. Co/Fe-doped MoS₂ Nanoparticles on Carbon Support as a Catalyst for Hydrogen Evolution Reaction. (Under the direction of Dr. Peter S. Fedkiw).

The challenge to replace fossil fuel with clean and renewable energies has led the scientific community to research alternative sources of energy. Because of the low-environmental impact and high-specific energy of hydrogen, interest in sustainable ways of producing it has increased. Water electrolysis is the best method to generate high-purity hydrogen without pollutants, but it is an energy-intensive route. The existing platinum (Pt) catalysts are highly efficient, but the cost and rarity of Pt limits its use. Therefore, seeking high-efficient and cost-effective catalyst for mass production of hydrogen is critical to the utilization of hydrogen energy. In 2005, Nørskov et al. reported that molybdenum disulfide (MoS₂) showed good activity for hydrogen evolution reaction (HER).

The work in this thesis aims to develop high-efficient molybdenum sulfide catalysts. Molybdenum trisulfide (MoS₃) was synthesized from acidification of ammonium tetrathiomolybdate [(NH₄)₂MoS₄] with the addition of sodium sulfide (Na₂S·9H₂O) to the reaction mixture. The synthesis parameters such as carbon support, S:Mo atomic ratio, solvent (H₂O, ethylene glycol (EG)), dopants (Co/Fe) and pH were systematically studied. The physical and chemical properties of the prepared catalysts were characterized by microscopy (SEM, TEM), x-ray spectroscopy (XPS), and elemental analysis and mapping (ICP, CHNS, STEM). The electrochemical activity toward HER was studied using voltammetry and impedance tests.

In the first section of the study, MoS₃ nanoparticles were synthesized on three carbon supports (graphene nanoplatelets (GNP), Ketjenblack EJ-300 and Vulcan XC 72R) with
various S:Mo atomic ratios (4:1, 5:1, 7:1, 10:1) using H₂O and EG as solvents. As a result, it was determined that 5:1 S:Mo ratio optimized the activity (-10 mA/cm² at -166 mV), because MoS₃ yield was increased yet the unbounded elemental sulfur was not enough to poison the catalyst. SEM and STEM showed that the dispersion of the elements (Mo, S, C) is uniform with Ketjenblack and Vulcan. In contrast to Vulcan and GNP supports, the composition of MoS₃/Ketjenblack was unvaried from surface (XPS) to bulk (ICP, CHNS); elemental sulfur was absent on the surface and the catalysts were more active than MoS₃/GNP (-10 mA/cm² at -183 mV), making Ketjenblack a more suitable support for MoS₃ nanoparticles. EG as a solvent improved the catalyst activity by allowing a better dispersion of carbon than H₂O as a solvent and by increasing the reaction temperature to 165°C, at which the thermal decomposition of (NH₄)₂MoS₄ occurs. The low solubility of the latter both in H₂O and EG was inferred by TEM images of the catalyst.

The best catalyst obtained from the previous section (MoS₃/Ketjenblack 5:1 S:Mo ratio in EG) was chosen to study dopant (Co/Fe) effects. Co/Fe acetates corresponding to 2%-5%-10 wt.% of Co/Fe were added during the synthesis of MoS₃. Although the final amount of dopants in the catalyst was significantly lower than expected (< 0.3 wt.%), the activity (-171/-184 mV at -10 mA/cm²) and STEM of doped catalysts provided an understanding of the role of dopants. The ineffective doping may be due to low temperature of the reaction and low solubility of (NH₄)₂MoS₄.

The incomplete dissolution of (NH₄)₂MoS₄ in a solvent mixture was further investigated and solved by changing the solvent to mixtures of dimethylformamide and H₂O/EG. As a result,
the particle size decreased (1-2 nm) but also so did the yield to MoS₃ (-8 wt.%); hence, the activity/catalyst mass improved (-169 mV at -10 mA/cm²).

Afterwards, sodium hydroxide was used to convert (NH₄)₂MoS₄ to Na₂MoS₄, which is soluble in H₂O and EG and reacts with acid as the (NH₄)₂MoS₄. The resulting catalysts deposited on Ketjenblack were homogenous and uniform (STEM). The higher activity (-159 mV at -10 mA/cm²) was a consequence of a completely dissolved Mo-precursor.
Co/Fe-doped MoS$_2$ Nanoparticles on Carbon Support as a Catalyst for Hydrogen Evolution Reaction.

by
Salvatore Luiso

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the degree of
Master of Science

Chemical and Biomolecular Engineering

Raleigh, North Carolina

2015

APPROVED BY:

_______________________________  _______________________________
Saad A. Khan             Stefano Menegatti

_______________________________
Peter S. Fedkiw
Committee Chair
DEDICATION

Ad Angela

“Ti amo.

Non ho nessun pensiero che non sia tuo;
non ho nel sangue nessun desiderio che non sia per te.
Lo sai. Non vedo nella mia vita altra compagna, non vedo altra gioia.

Rimani.

Riposati. Non temere di nulla.

Dormi stanotte sul mio cuore...”

“I love you,

I don’t have any thoughts that are not yours;

I don’t have in my blood any desires that are not for you,

You know. I don’t see in my life any other partners, I don’t see any other joy.

Stay.

Have rest. Don’t fear anything.

Sleep on my hearth tonight...”

(“Rimani”, G. D’Annunzio)
BIOGRAPHY

Salvatore Luiso was born on March 8th, 1991, in Rimini, a city on the North-Eastern coast of Italy. Salvatore attended the high school “Liceo Classico G. Cesare” in Rimini, where he was fascinated by the studies on ancient greek and latin culture and philosophy. Meanwhile, Salvatore attended the School of Clarinet at the State Academy of Music in Pesaro, where he got his master’s degree in 2010. In the same year, Salvatore moved to Bologna, to pursue his undergraduate studies in the Department of Chemical and Biochemical Engineering at the School of Advanced Studies Alma Mater Studiorum. These studies drove his mind toward the world of electrochemical engineering. Salvatore took his bachelor’s degree in 2013 under the advisory of Prof. Carlo Stramigioli with his thesis “Hydrogen production in water electrolysis with photovoltaic panels system”. Then, Salvatore started his master in Chemical Engineering, curriculum in Sustainable Technology for Environment and Materials (STEM), during which he was able to conduct his research on photocatalysis of TiO$_2$ thanks to his advisor Dr. Giovanni Camera Roda. With the help of Dr. Giulio Sarti, who was professor of Thermodynamics at University of Bologna, Salvatore’s interest in North Carolina State University raised, so that in 2014 he joined the Department of Chemical and Biomolecular Engineering at NC State for pursuing his third master’s degree. Salvatore joined Dr. Peter Fedkiw’s group to conduct research on MoS$_2$ as a catalyst for hydrogen evolution reaction. After one year of intense work, Salvatore defends his master’s thesis, after which he intends to join the PhD program in the same department.
ACKNOWLEDGMENTS

I would like to gratefully and sincerely thank my advisor Dr. Peter S. Fedkiw for his guidance, understanding, patience, and most importantly, his friendship during my graduate studies at North Carolina State University. His mentorship was paramount in providing a well-rounded experience consistent my long-term career goals. He encouraged me to not only grow as an experimentalist and an engineer but also as an instructor and an independent thinker. I look forward to working with him in the years to come. Not all graduate students are given the opportunity to develop their own individuality and self-sufficiency by being allowed to work with such independence. For everything he has done for me I thank Dr. Saad Khan. He was my first contact in the department and he always helped me in so many different ways. I would also like to thank Dr. Stefano Menegatti, who was a pioneer to successfully continue his studies at NC State after the degree at University of Bologna. I thank Stefano for his advises and his necessary help.

A special thanks goes to professors Giulio Cesare Sarti and Valerio Cozzani, who allowed and suggested me to leave my country to gain experience and knowledge at NC State. Without them I would have never realized my American dream.

I would like to thank all of the members of the Fedkiw research group, especially ShengYang Huang, Christine Rinne and David Ho. These three friends and co-workers also provided for some much needed humor and entertainment in what could have otherwise been a somewhat stressful laboratory environment. To them goes my gratitude for the time they kindly spent with me discussing and conducting experiments.
I also would like to thank the administrative staff, Saundra, Shirley, and Angela. Special thanks to Sandra for having been my magic wand to solve all the problems and paperwork required. I couldn’t make it without her advices and help.

A big thank goes also to my lovely friends from the PhD program, Barbara, Ria and Russell, in memory of the days and nights we spent together, studying, enjoying life and sharing wonderful moments, which made my life in Raleigh as beautiful as at home.

A very warm thank is for Deborah and Robert, my American parents, who treated me as their son, and who helped, served and advised me in so many ways that I will never forget. Their love and their humanity opened my mind to a more beautiful world.

Finally, I want to write a special dedication to my loved ones. I thank my parents, Giacomo and Viola, for their faith in me and allowing me to be as ambitious as I wanted. It was under their watchful eye that I gained so much drive and an ability to tackle challenges head on. They dedicated all their lives to raise, help and serve their sons. My life is full of gratitude and love for them and I value them as great and generous people and wonderful parents.

Besides my parents, the most important dedication goes to Angela. Her support, encouragement, quiet patience and unwavering love were undeniably the bedrock upon which the past five years of my life have been built. Her tolerance of my occasional tough life decisions is a testament in itself of her unyielding devotion and love. She is my love, my inspiration and my guidance. I’m greatly thankful to have met such a divine soulmate and I’m looking forward to spend my life with her. To her goes every achievement, every joy, every single moment of my whole life.
TABLE OF CONTENTS

LIST OF TABLES ............................................................................................................. x

LIST OF FIGURES .......................................................................................................... xiii

CHAPTER 1: HYDROGEN PRODUCTION BY WATER ELECTROLYSIS THROUGH
ADVANCED LOW-COST CATALYSTS ................................................................. 1

1.1 INTRODUCTION ................................................................................................. 1
  1.1.1 Water electrolysis .......................................................................................... 2
  1.1.2 MoS₂ as an electrocatalyst for the HER ....................................................... 5
  1.1.3 Amorphous, crystalline and clusters of Molybdenum sulfides ...................... 9
  1.1.4 Doping MoSₓ with Fe, Co and Ni ................................................................. 10
  1.1.5 MoS₂ Nanoparticles grown on carbon materials ....................................... 14

1.2 HYPOTHESIS ...................................................................................................... 21

1.3 OPERATIONAL STATEMENT ........................................................................... 21

1.4 REFERENCES ..................................................................................................... 23

CHAPTER 2: EQUIPMENT AND EXPERIMENTS: NEW RECIPE FOR THE
SOLVOTHERMAL SYNTHESIS OF MOS₃ NANOPARTICLES ............. 29

2.1 OLD PROCEDURE .............................................................................................. 29
  2.1.1 The reactants ............................................................................................... 29
  2.1.2 The synthesis .............................................................................................. 30
  2.1.3 The ink ......................................................................................................... 33
  2.1.4 Electrode loading ........................................................................................ 34
2.2 Variations to the Old Procedure ................................................................. 35
  2.2.1 Reactants ................................................................................................. 35
  2.2.2 Solvents .................................................................................................. 37
2.3 Electrochemical Tests ..................................................................................... 39
  2.3.1 iR compensation ..................................................................................... 40
2.4 Organization of Experiments ......................................................................... 41
2.5 Data Processing ............................................................................................. 44
2.6 Physical Characterization .............................................................................. 45
2.7 References .................................................................................................... 47

CHAPTER 3: RESULTS AND DISCUSSION .......................................................... 49

3.1 Effects of Carbon Supports, Solvents and Initial Compositions on MoS₃ Catalysts for Hydrogen Evolution Reaction .......................................................................................................................... 49
  3.1.1 Electrochemical results: GNP support at different S:Mo ratio in water ..... 50
  3.1.2 Thermogravimetric analysis results .......................................................... 67
  3.1.3 Electrochemical results: GNP support at different S:Mo ratio in ethylene glycol .......................................................................................................................... 71
  3.1.4 Electrochemical results: KETJENBLACK support at different S:Mo ratio in water ........................................................................................................................... 76
  3.1.5 Electrochemical results: KETJENBLACK support at different S:Mo ratio in ethylene glycol .......................................................... 87
  3.1.6 Electrochemical results: VULCAN support at different S:Mo ratio in water ... 96
3.1.7 Electrochemical results: VULCAN support at different S:Mo ratio in ethylene glycol .......................................................... 105
3.1.8 Loading effect: GNP, KETJENBLACK and VULCAN supports .............. 111
3.1.9 Material characterization: GNP, KETJENBLACK and VULCAN supports ... 115
3.1.10 Discussion .......................................................................................... 125

3.2 EFFECTS OF IRON AND COBALT AS DOPANTS FOR MOS₃/KETJENBLACK...
.................................................................................................................. 130
3.2.1 Electrochemical results: Co-doped MoS₃/Ketjenblack ......................... 131
3.2.2 Materials characterization: Co-doped MoS₃/Ketjenblack ....................... 136
3.2.3 Electrochemical results: Fe-doped MoS₃/Ketjenblack ............................ 140
3.2.4 Materials characterization: Fe-doped MoS₃/Ketjenblack ....................... 146
3.2.5 Discussion .......................................................................................... 150

3.3 DIMETHYLFORMAMIDE AS A SOLVENT FOR MOS₃/KETJENBLACK... 154
3.3.1 Electrochemical results ........................................................................ 155
3.3.2 Materials characterization .................................................................... 159
3.3.3 Discussion .......................................................................................... 162

3.4 SODIUM HYDROXIDE: THE KEY COMPOUND FOR THE DISSOLUTION OF
(NH₄)₂MOS₄ .................................................................................................. 164
3.4.1 Electrochemical results ........................................................................ 165
3.4.2 Materials characterization .................................................................... 169
3.4.3 Discussion .......................................................................................... 173

3.5 REFERENCES ......................................................................................... 177
CHAPTER 4: CONCLUSIONS ............................................................................................................. 181

4.1 EFFECT OF S:MO RATIO ............................................................................................................. 182

4.2 EFFECT OF CARBON SUPPORT ............................................................................................... 184

4.3 EFFECT OF DOPANTS ................................................................................................................. 185

4.4 CHANGE IN THE CATALYST SYNTHESIS CONDITION: SOLVENT AND MO- PRECURSOR ................................................................................................................................. 187

4.5 REFERENCES ............................................................................................................................... 190

CHAPTER 5: FUTURE WORK ............................................................................................................. 192

APPENDICES ....................................................................................................................................... 195

Appendix A – CHN/S Analysis .......................................................................................................... 196

Appendix B – ICP ................................................................................................................................ 201
Tab. 1.1 Summary of relevant studies on the MoS$_2$ as a catalyst for the hydrogen evolution reaction. ................................................................. 18
Tab. 2.1 Carbons surface area. .............................................................. 37
Tab. 2.2 Characteristics of water and ethylene glycol in the synthesis of MoS$_3$. .................................................. 38
Tab. 3.1 Matrix of the first series of experiments to synthesize MoS$_3$ on a carbon support and at different S:Mo ratio. ................................................................. 49
Tab. 3.2 Summary of results for MoS$_3$/GNP, S:Mo = 4:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 53
Tab. 3.3 Summary of results for MoS$_3$/GNP, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 57
Tab. 3.4 Summary of results for MoS$_3$/GNP, S:Mo = 7:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 61
Tab. 3.5 Summary of results for MoS$_3$/GNP, S:Mo = 10:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 64
Tab. 3.6 Summary data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm$^2$ for MoS$_3$/GNP, S:Mo = 4/5/7/10:1 after 0 cycles of CV stability tests. ................................................................. 66
Tab. 3.7 Summary of results for MoS$_3$/GNP, S:Mo = 4:1 in EG after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 72
Tab. 3.8 Summary of results for MoS$_3$/GNP, S:Mo = 5:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 75
Tab. 3.9 Summary of results for MoS$_3$/KETJEN, S:Mo = 4:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 cycles of CV stability tests. .................................................. 78
Tab. 3.10 Summary of results for MoS$_3$/KETJEN, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 81
Tab. 3.11 Summary of results for MoS$_3$/KETJEN, S:Mo = 7:1 at 250, 350 and 500 μg/cm$^2$ loading. ................................................................. 84
Tab. 3.12 Summary of results for MoS$_3$/KETJEN, S:Mo = 4:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 88
Tab. 3.13 Summary of results for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 91
Tab. 3.14 Summary of results for MoS$_3$/KETJEN, S:Mo = 7:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests. .................................................. 93
Tab. 3.15 Summary of results for MoS$_3$/VULCAN, S:Mo = 4:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 cycles of CV stability tests. .................................................. 97
Tab. 3.16 Summary of results for MoS$_3$/VULCAN, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50 cycles of CV stability tests. ................................................................. 100

Tab. 3.17 Summary of results for MoS$_3$/VULCAN, S:Mo = 7:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50 cycles of CV stability tests. ................................................................. 103

Tab. 3.18 Summary of results for MoS$_3$/VULCAN, S:Mo = 4:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 cycles of CV stability tests. ................. 106

Tab. 3.19 Summary of results for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 and 200 cycles of CV stability tests. .... 109

Tab. 3.20 Summary data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm$^2$ for MoS$_3$ on GNP, Ketjenblack and Vulcan, S:Mo = 5:1 in ethylene glycol after 0 cycles of CV stability tests .............................................. 116

Tab. 3.21 Compositions analysis of MoS$_x$ electrocatalysts from XPS (top) and ICP-CHNS (bottom) made on GNP, Ketjen, Vulcan at S:Mo 5:1 in ethylene glycol. ............. 122

Tab. 3.22 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoS$_x$ electrocatalysts pure from Sigma-Aldrich, supported on GNP, KetjenBlack and Vulcan, at S:Mo 5:1 in ethylene glycol .... 122

Tab. 3.23 Chemical states and peak area ratios of MoS$_x$ electrocatalysts pure from Sigma-Aldrich, supported on GNP, KetjenBlack and Vulcan, at S:Mo 5:1 in ethylene glycol. .......................................................... 123

Tab. 3.24 Matrix of the second series of experiments ............................................................................................................. 131

Tab. 3.25 Reactants needed to obtain the desired doped products at S:Mo 5:1. ...................... 132

Tab. 3.26 Reactants needed to obtain the desired doped products at S:Mo 7:1. ...................... 132

Tab. 3.27 Summary of results for Co-doped MoS$_3$/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 after 0 cycles of CV stability tests. ...................................................... 135

Tab. 3.28 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm$^2$ for Co-doped MoS$_3$/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 .................................................................................................................. 136

Tab. 3.29 Compositions analysis of MoS$_x$ electrocatalysts from XPS (top) and ICP-CHNS (bottom) doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol. ............................................................................................................................... 138

Tab. 3.30 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoS$_x$ electrocatalysts pure from Sigma-Aldrich, and doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol. ................................................................................................................................................. 139

Tab. 3.31 Chemical states and peak area ratios of MoS$_x$ electrocatalysts pure from Sigma-Aldrich, and doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol. ................................................................................................................................................. 139
Tab. 3.32 Reactants needed to obtain the desired doped products at S:Mo 5:1. ................. 141
Tab. 3.33 Reactants needed to obtain the desired doped products at S:Mo 7:1. ................. 141
Tab. 3.34 Summary of results for Fe-doped MoS\textsubscript{3}/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 after 0 cycles of CV stability tests. ............................................................... 144
Tab. 3.35 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm\textsuperscript{2} for Fe-doped MoS\textsubscript{3}/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 .................................................................................................................. 146
Tab. 3.36 Compositions analysis of MoS\textsubscript{x} electrocatalysts from XPS (top) and ICP-CHNS (bottom) doped with 2\%Fe and 5\%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol. .......................................................................................................................... 148
Tab. 3.37 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoS\textsubscript{x} electrocatalysts pure from Sigma-Aldrich, and doped with 2\%Fe and 5\%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol. .......................................................................................................................... 149
Tab. 3.38 Chemical states and peak area ratios of MoS\textsubscript{x} electrocatalysts pure from Sigma-Aldrich, and doped with 2\%Fe and 5\%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol. .......................................................................................................................... 149
Tab. 3.39 Mixtures of solvents used in the attempt to completely dissolve (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4}. .... 155
Tab. 3.40 Summary of solvents, amount of sulfuric acid and S:Mo ratio used in the DMF experiments. The final pH, color of the filtrate solution and weight of the catalysts are reported. .......................................................................................................................... 156
Tab. 3.41 Summary of results for MoS\textsubscript{3}/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H\textsubscript{2}O and DMF+EG after 0 cycles of CV stability tests. ................................................................. 159
Tab. 3.42 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm\textsuperscript{2} for MoS\textsubscript{3}/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H\textsubscript{2}O and DMF+EG. .......................................................................................................................... 160
Tab. 3.43 Summary of results for MoS\textsubscript{3}/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs after 0 cycles of CV stability tests. ................................. 168
Tab. 4.1 Summary data of relevant studies on the MoS\textsubscript{2} as a catalyst for the hydrogen evolution reaction. .......................................................................................................................... 189
LIST OF FIGURES

Fig. 1.1 Scheme of an electrolytic cell for hydrogen production ........................................ 3
Fig. 1.2 Exchange current density as a function of hydrogen adsorption free energy for various HER catalyst materials. The trend in the data defines a so-called “volcano plot” for the HER. Platinum, with slightly negative hydrogen absorption energy, has the highest HER activity. .................................................................................................................. 5
Fig. 1.3 Schematic of the difference in conductivity to the active sites on nanoplatelets (a) and nanoparticles (b)........................................................................................................................................................................... 7
Fig. 1.4 a) Hopping of electrons in the vertical direction of MoS2 layers. The right side illustrates the potential distribution in the multilayer film and the hopping of electrons through the potential barrier in the interlayer gap. b) The exchange current density of the MoS2 film as a function of the layer number. ................................. 8
Fig. 1.5 Structure of molybdenum trisulfide. .................................................................................. 10
Fig. 1.6 (a) and (d) are the schematic diagram of Co/MoS2 and Ni/MoS2 systems. The corresponding partial density of states projected on sd orbitals are given in (b) and (e); the corresponding electronic deformation densities are shown in (c) and (f). The yellow and green denote S and Mo, the blue and pink are Co and Ni, respectively 12
Fig. 1.7 (a) Molecular model of MoS2 showing its lamellar structure and (b) molecular model of the interface region between MoS2 and CoS8 as present on unsupported Co/MoS2 catalyst. .......................................................................................................................... 13
Fig. 1.8 LSV polarization curves for GCEs modified with (A) MoS2/MCNs, (B) a mixture of MoS2 and MCNs, (C) pure MoS2 and (D) MCNs in 0.5 M H2SO4; scan rate: 2 mV/s ........................................................................................................................................................................... 17
Fig. 2.1 Scheme of the synthesis procedure for MoS3 nanoparticles on carbon support ...... 33
Fig. 2.2 Glassy carbon electrode with Teflon coat. Radius = 0.25 cm. ........................................ 34
Fig. 2.3 Set-up configuration for the electrochemical tests system. ................................. 40
Fig. 2.4 Equivalent Randles circuit R1(QR2) where R1 = solution resistance, R2 = charge-transfer resistance and Q = constant phase element (CPE). .......................................................... 44
Fig. 3.1 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS3/GNP, S:Mo = 4:1. ........................................................................................................ 51
Fig. 3.2 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS3/GNP, S:Mo = 4:1. ........................................................................................................ 51
Fig. 3.3 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS3/GNP, S:Mo = 4:1 .................................................................................................................. 52
Fig. 3.4 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS3/GNP, S:Mo = 4:1 .................................................................................................................. 52
Fig. 3.5 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1. .......................................................... 55
Fig. 3.6 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1. .......................................................... 55
Fig. 3.7 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1.......................................................... 56
Fig. 3.8 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1.......................................................... 56
Fig. 3.9 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 7:1. .......................................................... 58
Fig. 3.10 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 7:1. .......................................................... 59
Fig. 3.11 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 7:1.......................................................... 60
Fig. 3.12 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 7:1.......................................................... 60
Fig. 3.13 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 10:1. .......................................................... 62
Fig. 3.14 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 10:1. .......................................................... 62
Fig. 3.15 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 10:1.......................................................... 63
Fig. 3.16 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 10:1.......................................................... 63
Fig. 3.17 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_2$/GNP, at 4:1, 5:1, 7:1 and 10:1 S:Mo ratio. Pt data are also reported. ....... 65
Fig. 3.18 TGA of Thiomolybdate and Molybdate run in air from room T to 250°C at 5°C/min (a), with 1 hour hold at 250°C (b). .......................................................... 69
Fig. 3.19 TGA run in nitrogen from room T to 500°C at 5°C/min and hold at 500°C for 2 hours of Ammonium Tetrathiomolybdate (a) and MoS$_2$/Ketjenblack carbon (b).... 70
Fig. 3.20 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 4:1 in ethylene glycol. ............................................. 71
Fig. 3.21 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1 in ethylene glycol. ............................................. 73
Fig. 3.22 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1 in ethylene glycol. ............................................. 73
Fig. 3.23 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1 in ethylene glycol. ............................................. 74
Fig. 3.24 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 5:1 in ethylene glycol.

Fig. 3.25 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/GNP, at 4:1 and 5:1, made in water and ethylene glycol. Pt data are also reported.

Fig. 3.26 Current density-potential curves from LSV after 0,10,50,100 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 4:1.

Fig. 3.27 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.28 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.29 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.30 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.31 Current density-potential curves from LSV at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.

Fig. 3.32 Current density vs Potential curves from CV at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.

Fig. 3.33 Impedance curves from EIS at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.

Fig. 3.34 Tafel plot from LSV at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.

Fig. 3.35 Curves for potential at -10 mA/cm$^2$ and capacitance at different loadings for MoS$_3$/Ketjenblack at S:Mo = 7:1.

Fig. 3.36 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/KETJENBLACK, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported.

Fig. 3.37 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 4:1 in ethylene glycol.

Fig. 3.38 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Fig. 3.39 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Fig. 3.40 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Fig. 3.41 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Fig. 3.42 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 7:1 in ethylene glycol.
Fig. 3.43 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/KETJENBLACK in ethylene glycol, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported. .............................................................. 94

Fig. 3.44 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/KETJEN, at 4:1, 5:1 and 7:1, made in water and ethylene glycol. Pt data are also reported. .............................................................. 95

Fig. 3.45 Current density-potential curves from LSV after 0,10,50,100 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 4:1. .............................................................. 96

Fig. 3.46 Current density-potential curves from LSV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1. .............................................................. 98

Fig. 3.47 Current density vs Potential curves from CV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1. .............................................................. 98

Fig. 3.48 Impedance curves from EIS after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1. .............................................................. 99

Fig. 3.49 Tafel plot from LSV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1. .............................................................. 99

Fig. 3.50 Current density-potential curves from LSV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1. .............................................................. 101

Fig. 3.51 Current density vs Potential curves from CV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1. .............................................................. 101

Fig. 3.52 Impedance curves from EIS after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1. .............................................................. 102

Fig. 3.53 Tafel plot from LSV after 0,10,50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1. .............................................................. 102

Fig. 3.54 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/VULCAN, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported. ....... 104

Fig. 3.55 Current density-potential curves from LSV after 0,10,50,100 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 4:1........................................... 106

Fig. 3.56 Current density-potential curves from LSV after 0,10,50, 100, 200 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1........................................... 107

Fig. 3.57 Current density vs Potential curves from CV after 0,10,50, 100, 200 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1........................................... 107

Fig. 3.58 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1........................................... 108

Fig. 3.59 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1........................................... 109

Fig. 3.60 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/VULCAN, at 4:1, 5:1 and 7:1, made in water and ethylene glycol. Pt data are also reported. .............................................................. 110
Fig. 3.61 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 μg/cm² loading for MoS₃/GNP, S:Mo = 5:1. .......................... 112

Fig. 3.62 Summary of capacitance and potential at -10 mA/cm² vs loading for MoS₃/GNP, S:Mo = 5:1 ........................................... 112

Fig. 3.63 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 μg/cm² loading for MoS₃/KETJEN, S:Mo = 5:1 .......................... 113

Fig. 3.64 Summary of capacitance and potential at -10 mA/cm² vs loading for MoS₃/KETJEN, S:Mo = 5:1 ........................................... 113

Fig. 3.65 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 μg/cm² loading for MoS₃/VULCAN, S:Mo = 5:1 .......................... 114

Fig. 3.66 Summary of capacitance and potential at -10 mA/cm² vs loading for MoS₃/VULCAN, S:Mo = 5:1 ........................................... 114

Fig. 3.67 SEM images of MoS₃ on GNP in water S:Mo ratio 4:1 (a), 5:1 (b), 7:1 (c), 10:1 (d) Location: center of the plate; Zoom: x50 .................................................. 117

Fig. 3.68 SEM images of MoS₃ on GNP: S:Mo 4:1 ratio in water (a) and Ethylene Glycol (b), S:Mo ratio 5:1 in water (c) and Ethylene Glycol (d). Location: center of the plate; Zoom: x50 ............................ 118

Fig. 3.69 SEM images of MoS₃ in Ethylene Glycol, S:Mo ratio 5:1 on GNP (a), KETJENBLACK (b) and VULCAN (c). Location: center of the plate; Zoom: x50 118

Fig. 3.70 Profile of MoS₃/Ketjenblack film 5:1 in ethylene glycol deposited on a glassy carbon plate. .............................................................................. 120

Fig. 3.71 TEM images at two different spots for each sample of xGNP (a) and (b), Ketjenblack (c) and (d), Vulcan (e) and (f), MoS₃/Ketjenblack in ethylene glycol, S:Mo ratio 5:1 (g) and (h). ...................................................... 121

Fig. 3.72 X-ray photoelectron spectra of MoS₃/GNP 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV. ............................................................................. 124

Fig. 3.73 X-ray photoelectron spectra of MoS₃/Ketjenblack 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV ......................................................... 124

Fig. 3.74 X-ray photoelectron spectra of MoS₃/Vulcan 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV. ............................................................................. 125

Fig. 3.75 Current density vs potential from LSV after 0 cycles of CV stability for MoS₃/Ketjenblack doped with 2 wt%, 5 wt% and 10 wt% cobalt., at 5:1 S:Mo ratio. Pt data are also reported. ...................................................... 133

Fig. 3.76 Current density vs potential from LSV after 0 cycles of CV stability for MoS₃/Ketjenblack doped with 2 wt% and 5 wt% cobalt., at 7:1 S:Mo ratio. Pt data are also reported. ...................................................... 133

Fig. 3.77 Tafel plot from LSV after 0 of CV stability tests for Co-doped MoS₃/Ketjenblack at 5:1 and 7:1 S:Mo ratio. ...................................................... 134
Fig. 3.78 Current density vs Potential curves from CV after 0 cycles of CV stability tests Co-doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. ................................................. 134
Fig. 3.79 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_3$/Ketjenblack 5:1 ratio with 2% Co (top) and 5% Co (bottom). ......................................................... 137
Fig. 3.80 X-ray photoelectron spectra of 2%Co-MoS$_3$/KETJENBLACK 5:1 in ethylene glycol from (a) Mo(3d) and (b)S(2p). C1s 285.0 eV. ......................................................... 140
Fig. 3.81 X-ray photoelectron spectra of 5%Co-MoS$_3$/KETJENBLACK 5:1 in ethylene glycol from (a) Mo(3d) and (b)S(2p). C1s 285.0 eV. ......................................................... 140
Fig. 3.82 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt%, 5 wt% and 10 wt% of iron, at 5:1 S:Mo ratio. Pt data are also reported. ......................................................... 142
Fig. 3.83 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt% and 5 wt% of iron, at 7:1 S:Mo ratio. Pt data are also reported. ......................................................... 142
Fig. 3.84 Tafel plot from LSV after 0 of CV stability tests for Fe-doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. ........................................................................................................... 143
Fig. 3.85 Current density vs Potential curves from CV after 0 cycles of CV stability tests Fe-doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. ......................................................... 143
Fig. 3.86 Current density vs potential from LSV after 0 cycles of CV stability for Co/Fe doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. Pt data are also reported. ... 145
Fig. 3.87 Impedance curves from EIS after 0 cycles of CV stability tests for Co/Fe doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. ........................................................................................................... 145
Fig. 3.88 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_3$/Ketjenblack 5:1 ratio with 2% Fe (top) and 5% Fe (bottom). ......................................................... 147
Fig. 3.89 X-ray photoelectron spectra of 2%Fe-MoS$_3$/KETJENBLACK 5:1 in ethylene glycol from (a) Mo(3d) and (b)S(2p). C1s 285.0 eV. ......................................................... 150
Fig. 3.90 X-ray photoelectron spectra of 5%Fe-MoS$_3$/KETJENBLACK 5:1 in ethylene glycol from (a) Mo(3d) and (b)S(2p). C1s 285.0 eV. ......................................................... 150
Fig. 3.91 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG. Pt data are also reported. ........................................................................................................... 157
Fig. 3.92 Impedance curves from EIS after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG. ................................................. 158
Fig. 3.93 Tafel plot from LSV after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG. ................................................. 158
Fig. 3.94 TEM images of MoS$_3$/Ketjenblack 5:1 made in DMF + EG at two different magnifications. Particle sizes: 1-2 nm. ........................................................................................................... 161
Fig. 3.95 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_3$/Ketjenblack 5:1 made in DMF + EG. ........................................................................................................... 161
Fig. 3.96 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs. Pt data are also reported. ................................................................. 166
Fig. 3.97 Tafel plot from LSV after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs. ......................... 166
Fig. 3.98 Current density vs potential from CV after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs. ................................................................. 166
Fig. 3.99 Impedance curves from EIS after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs. ................. 167
Fig. 3.100 Filtrate solutions after the synthesis and filtration of MoS$_3$/Ketjenblack at 5:1 S:Mo in ethylene glycol at pH higher (left) and lower (right) than 2.65. .............. 169
Fig. 3.101 TEM images of MoS$_3$/Ketjenblack 5:1 made in EG + NaOH at two different magnifications. pH = 3-4 H$_2$SO$_4$. Particle size < 1 nm. ................................. 170
Fig. 3.102 TEM images of MoS$_3$/Ketjenblack 4:1 made in EG + 120 mg NaOH at two different magnifications. pH = 4-5 HCl. Particle size < 1 nm. .............................. 171
Fig. 3.103 STEM elemental mapping of MoS$_3$/Ketjenblack 5:1 in EG + NaOH. pH = 3-4 H$_2$SO$_4$. ........................................................................................................ 172
Fig. 3.104 STEM elemental mapping of MoS$_3$/Ketjenblack 4:1 in EG + NaOH. pH = 4-5 HCl ........................................................................................................ 172
Fig. 3.105 Effect of final pH on molybdenum precipitation by the rapid acidification technique. ........................................................................................................ 175
Fig. 6.1 2400 Series II CHNS/O Schematic. ................................................................. 197
Fig. 6.2 Chromatogram PE 2400. .................................................................................. 198
CHAPTER 1: HYDROGEN PRODUCTION BY WATER ELECTROLYSIS THROUGH ADVANCED LOW-COST CATALYSTS

1.1 INTRODUCTION

In the last few decades the challenge of clean energies gave rise to debates about fossil fuel combustion processes, which led to the proclamation of stricter international requirements for toxic emissions. In this framework two pathways were followed by scientists: on one side better technologies were exploited for the fossil fuel combustion processes, to increase the efficiency and decrease the emitted pollutants; on the other side renewable and cleaner energy sources have been introduced into the market. The proposed use of hydrogen represents an interesting alternative source of energy not only because of its very low environmental impact, high-specific energy, and the possibility to store, transfer and distribute it, but also because of its intrinsic characteristic as a major energy carrier\textsuperscript{1,2}. This raised the interest in the sustainable ways of producing it to promote a renewable clean energy cycle. Indeed, hydrogen can’t be considered as a primary source of energy (because it is not naturally found in its pure state), but as a means of storing and using energy later in time, \textit{i.e.} hydrogen is truly an energy carrier. Thus, it is clearly necessary to produce hydrogen by spending energy to chemically generate it from other compounds: this is usually the reason of the high cost of the final product.


Electricity is nowadays only a secondary source of energy to produce hydrogen by water electrolysis or chlor-alkali electrolysis, where hydrogen is a side product. Electrochemical water splitting is actually the best method to generate high-purity hydrogen and without pollutants, although only 4% of the total hydrogen is produced with this method\textsuperscript{3}. Electricity is the main reason of the high cost of the process, because of the high energy required to split the water.

Hydrogen can be exploited in different ways. First, as an energy carrier, it could be sent to power plants, stored and later burnt for producing energy. Second, it could be used in the automotive industry: BMW already showed an entirely automatic early hydrogen station prototype\textsuperscript{4}. Last but not least, hydrogen is already applied as a fuel for fuel cells, \textit{i.e.} it is used to produce electric and thermal energy in cogeneration plants.

\textit{1.1.1 Water electrolysis}

Water electrolysis happens when current is allowed to flow through two electrodes immersed in an aqueous electrolyte (Fig. 1.1), thus by electrochemically decomposing water with the overall reaction:

\[
(1) \quad \text{H}_2\text{O} + \text{electric energy} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2
\]

This reaction requires an energy input of $\Delta G = 237.1$ kJ/mol at standard conditions, which corresponds to a thermodynamic voltage requirement of 1.23 V.


The electrolytic cell is a container with an electrolyte, where the two electrodes (anode and cathode) are immersed. The electric field created by the applied potential makes the anions to move toward the anode and the cations to move toward the cathode.

At the same time, the protons are reduced at the cathode and the water is oxidized at the anode.

In a water splitting cell, the two half reactions are:

- the Hydrogen Evolution Reaction (HER), at the cathode:
  \[ 2H^+ + 2e^- \rightarrow H_2 \]  

- the Oxygen Evolution Reaction (OER), at the anode:
  \[ H_2O \rightarrow \frac{1}{2} O_2 + 2H^+ + 2e^- \]

However, electrochemical water splitting requires a significant amount of energy without the use of advanced catalysts, so to have a high current density at a low overpotential.
The HER is thought to involve three possible reaction steps which lead to two possible mechanisms: the Volmer–Heyrovsky or the Volmer–Tafel mechanism.

- **Volmer step**: \( H^+ + e^- \rightarrow H_{ad} \)
- **Heyrovsky step**: \( H^+ + H_{ad} + e^- \rightarrow H_2 \)
- **Tafel step**: \( 2H_{ad} \rightarrow H_2 \)

In both cases, the reaction proceeds through hydrogen atoms adsorbed at the electrode surface, \( H_{ad} \), and thus the rate of the overall reaction is influenced by the free energy of hydrogen adsorption, \( \Delta G_H \). The rate-limiting step could be the adsorption, in case of a weak hydrogen-to-surface bond, or the desorption, in case of a strong hydrogen-to-surface bond. The best HER catalysts have hydrogen adsorption energies close to \( \Delta G_H = 0 \). This principle gives rise to the “volcano” shape in Fig. 1.2:

---

Fig. 1.2 Exchange current density as a function of hydrogen adsorption free energy for various HER catalyst materials. The trend in the data defines a so-called "volcano plot" for the HER. Platinum, with slightly negative hydrogen absorption energy, has the highest HER activity.

The most effective catalysts for the HER are Pt-based, but Pt is a rare metal on Earth and its cost is high for practical application. In recent years, molybdenum sulfides, capable of accepting electrons and protons, were highlighted as promising hydrogen evolution catalysts.

1.1.2 MoS2 as an electrocatalyst for the HER

The studies of Nidola and Schira in 1986 on sulphide coatings showed for the first time that a MoS2 pigmented NiSx coating had higher catalytic activity and higher stability for the

---

Hydrogen Evolution Reaction than the non-pigmented one. MoS$_2$ was already known for its catalytic properties for hydrodesulfurization reactions and Raybaud et al. demonstrated with a local-density-functional study that the active sites are not situated on the basal planes but on the edges of the structure of MoS$_2$. The latter was investigated firstly by Jaegermann and Trubutsch in 1988 together with other transition metal chalcogenides. MoS$_2$ is trigonal prismatic coordinated and its structure is characterized by sheets of covalently bound S-Mo-S sandwiches. Several years later Topsøe et al. showed that the structure of the MoS$_2$ catalyst is composed almost entirely of flat polygons of S-Mo-S trilayers. These layers can be stacked in a structure similar to graphite or remain as single trilayers, in which two kinds of surface sites can be observed: terrace sites (on the basal plane) and edge sites (on edges of the nanoparticles). Scanning tunneling microscopy studies on thiophene have shown that the active sites for hydrodesulfurization reaction (HDS) are on the nanoparticle edges.

A combination of surface resolving methods and electrochemical studies determined the active sites of molybdenum sulfide for the HER. By preparing MoS$_2$ nanoparticles of different sizes (thus varying the distribution of surface sites on MoS$_2$ nanoparticles), it has...
been observed that the electrocatalytic activity of MoS$_2$ for HER correlates linearly with the number of edge sites on the MoS$_2$ catalyst$^{15,16}$.

One of the problems resulting when using MoS$_2$ in any electrochemical reaction is the extremely low conductivity between adjacent Van Der Waals bonded S–Mo–S sheets. So if we look at the single layer nanoplatelets [Fig.1.3a], we can understand that they have an optimal structure compared to a multi-layer nanoparticle [Fig.1.3b], because electrons only need to be transferred from the support to the platelets. The electrons transferred in a nanoparticle from the support to the bottom layer have to keep going then through four platelet interfaces to reach all the edges. This increases the resistance for each traversed layer$^{17}$.

![Fig. 1.3 Schematic of the difference in conductivity to the active sites on nanoplatelets (a) and nanoparticles (b)$^{17}$](image)


Thus, there are two general strategies to improve MoS$_2$ electrocatalysts. The first is to improve the intrinsic reactivity of the catalyst, \textit{i.e.} optimizing the binding energy of hydrogen, for example, by doping the MoS$_2$ nanoplatelets with transition metal ions. The second approach to improve the electrocatalytic activity of MoS$_2$ is to increase the amount of edges per mole MoS$_2$.

The number of edge sites is not the sole important factor which affects the catalytic activity of the MoS$_2$ for the HER. The activity is also dependent on the number of layers of its thin film structure. In particular, its catalytic activity decreases by a factor of \(~4.47\) for each additional layer. This behavior is likely correlated to the “jumping” of electrons in the vertical direction of MoS$_2$ layers (Fig. 1.4) over an interlayer potential barrier that has been calculated, and then observed, as 0.119 V$^{18}$.

\[\text{Fig. 1.4 a) Hopping of electrons in the vertical direction of MoS}_2\text{ layers. The right side illustrates the potential distribution in the multilayer film and the hopping of electrons through the potential barrier in the interlayer gap. b) The exchange current density of the MoS}_2\text{ film as a function of the layer number}.\]

1.1.3 Amorphous, crystalline and clusters of Molybdenum sulfides

Molybdenum sulfides can be produced in different grades of crystallinity. The highly crystalline sulfide is MoS2, which is the first one studied and whose nanoparticles are mostly synthesized by high-temperature sulfidation reactions or hydrothermal reactions. On the contrary, amorphous molybdenum sulfides (MoSx) can be produced under milder conditions and they have been found to be active catalysts toward the HER19,20,24. However, Merki et al. showed that a pre-activation process is occurring when amorphous MoS3 was used as a catalyst for the HER20. The XPS and UV-Vs spectra showed that after multiple polarization scans, the major part of the catalyst was a reduced MoSx species (where 3 > x ≥ 2), which is the real molybdenum sulfide active toward the HER.

MoS3 was believed to be a mixture of MoS2 and elemental S, but Hibble et al. showed theoretically21 and Wang et al. confirmed with electrochemical tests22 that molybdenum trisulfide exists as Mo3S9 clusters (Fig. 1.5).

---

An interesting result about molybdenum sulfides was obtained by Kibsgaard et al. when they studied thiomolybdate [Mo$_3$S$_{13}$]$^{2-}$ nanoclusters$^{23}$. The basic idea is that, since the active sites of the Mo sulfides catalysts are on the edge of the nanoparticles, a compound with higher edge sulfur atoms would have more active sites. Indeed, the clusters contain three different kind of sulfur ligands, all situated on the edges, and can be considered as Mo sulfide with a higher amount of active sites, since the catalysis could theoretically happen at nearly all the sulfur atoms.

1.1.4 Doping MoS$_x$ with Fe, Co and Ni

The MoS$_2$ nanoparticles are often difficult to prepare with conventional methods that use elevated temperature, pressure, or vacuum, so there are studies showing interesting properties of the amorphous MoS$_x$ films that are prepared by simple solution electrochemistry under

---

ambient conditions. These studies showed also that doping the catalyst with Fe, Co and Ni improves the catalytic activity of the MoS\textsubscript{x}, by optimizing the binding energy of hydrogen. The Co/Fe/Ni–Mo–S films are active HER catalysts. The Co-promoted MoS\textsubscript{3} film was prepared by electropolymerization of (NH\textsubscript{4})\textsubscript{2}[Co(MoS\textsubscript{4})\textsubscript{2}], which can be prepared in situ immediately upon the mixing of CoCl\textsubscript{2} with (NH\textsubscript{4})\textsubscript{2}[MoS\textsubscript{4}]. The Co-MoS\textsubscript{3} film showed optimal catalytic activity when the initial Co:Mo ratio was about 1:3. The catalytic activities of these ternary M–MoS\textsubscript{3} (where M=Co/Fe/Ni) films towards HER were measured using linear sweep voltammetry: Fe\textsuperscript{2+} appears to significantly promote the activity of MoS\textsubscript{3} film at both acidic and neutral pHs, and Ni\textsuperscript{2+} has a pronounced promotional effect at pH = 7. Other ions have a smaller or negligible influence on the activity.

The electrochemical impedance responses of these films support the idea that the HER catalyzed by amorphous MoS\textsubscript{3} and M–MoS\textsubscript{3} (where M= Mn, Fe, Cu, Zn) in acidic solutions exploits a fast Volmer step and then a rate-determining Heyrovsky step. SEM results showed a morphological change when Fe, Co, or Ni are incorporated into the amorphous MoS\textsubscript{3} film. In the electropolymerization technique the addition of the above transition metals improved the growth of the film, increasing its surface area, the catalyst loading and then its activity.

The addition of Co or Ni in particular modifies the shape of the Molybdenum sulfide clusters, to one closer to hexagonal. The doped catalyst tend to expose more promoted (\(\bar{1}010\)) S-type edges and HAADF-STEM results showed also the Co- and Ni- promoted catalysts may expose other high index facets.


Merki et al. suggest that HER occurs at defect sites in the amorphous MoS$_3$, which are unsaturated Mo and S sites. The presence of Fe, Ni and Co ions can enhance the activity of these unsaturated sites, leading to higher intrinsic activity$^{24}$. 

In fact, the dopant ions may be incorporated into the catalyst structure in different ways. Xiao et al. performed a DFT study to show that, in Co/MoS$_2$ and Ni/MoS$_2$, the doped metal atom is located on the S vacancy site and it’s bonded with the nearest Mo atom$^{26}$ (Fig. 1.6).

![Fig. 1.6](image)

*Fig. 1. 6(a) and (d) are the schematic diagram of Co/MoS$_2$ and Ni/MoS$_2$ systems. The corresponding partial density of states projected on sd orbitals are given in (b) and (e); the corresponding electronic deformation densities are shown in (c) and (f). The yellow and green denote S and Mo, the blue and pink are Co and Ni, respectively$^{26}$.***

A similar study was performed on Fe/MoS$_2$ and reached the same conclusion$^{27}$. However, the number of vacancies in the lattice can be increased only with the use of specific techniques (such as low-argon sputtering$^{28}$ or electron irradiation$^{29}$). In all other cases, it’s unlikely to have a high concentration of dopants in the lattice vacancies. More frequently, the dopants ions go inside the MoS$_2$ structure as sulfides (i.e. Co as Co$_9$S$_8$), leading to the so-called surface promoted M-Mo-S phase (where M is the dopant metal ion)$^{30}$ (Fig. 1.7).

![Molecular model of MoS$_2$ showing its lamellar structure and molecular model of the interface region between MoS$_2$ and Co$_9$S$_8$ as present on unsupported Co/MoS$_2$ catalyst](image)

Fig. 1.7(a) Molecular model of MoS$_2$ showing its lamellar structure and (b) molecular model of the interface region between MoS$_2$ and Co$_9$S$_8$ as present on unsupported Co/MoS$_2$ catalyst$^{30}$.

Depending on the synthesis procedure, the promoting ions could compete with the Mo in forming sulfides. Cobalt sulfide has been studied to see if this side product enhances even more the activity or if it poisons the catalyst\textsuperscript{31}. Electrochemical tests showed that CoS\(_x\) is actually a catalyst itself but it is also unstable in acidic solution and its activity decreases after few potential sweeps. However, the Co-promoted molybdenum sulfide looks more stable, which means that it retains the same electrochemical and morphological properties after several polarization sweeps. The activity, which decreases after these tests due to the presence of CoS\(_x\), eventually reaches a stable value, which is higher than the unpromoted catalyst. DFT calculations confirm this hypothesis by showing that the hydrogen binding energy (\(\Delta G_{\text{H}}\)) is decreased after the doping with Co ions\textsuperscript{31}.

1.1.5 \textit{MoS\(_2\) Nanoparticles grown on carbon materials}

A second strategy used to enhance the activity of molybdenum sulfides is to improve the electronic contact between the active sites and the underlying electrode. From this point of view, carbon materials are good candidates as catalyst supports due to their unique physicochemical properties, such as high conductivity, good electronic coupling and chemical stability. The electrocatalytic activity of MoS\(_2\) mainly depends on the MoS\(_2\) morphology and MoS\(_x\)-support electrical coupling. In this regard, forming highly dispersed nanoparticulate (\textit{i.e.}, edge rich) MoS\(_2\) on a conducting matrix is an ideal protocol to lower the activation potential for HER.

MoS\(_2\) loaded on graphene, graphite, and carbon nanotubes have been used as catalysts for HER\(^{17,32,33}\). To improve the electrocatalytic HER efficiency, it is crucial to increase the surface area for catalyst loading. Different morphological MoS\(_2\) shapes were developed on different carbon matrices. Recent studies focused on the catalytic activity more than on the stability, by exploiting molybdenum sulfides on multi-walled carbon nanotubes\(^{34}\), on conducting carbon fiber network\(^{35}\) and on Reduced Graphite Oxide\(^{36}\).

Although HER is involved in most of the recent studies on Molybdenum sulfides, it is sometimes interesting to have a look at developments of the same catalyst for other electrochemical purposes. MoS\(_2\)–reduced graphene oxide nanosheet–nanosheet hybrids (MoS\(_2\)NS–RGO), prepared via a lithiation-assisted exfoliation process and a hydrazine monohydrate vapour reduction technique, showed in lithium batteries higher capacity, improved rate capability, and increased endurance, confirming a synergistic effect between MoS\(_2\) and graphene nanosheets\(^{37}\). A future work of this compound applied to HER may be relevant.

---

Various three-dimensional (3D) electrode structures have been created and resulted in particularly interesting materials. Thanks to the 3D structures the graphene sheets do not restack and the specific surface area is increased in graphene materials; an interconnected conductive network and a specific microenvironment are created thanks to the optimal intrinsic properties of graphene\textsuperscript{38}. A three-dimensional graphene foam synthesized on a Ni foam skeleton by chemical vapor deposition (CVD) has been reported\textsuperscript{39}. The graphene foam without the support of a Ni skeleton is brittle and is not able to serve as a 3D electrode for hosting catalysts. The 3D Ni foam is a low cost, conductive metal with a high surface area, which is ideal for use as a template to host catalysts with increased reaction sites\textsuperscript{39}.

Another example of the effect of increasing the amount of edges was published by Li et al.\textsuperscript{33}. By adding ammonium tetrathiomolybdate \((\text{NH}_4)_2\text{MoS}_4\) and hydrazine to a solution with Graphene Oxide (GO) dispersed in DMF, they were able to produce MoS\textsubscript{2} nanocrystals, via a hydrothermal reduction of the Mo-precursor, and deposit them on GO, which was itself reduced during the process to Reduced Graphene Oxide (RGO). The composite is a material with an abundance of small MoS\textsubscript{2} crystals dispersed on the conductive graphene. The amount of edges are now increased as the particles are very small (from 2 to 100 nm) and the conductivity of graphene ensures an efficient electronic contact between the particles and the electrode. This allows for a high loading of MoS\textsubscript{2} per unit area, essentially resulting in a smaller electrode footprint.


Bian et al. focused on \textit{in situ} reduction of \((\text{NH}_4)_2\text{MoS}_4\) to MoS\textsubscript{2} on ordered mesoporous carbon nanospheres (MoS\textsubscript{2}/MCNs), and an electrochemical characterization was obtained for MoS\textsubscript{2}/MCNs modified glassy carbon electrodes (GCE). They tested pure MoS\textsubscript{2}, a mixture of MoS\textsubscript{2} and MCNs modified GCEs (MoS\textsubscript{2}–MCNs), pure MCNs, and MoS\textsubscript{2} supported on MCNs modified GCEs (MoS\textsubscript{2}/MCNs). The latter resulted to be the best one in terms of catalytic activity, HER onset potential and observed current densities (Fig. 1.8). The improved electrocatalysis exhibited by the MoS\textsubscript{2}/MCNs-GCE suggests a smaller activation energy for HER. Nanoparticulate growth on MCNs is confined such that very small and thereby edge-rich, MoS\textsubscript{2} particles are formed in comparison to the large aggregated MoS\textsubscript{2} grown freely in solution. Additionally, the intimate coupling between MoS\textsubscript{2} and the highly conductive MCNs should permit efficient electrical communication between the catalytic edge sites and underlying electrode\textsuperscript{40}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1a.png}
\caption{LSV polarization curves for GCEs modified with (A) MoS\textsubscript{2}/MCNs, (B) a mixture of MoS\textsubscript{2} and MCNs, (C) pure MoS\textsubscript{2} and (D) MCNs in 0.5 M H\textsubscript{2}SO\textsubscript{4}; scan rate: 2 mV/s.}
\end{figure}

**Tab. 1.1 Summary of relevant studies on the MoS\(_2\) as a catalyst for the hydrogen evolution reaction.**

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Year</th>
<th>Compound studied</th>
<th>Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MoS(_2) structure</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jaegermann <em>et al.</em>(^{12})</td>
<td>1988</td>
<td>Transition metal chalcogenides</td>
<td>MoS(_2) basic structure</td>
</tr>
<tr>
<td>Topsøe <em>et al.</em>(^{13})</td>
<td>1996</td>
<td>MoS(_2)</td>
<td>MoS(_2) S-Mo-S trilayers structure</td>
</tr>
<tr>
<td>Hibble <em>et al.</em>(^{21})</td>
<td>1998</td>
<td>MoS(_3)</td>
<td>MoS(_3) as Mo(_3)S(_9) clusters (theoretical study)</td>
</tr>
<tr>
<td>Wang <em>et al.</em>(^{22})</td>
<td>2007</td>
<td>MoS(_3)</td>
<td>MoS(_3) as Mo(_3)S(_9) clusters (electrochemical tests)</td>
</tr>
<tr>
<td>Laursen <em>et al.</em>(^{17})</td>
<td>2012</td>
<td>Molybdenum sulfides</td>
<td>Single/multi-layer MoS(_2) nanoparticles structure</td>
</tr>
<tr>
<td><strong>MoS(_2) as a catalyst for the HER</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nidola <em>et al.</em>(^{10})</td>
<td>1986</td>
<td>MoS(_2) pigmented NiS(_x) coating</td>
<td>First time MoS(_2) is found active toward HER</td>
</tr>
<tr>
<td>Raybaud <em>et al.</em>(^{11})</td>
<td>2000</td>
<td>DFT on MoS(_2)</td>
<td>MoS(_2) active sites are on the edges</td>
</tr>
<tr>
<td>Jaramillo <em>et al.</em>(^{16})</td>
<td>2007</td>
<td>MoS(_2)</td>
<td>Active edge sites</td>
</tr>
<tr>
<td>Merki <em>et al.</em>(^{15})</td>
<td>2011</td>
<td>Mo- and W- sulfides</td>
<td>Relation activity/ active edge sites</td>
</tr>
<tr>
<td>Yu <em>et al.</em>(^{18})</td>
<td>2014</td>
<td>MoS(_2)</td>
<td>Relation activity/ n. of layers in MoS(_2) structure</td>
</tr>
<tr>
<td>Kibsgaard <em>et al.</em>(^{23})</td>
<td>2014</td>
<td>[Mo(<em>3)S(</em>{13})](^{-2})-nanoclusters</td>
<td>Relation edge S atoms/ active sites</td>
</tr>
</tbody>
</table>
Tab. 1.1 continued

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Year</th>
<th>Compound studied</th>
<th>Relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Amorphous MoS(_x)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merki et al.(^{20})</td>
<td>2011</td>
<td>Amorphous MoS(_x)</td>
<td>Preactivation process in amorphous MoS(_x)</td>
</tr>
<tr>
<td>Vrubel et al.(^{19})</td>
<td>2012</td>
<td>MoS(_2)/ MoS(_3)</td>
<td>Amorphous MoS(_x) is active toward HER</td>
</tr>
<tr>
<td><strong>MoS(_2) doped with transition metal ions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brorson et al.(^{25})</td>
<td>2007</td>
<td><em>MoS(_2), WS(_2), Co-Mo-S, Ni-Mo-S, Ni-W-S</em></td>
<td>Shape modifications of the MoS(_2) clusters due to Co/Ni</td>
</tr>
<tr>
<td>Bonde et al.(^{31})</td>
<td>2008</td>
<td>Transition metal sulfides</td>
<td>CoS(_x) is active toward the HER</td>
</tr>
<tr>
<td>Merki et al.(^{24})</td>
<td>2012</td>
<td>Co-, Fe-, Ni-MoS(_2)</td>
<td>Effect of transition metal dopants on activity</td>
</tr>
<tr>
<td>Ramos et al.(^{30})</td>
<td>2013</td>
<td>Co-MoS(_2)</td>
<td>Co as CoS(_8) in Co-MoS(_2), Co-Mo-S phase</td>
</tr>
<tr>
<td>Xiao et al.(^{26})</td>
<td>2014</td>
<td>Co-, Ni-MoS(_2)</td>
<td>Co/Ni atoms are on the S vacancy sites</td>
</tr>
<tr>
<td>Ma et al.(^{27})</td>
<td>2015</td>
<td>Fe-embedded monolayer MoS(_2)</td>
<td>Fe atoms are on the S vacancy sites</td>
</tr>
<tr>
<td>Researchers</td>
<td>Year</td>
<td>Compound studied</td>
<td>Relevance</td>
</tr>
<tr>
<td>-----------------</td>
<td>------</td>
<td>--------------------------------------------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>Li et al. (^{33})</td>
<td>2011</td>
<td>MoS(_2)/graphene</td>
<td>MoS(_2) on graphene active toward the HER</td>
</tr>
<tr>
<td>Bian et al. (^{40})</td>
<td>2012</td>
<td>MoS(_2)/mesoporous carbon</td>
<td>MoS(_2) on ordered mesoporous carbon nanospheres active toward the HER</td>
</tr>
<tr>
<td>Chang et al. (^{32})</td>
<td>2013</td>
<td>MoS(_x) on Graphene-Protected 3D Ni Foam</td>
<td>MoS(_2) on graphene active toward the HER</td>
</tr>
<tr>
<td>Laursen et al. (^{35})</td>
<td>2013</td>
<td>MoS(_2)/carbon fiber network</td>
<td>MoS(_2) on carbon fibers active toward the HER</td>
</tr>
<tr>
<td>Lin et al. (^{34})</td>
<td>2013</td>
<td>MoS(_3)/carbon nanotubes</td>
<td>MoS(_3) on carbon nanotubes active toward the HER</td>
</tr>
<tr>
<td>Zhou et al. (^{38})</td>
<td>2013</td>
<td>MoS(_2)/Mesoporous Graphene</td>
<td>MoS(_2) on Mesoporous Graphene active toward the HER</td>
</tr>
<tr>
<td>Zheng et al. (^{36})</td>
<td>2014</td>
<td>MoS(_2)/Reduced Graphite Oxide</td>
<td>MoS(_2) on Reduced Graphite Oxide active toward the HER</td>
</tr>
</tbody>
</table>
1.2 HYPOTHESIS

Owing to MoS$_2$‘s hydrogen binding energy similar to that of Pt’s, we hypothesize that enhanced level of the MoS$_2$ catalytic activity toward the Hydrogen Evolution Reaction (HER) will be achieved by synthesizing the MoS$_2$ as nanoparticles on a mesoporous carbon support and by doping the catalyst with particular transition metal ions (i.e. Co/Fe), so to increase the surface area while maintaining high conductivity.

1.3 OPERATIONAL STATEMENT

We decompose ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$) to obtain MoS$_3$ nanoparticles via acidification reaction in liquid solution through sulfuric acid in different concentration and at temperatures between 165°C and 170°C, where also the thermal decomposition of the Mo-precursor starts. Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O) is added to increase the S:Mo ratio and so the yield to MoS$_3$. The nanoparticles are synthesized on various carbon supports: Graphene Nanoplatelets (GNP), Ketjenblack EJ-300 and Vulcan XC 72R mesoporous carbon. Different solvents are studied (mostly water, ethylene glycol) to obtain different size nanoparticles in order to increase the surface area and hence the activity.

We choose to incorporate transition metal ions as dopants during the synthesis process: Co and Fe will be exploited for this purpose and the respective acetates are used as reactants. Then, the catalyst obtained is characterized first by electrochemical analysis (i.e. linear sweep and cyclic voltammetry and electrochemical impedance spectroscopy), where 0.5 M H$_2$SO$_4$ is the electrolyte and then by physical analysis (e.g. SEM, XPS, ICP, CHNS analysis, S/TEM, elemental mapping).
The catalyst powder is added to a solution of ethanol and Nafion solution to create the ink. The electrode is loaded with the drop casting technique and is let dry in the oven. The loading routinely used is 250 μg/cm², meaning that the drop casting technique is repeated 5 times, although some tests required higher loadings. During the electrochemical tests MoS₃ is reduced to MoS₂, which is the active catalyst toward the HER.
1.4 REFERENCES


=node__5236


Chapter 2: Equipment and experiments: new recipe for the solvothermal synthesis of MoS$_3$ nanoparticles

2.1 OLD PROCEDURE

MoS$_3$ has been synthesized in several different ways, each one focused on improving a particular aspect of the procedure. Here we show how a simple process involving the dissolution of the reactants in a solvent and a following acidification reaction at a relatively low temperature can be exploited to obtain MoS$_3$ nanoparticles. Not only the synthesis is straightforward but it is scalable and creates stable and highly active catalysts.

This group previously developed a procedure for synthesizing MoS$_3$ nanoparticles on Graphene NanoPlatelets (xGNP)\textsuperscript{1}. The majority of the steps in this procedure comes from the combination of other different procedures found in literature, plus some innovative adjustments.

2.1.1 The reactants

The reactants used are listed below:

- Sodium sulfide nonahydrate: Na$_2$S$\cdot$9H$_2$O ($\geq$ 98.0%);
- Ammonium molybdate tetrahydrate: Mo$_7$O$_{24}$(NH$_4$)$_6$$\cdot$4H$_2$O (99.95% metal basis);
- Ammonium tetrathiomolybdate: (NH$_4$)$_2$MoS$_4$ (99.95% metal basis);
- Sulfuric acid solution: 0.5 M H$_2$SO$_4$ in H$_2$O;
- Cobalt (II) acetate: Co(C$_2$H$_3$O$_2$)$_2$ ($\geq$ 99.99% metal basis);

- Iron (II) acetate: C₄H₆FeO₄ (≥ 99.99% metal basis);
- Sodium hydroxide (98.9%);
- Graphene NanoPlatelets (xGNP® GRADE C 100%);
- Ketjenblack EJ-300 (Ketjenblack 98-100%);
- Vulcan XC 72R (Vulcan 100%);
- Ethanol (≥ 99.5%);
- Deionized water;
- Nafion® solution (0.25 wt% Nafion in ethanol).

The use of ammonium molybdate tetrahydrate (Mo₇O₂₄(NH₄)₆·4H₂O) has been reported by Benck et al.² They dispersed the molybdenum precursor in a solution with water and 0.2 M sulfuric acid and then added a solution containing sodium sulfide (Na₂S).

Lin et al. reported ammonium tetrathiomolybdate ((NH₄)₂MoS₄) on Multi-Walled Carbon NanoTubes (MWCNTs)³. First, they dispersed the carbon and the Mo precursor in the solvent, then they sonicated the solution and finally they added the acid.

2.1.2 The synthesis

By following the same steps, in our old procedure 0.05 g of Graphene NanoPlatelets (GNP) is dispersed in 200 ml H₂O and sonicated for 1 hr at room temperature. Then, 0.3169 g of sodium sulfide nonahydrate (Na₂S·9H₂O) is added to the solution so to have a S:Mo mole

ratio of 5:1 and the pH value is recorded. Finally, 0.046 g of ammonium molybdate tetrahydrate (Mo\textsubscript{7}O\textsubscript{24}(NH\textsubscript{4})\textsubscript{6}⋅4H\textsubscript{2}O) is added to the solution. The recipe was developed to obtain 100 mg of MoS\textsubscript{3} catalyst. All these compounds are solid particles and it is recommended to wash their containers with water in order to make sure that all the amount of each compound falls down in the flask.

Sulfuric acid (10 ml of aqueous 0.5 M H\textsubscript{2}SO\textsubscript{4}) is then added to maintain the pH low (< 2). The reaction occurs in four steps and molybdenum oxide (MoO\textsubscript{3}) is an intermediate compound\textsuperscript{4,5}:

1. \[ \text{Mo}_7\text{O}_{24}^{6-} + 6H^+ \rightarrow 7\text{MoO}_3 + 3H_2O \]
2. \[ \text{MoO}_3 + H_2O \leftrightarrow \text{MoO}_4^{2-} + 2H^+ \]
3. \[ \text{MoO}_4^{2-} + 4H_2S \leftrightarrow \text{MoS}_4^{2-} + 4H_2O \]
4. \[ \text{MoS}_4^{2-} + H^+ \leftrightarrow \text{MoS}_3 + HS^- \]

where the hydrogen ion comes from the sulfuric acid and the sulfur ion comes from the Na\textsubscript{2}S reactant.

While Benck \textit{et al.}\textsuperscript{2} at this point centrifuged the solution, Vrubel \textit{et al.}\textsuperscript{6} boiled it and let it cool down to room temperature. We found the latter procedure more appropriate. Hence, the flask with the solution is put in a hood on an electric heater and boiled for 1 hr while the solution is continuously mixed by a magnetic stirrer. The flask is capped to prevent H\textsubscript{2}S gas from escaping, the hood’s sash is left down and a thermometer is used to monitor the


\textsuperscript{5} “Synthesis of highly active unsupported molybdenum sulfide catalysts for hydrodesulfurization and hydrodeoxygenation” H. Zhang, PhD thesis, Tianjin University, P. R. China.

temperature of the solution, which is kept at ~100°C with a variable transformer (Variac) and a heating mantle. The cap has one small extra hole for pressure relief. It is important to maintain a gas phase rich in \( \text{H}_2\text{S} \): every uncontrolled loss of sulfur could determine a big variation in the final product.

Next step is to filter and wash the solution. A metal grid and a new membrane filter (Whatman–Nylon–47 mm–porosity ~2/4.5/8 nm) are put on a filter flask. A vacuum pump (WELCH® 115 V – up to 0.9 atm) is connected to the flask and the solution is poured. When the liquid is almost all drained, more water is added to the graduated glass funnel (Fig. 2.1) and the procedure is repeated until the flask is full. It is recommended to be sure that there is always liquid on the filter because the catalyst should constantly be in the form of a dense mud. The reason is that the catalyst no more wet by the water is likely to create cracks in its film, thus allowing the water to go through the filter without washing the catalyst itself.

Now, it’s time to remove the water from the catalyst mud. So the membrane filter with the catalyst is put in the oven at ~50°C for several hours and visually checked by naked eye every hour if it’s dry. A scheme of the synthesis procedure is shown in Fig. 2.1.
**2.1.3 The ink**

The catalyst is removed from the filter membrane with a spatula and the weight is measured to know the yield of the process. Afterwards, the catalyst is added to a solution of 0.33 ml of ethanol and 0.0238 ml of water per every mg of catalyst. We intend to use 4.2 mg of catalyst, so we need 1.4 ml of ethanol and 0.1 ml of water. The water is necessary to help with dispersion. The ink is thus sonicated for 30 min.
2.1.4 Electrode loading

As far as the ink deposition is concerned, we intend to load the electrode with 250 μg MoS₃/cm². The glassy carbon working electrode has a cylindrical shape and a radius equal to 0.25 cm; a Teflon shroud insulates the disk (Fig. 2.2).

![Fig. 2.2 Glassy carbon electrode with Teflon coat. Radius = 0.25 cm.](image)

The surface tension of the ink on the glassy carbon is able to hold without spilling a droplet of no more than 7 μL (50 μg MoS₃/cm²). Thus, in order to obtain the desired loading we need to deposit five times 7 μL of catalyst each time (total 250 μg MoS₃/cm²) and then let the electrode dry in an oven (~ 45°C) after every deposition. Two processes were used to deposit the Nafion on the electrode, which were later determined to produce essentially identical electrochemical results:
1) 5 μL of Nafion solution is deposited after every second catalyst deposition. Increasing the quantity of Nafion and adding it amongst the catalyst depositions can significantly reduce the issues with binding.

2) The ink composition was modified to 0.2 ml of H₂O, 0.8 ml of ethanol and 0.5 ml Nafion solution. It was faster and easier to add the Nafion to the ink, thus loading the electron just with ink droplets.

2.2 VARIATIONS TO THE OLD PROCEDURE

2.2.1 Reactants

(a) Mo-precursor

The Mo-precursor is the most important variation to the old procedure. Ammonium molybdate tetrahydrate (Mo₇O₂₄(NH₄)₆·4H₂O) produces oxygen atoms, which eventually form molybdenum trioxide (MoO₃), a reaction intermediate (reaction 1). The latter is an impurity for our catalyst and decreases the yield to MoS₃.

Recently, ammonium tetrathiomolybdate ((NH₄)₂MoS₄) has been used by Jaramillo group as a new Mo precursor to synthesize MoS₃. Since there are less chances than in the old one (Mo₇O₂₄(NH₄)·4H₂O) to have impurities dispersed in MoS₃, such as unbonded S or MoO₃, we chose to use (NH₄)₂MoS₄ as our new Mo-precursor for all our experiments. One important difference we noticed in using this compound is that it is less soluble in water than the previous one. Rather than being completely dissolved into NH₄⁺ and MoS₄²⁻ ions, the ammonium tetrathiomolybdate tends to remain as a suspension of tiny particles.

---

The acidification of the new molybdenum precursor can be described as follow:

6. \( \text{MoS}_4^{2-} + 2H^+ \rightarrow \text{MoS}_3 + H_2S \)

We still keep the flask capped to prevent the \( H_2S \) to escape. Then, either the heating of \( \text{MoS}_3 \) up to ~623-673K or the electrochemical reduction provokes the reaction leading to \( \text{MoS}_2 \) according to:

7. \( \text{MoS}_3 \rightarrow \text{MoS}_2 + (1/\text{x})S_x \)

We use the electrochemical reaction to obtain the final catalyst.

\( a \) Sodium hydroxide

We mentioned that \((\text{NH}_4)\text{MoS}_4\) is hardly soluble in water, so one more variation we performed with respect to the old procedure was the addition of sodium hydroxide (NaOH). The reaction between the Mo-precursor and NaOH leads to sodium thiomolybdate (\( \text{Na}_2\text{MoS}_4 \)) which has high solubility in water and organic solvents:

8. \( (\text{NH}_4)\text{MoS}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{MoS}_4 + 2\text{H}_2\text{O} + 2\text{NH}_3 \)

\( c \) Carbon

The carbon support of the previous procedure was GNP, which creates relatively weak bonds with \( \text{MoS}_3 \) and is not highly soluble in water. The new carbon chosen for the synthesis are Ketjenblack EJ-300 and Vulcan XC 72R. The former has the highest surface area, as summarized in Table 2.1. However, we performed a series of experiments involving all three different carbons, in order to examine the effect on the activity of the catalyst.

---


Tab. 2.1 Carbons surface area.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
<td>750</td>
</tr>
<tr>
<td>Vulcan XC 72R</td>
<td>240</td>
</tr>
<tr>
<td>Ketjenblack EJ-300</td>
<td>800</td>
</tr>
</tbody>
</table>

The reason why we want to exploit these mesoporous carbons is that we hope that their high and various-sized porosity will help to deposit the nanoparticles on the carbon structure, in particular in the nanopores. In this way we can significantly improve the electronic coupling and the charge transfer of the entire system.

2.2.2 Solvents

The solvent is an extremely important factor in this process. By changing the solvent we were able to change the boiling temperature, the solubility of the molybdenum precursor, the interactions and side reactions of the molecules in the flask, and the yield to MoS₃. The two main solvents we used were deionized water and ethylene glycol. Their characteristics are summarized in Table 2.2.
**Tab. 2.2 Characteristics of water and ethylene glycol in the synthesis of MoS₃.**

<table>
<thead>
<tr>
<th></th>
<th>WATER</th>
<th>ETHYLENE GLYCOL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Boiling point with the reactants and sulfuric acid in water</td>
<td>Boiling point with the reactants and sulfuric acid in water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Boiling point with the reactants and sulfuric acid in EG</td>
</tr>
<tr>
<td>Capability of dissolving (NH₄)₂MoS₄</td>
<td>Very low</td>
<td>Capability of dissolving (NH₄)₂MoS₄</td>
</tr>
<tr>
<td>Capability of dispersing Carbon</td>
<td>Very low</td>
<td>Capability of dispersing Carbon</td>
</tr>
<tr>
<td>Polarity</td>
<td>Polar</td>
<td>Polarity</td>
</tr>
<tr>
<td>Speed of filtration/probability of residual</td>
<td>High/Low</td>
<td>Speed of filtration/probability of residual</td>
</tr>
</tbody>
</table>

Other solvents were used in the attempt to completely dissolve the ammonium tetrathiomolybdate, such as mixtures of water and ethylene glycol in different ratios, N-Methyl-2-pyrrolidone, N,N-Dimethylformamide (DMF), mixtures of DMF and water and DMF and Ethylene Glycol. It’s remarkable to say that DMF is widely used in literature for this purpose because is able to completely dissolve the Mo-precursor. However, DMF
solvent forms stable H-bonded complexes with Sulfuric Acid: \((\text{H}_2\text{SO}_4)_2\text{-DMF}\)^{10}. Without the correct amount of free acid in solution, the acidification reaction occurs at a lower extent. Eventually, this leads to unreacted Mo-precursor and so to a decreased yield to MoS\(_3\).

2.3 ELECTROCHEMICAL TESTS

We defined a structure for our electrochemical tests by allowing the catalyst to be activated before analyzing its characteristics. The equipment we use is listed below:

- PINE AFCBP1 bipotentiostat;
- PRINCETON APPLIED RESEARCH VERSASTAT 4 potentiostat;
- Three electrode configuration flask;
- Ag/AgCl single junction reference electrode (potential = 0.222 vs RHE);
- Platinum coil counter electrode;
- Argon source;

We used the Versastat potentiostat because the AFCBP1 is not able to perform an impedance test. Argon is introduced in solution to remove oxygen. The set-up of the experiment is shown in Fig. 2.3.

---

2.3.1 iR compensation

We are interested in finding the potential at the working electrode, which is shifted by the uncompensated resistance of the cell. Thus, when we process the data we need to subtract the potential drop in the cell: this is called iR compensation. We ran all the experiment but the Electrochemical Impedance Spectroscopy (EIS) with the Pine Bipotentiostat AFCBP1, which is unable to perform impedance tests. We ran the EIS with the Princeton Applied Research VERSASTAT 4 Potentiostat. From EIS data we are able to know the resistance of the cell. However, this procedure could imply some analytical risks because the reference electrode could shift a bit from one measurement to another. So we tried to find a way to obtain the resistance with the Pine potentiostat, i.e. we searched for the “current interrupt” method.
Unfortunately, the Pine bipotentiostat is unable to perform the current interrupt method or any other experiments which could let us know the resistance. However, to be sure of our results we measured the reliability of this procedure by testing the resistance of the cell with a 16 Channel BioLogic VMP3 potentiostat (which is able to perform all the tests we need, the current interrupt method and the EIS), and we compared the results with the VERSASTAT 4 we have in the lab: they both give the same resistance with the EIS; the current interrupt method was found less reliable. So we can now proceed safely by doing iR compensation with the uncompensated resistance taken from EIS tests with the VERSASTAT 4 potentiostat.

2.4 ORGANIZATION OF EXPERIMENTS

As far as the electrochemical experiments are concerned, basically we are going to perform and repeat four categories of tests:

- **Cyclic Voltammetry (CV), with the following parameters:**
  - Segments (2 segments = 1 cycle): 6
  - Initial potential: 0.4 V
  - Final potential: -0.1 V
  - Sweep rate: 50 mV/s
  - Electrode range: 2 mA/cm²

- **Linear Sweep Voltammetry (LSV), with the following parameters:**
  - Segments: 1
  - Initial potential: 0.2 V
- Final potential: -0.55 V
- Sweep rate: 5 mV/s
- Electrode range: 5 mA/cm²

- Cyclic Voltammetry – stability tests, with the following parameters:
  - Segments: 20/80/100/200
  - Initial potential: 0 V
  - Final potential: variable – from previous LSV take a potential that gives you a current density close to 2 mA/cm²
  - Sweep rate: 50 mV/s
  - Electrode range: 5 mA/cm²

- Electrochemical Impedance Spectroscopy (EIS), with the following parameters:
  - Start Frequency: 100 kHz
  - End Frequency: 0.1 Hz
  - Amplitude: 5 mV
  - Point Spacing: Logarithmic
  - Number of points: 30
  - Points Per Decade: 10
  - Measurement Delay: 0 s
  - Step or Scan: Step
  - Potential: first at -0.1 V, followings at -0.15 V.
CV, LSV and CV-stability data are taken from the potentiostat with AfterMath software from PINE Company, EIS data are taken with VersaStudio software from Princeton Applied Research.

The structure of our experiments is the following:

- **1**\textsuperscript{st} series:
  - CV, EIS (before **1**\textsuperscript{st} LSV)
  - LSV
  - CV, EIS (after **1**\textsuperscript{st} LSV)

- **2**\textsuperscript{nd} series - after **10** cycles (20 segments) of CV stability tests:
  - LSV, CV, EIS

- **3**\textsuperscript{rd} series - after **50** cycles (100 segments) of CV of stability tests:
  - LSV, CV, EIS

- **4**\textsuperscript{th} series - after **100** cycles (200 segments) of CV of stability tests:
  - LSV, CV, EIS

- **5**\textsuperscript{th} series - after **200** cycles (400 segments) of CV of stability tests:
  - LSV, CV, EIS

Thus, the plots will show a legend with 0-1 (\textit{i.e.} CV and EIS before the **1**\textsuperscript{st} LSV after **0** cycles), 0-2 (\textit{i.e.} CV and EIS after the **1**\textsuperscript{st} LSV after **0** cycles), **10**, **50**, **100**, **200** (\textit{i.e.} LSV, CV and EIS after **10**, **50**, **100**, **200** cycles respectively).

The CVs are necessary to convert MoS\textsubscript{3} in MoS\textsubscript{2} and to detect three reactions. First, the oxidation/reduction of MoO\textsubscript{3}, then the reductions of MoS\textsubscript{3} and S. We use LSV to obtain the potential at -10 mA/cm\textsuperscript{2} as a term of comparison, the activity (current density), the Tafel...
slope, the exchange current density. The electrolyte resistance and capacitance of the electrocatalysts are characterized using EIS.

The electrochemical stability and performance of the MoS$_2$ electrocatalyst is examined using an accelerated durability test (ADT) by continuously cycling the potential between 0 and -0.2 V (the range in which hydrogen evolution occurs) with periodic measurements of impedance and catalytic activity, to evaluate the stability of the catalyst and see if there are impurities.

2.5 DATA PROCESSING

The raw data are taken from the two softwares and first converted from our reference electrode (single junction Ag/AgCl = 0.222 vs RHE) to the RHE. We usually see the reduction peak of the MoS$_3$ just in the first CV. In order to know the capacitance, the resistance of the cell and of the charge-transfer we perform the EIS. We use VersaStudio software to take the data from the potentiostat and an equivalent Randles circuit model is fit to the data with ZSimpWin software to determine the system resistance and the capacitance (Fig. 2.4).

![Equivalent Randles Circuit](image)

*Fig. 2.4 Equivalent Randles circuit $R_1(QR_2)$ where $R_1$ = solution resistance, $R_2$ = charge-transfer resistance and $Q$ = constant phase element (CPE).*

We take the resistance of the cell from EIS data at the real axis interception in Nyquist plot. The model of ZSimpWin provides us the data of the capacitance and the charge-transfer resistance $R_2$. LSV experiments provide us data for the current and the potential, which is
corrected by subtracting the ohmic drop of the cell (see section 2.3.1 \textit{iR compensation}). The same data of the polarization curves are plotted in the opposite and positive way and we take the logarithm of the current density, so to have the Tafel plot of log $i$ vs overpotential and clearly see the trend of the Tafel slope. From the Tafel plot we extrapolate the current at zero overpotential, \textit{i.e.} the exchange current.

We use Origin software to summarize and plot the processed data.

2.6 PHYSICAL CHARACTERIZATION

After the electrochemical analysis, if the catalyst showed good response, we carried out some physical characterizations such as XPS, TEM, CHN/S, ICP, and STEM.

X-ray photoelectron spectroscopy (XPS) is a surface chemical analysis technique that is used to analyze the surface chemistry of the material in its as-received state, so to obtain:

- composition
- binding energy of Mo and S
- valence of catalysts

Transmission electron microscopy (TEM) is used to obtain properties of the catalyst, in particular:

- morphology
- size
- dispersion

Inductively coupled plasma (ICP) and elemental CHNS analysis are performed to know the concentration of elements. Appendices A and B describe these last two techniques in details.
The FEI Titan 80-300 probe aberration corrected scanning transmission electron microscope (STEM) with monochromator is an advanced analytical workstation. The combination of field emission electron source (X-FEG) and SuperX Energy Dispersive Spectrometry (SuperX EDS) together is called ChemiSTEM Technology, which makes elemental mapping at atomic level possible.

The monochromator makes sure the energy resolution of the electron source is as narrow as 0.2 eV, which allows electron energy-loss spectrum (EELS) to be collected at atomic level. With this tool, we are able to look at the morphology and size of the nanoparticles and at the dispersion of the different elements in the catalyst structure.
2.7 REFERENCES


Chapter 3: Results and Discussion

3.1 EFFECTS OF CARBON SUPPORTS, SOLVENTS AND INITIAL COMPOSITIONS ON MoS$_3$ CATALYSTS FOR HYDROGEN EVOLUTION REACTION

The experiments were carried out by following a specific pathway, which is changing one variable at time and keeping all others fixed. After the procedure was fixed, we started the experiments by investigating the effects of the carbon support chosen (GNP, Ketjenblack and Vulcan) and the initial atomic S:Mo ratio, by changing the ratio of the amount of S-precursor and Mo-precursor. For this purpose, a table was developed to track the path chosen (Tab. 3.1).

Tab. 3.1 Matrix of the first series of experiments to synthesize MoS$_3$ on a carbon support and at different S:Mo ratio.

<table>
<thead>
<tr>
<th>S:Mo ratio</th>
<th>4:1</th>
<th>5:1</th>
<th>7:1</th>
<th>10:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GNP</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>KETJEN</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>VULCAN</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Together with the S:Mo ratio and the carbon, we also investigated the role of the solvent as an independent variable of the system. In particular, water and ethylene glycol are the two main solvents studied.

3.1.1 Electrochemical results: GNP support at different S:Mo ratio in water

The boiling step in the synthesis was controlled by allowing few small bubbles on the liquid surface (~ 105°C), thus by increasing the mixing and stirring but without perturbing the reaction.

Static electricity created problems after the ink was dried in the oven. The catalyst is charged and it is very difficult to keep it in the container. To avoid the problem, the filter membrane with the catalyst is put on a weighting paper in a glass container instead of a plastic one.

4:1 S:Mo ratio → Weight obtained: 102.6 mg from:

- 0.068 g \((\text{NH}_4)_2\text{MoS}_4\)
- 0 g \(\text{Na}_2\text{S}\cdot9\text{H}_2\text{O}\)
- 0.05 g GNP (GNP:Mo\(_3\) = 1:1)
- 10 ml 0.5 M \(\text{H}_2\text{SO}_4\) (in \(\text{H}_2\text{O}\))
- 200 ml water
Fig. 3.1 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 4:1.

Fig. 3.2 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 4:1.
Fig. 3.3 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 4:1.

Fig. 3.4 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 4:1.
Tab. 3.2 Summary of results for MoS₂/GNP, S:Mo = 4:1 after 0 (before and after the 1st LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_S$ (ohm)</th>
<th>$R_{ct}$ (ohm)</th>
<th>CPE/Area (μF/cm²)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm²)</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.6</td>
<td>63.9</td>
<td>20.2</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>6.4</td>
<td>52.3</td>
<td>19.5</td>
<td>43</td>
<td>-5.6 x 10⁻⁴</td>
<td>-184</td>
</tr>
<tr>
<td>10</td>
<td>6.6</td>
<td>56.4</td>
<td>19.4</td>
<td>42</td>
<td>-3.9 x 10⁻⁴</td>
<td>-185</td>
</tr>
<tr>
<td>50</td>
<td>6.6</td>
<td>59.2</td>
<td>19.9</td>
<td>42</td>
<td>-2.4 x 10⁻⁴</td>
<td>-186</td>
</tr>
<tr>
<td>100</td>
<td>5.8</td>
<td>62.0</td>
<td>19.9</td>
<td>43</td>
<td>-4.5 x 10⁻⁴</td>
<td>-187</td>
</tr>
<tr>
<td>200</td>
<td>6.5</td>
<td>64.5</td>
<td>19.2</td>
<td>41</td>
<td>-2.8 x 10⁻⁴</td>
<td>-187</td>
</tr>
</tbody>
</table>

One parameter which can be found in literature to compare different electrocatalysts is the onset potential, which is the potential at which the catalytic current is first observed. Without a strict definition, the ambiguity of the onset potential makes it a poor criterion for comparing different catalysts; thus, we decided to take a more relevant metric, that is the potential required to reach a current density of interest: the potential will be compared at -10 mA/cm².

Since the weight of this first catalyst is slightly above 100 mg, there must be a small percentage of unbonded elemental S. The results show a catalyst with good but not excellent activity, similar to the previous ones developed by this group. Since (NH₄)₂MoS₄ is cheaper than Mo₇O₂₄(NH₄)·4H₂O and also we avoided the S precursor, the cost of the catalyst is now decreased. The LSV data show that the catalyst is stable, although the charge-transfer resistance has a small increase after each cycles series. The CV data tells that all MoS₃ has been converted to MoS₂ and the Tafel slope ~ 40 mV/dec indicates that the hydrogen production happens mostly via the Volmer–Tafel mechanism (~ 30 mV/dec).
The idea of changing the S:Mo ratio of the reactants came from the assumption that, by following Le Châtelier’s principle, we can increase the yield to the product by increasing the amount of reactants. Of course this process is a balance between the increase in the activity due to the higher amount of MoS$_3$ and the decrease due to the presence of more unbonded elemental sulfur, which is a poison for the catalyst. We can’t change the S:Mo ratio by using only (NH$_4$)$_2$MoS$_4$ (as we did in this first experiment: S:Mo is always 4:1) but, since a good starting point for the S:Mo ratio may be to keep the same ratio of the old procedure, i.e. 5:1, we need to add the S-precursor. In order to do so, 0.063 g of Na$_2$S∙9H$_2$O are added to the solution. It is not easy to measure Na$_2$S∙9H$_2$O because the compound is kept in the fridge and is in the form of big crystals. Thus, an aqueous solution (10 mg Na$_2$S∙9H$_2$O/l) was made out of it.

We also chose to use less solvent (150 ml instead of 200 ml), which didn’t affect our results.

5:1 S:Mo ratio → Weight obtained: 103.3 mg from:

- 0.068 g (NH$_4$)$_2$MoS$_4$
- 0.063 g Na$_2$S∙9H$_2$O
- 0.05 g GNP (GNP:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml water
Fig. 3.5 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1.

Fig. 3.6 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1.
Fig. 3.7 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS\textsubscript{3}/GNP, $S$:$Mo = 5$:$1$.

Fig. 3.8 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS\textsubscript{3}/GNP, $S$:$Mo = 5$:$1$.
Tab. 3.3 Summary of results for MoS$_2$/GNP, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_S$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area mF/cm$^2$</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.7</td>
<td>44.1</td>
<td>19.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>6.6</td>
<td>43.7</td>
<td>20.6</td>
<td>42</td>
<td>-5.5 x 10$^{-4}$</td>
<td>-180</td>
</tr>
<tr>
<td>10</td>
<td>6.5</td>
<td>50.0</td>
<td>20.1</td>
<td>42</td>
<td>-4.4 x 10$^{-4}$</td>
<td>-183</td>
</tr>
<tr>
<td>50</td>
<td>6.6</td>
<td>55.8</td>
<td>19.5</td>
<td>38</td>
<td>-1.5 x 10$^{-4}$</td>
<td>-185</td>
</tr>
<tr>
<td>100</td>
<td>6.9</td>
<td>59.2</td>
<td>18.9</td>
<td>39</td>
<td>-1.8 x 10$^{-4}$</td>
<td>-187</td>
</tr>
<tr>
<td>200</td>
<td>7.0</td>
<td>61.6</td>
<td>19.2</td>
<td>41</td>
<td>-2.9 x 10$^{-4}$</td>
<td>-185</td>
</tr>
</tbody>
</table>

The catalyst is stable, although a small reduction in the performances can be observed after the stability tests.

The reduction peak of MoS$_3$ to MoS$_2$ in the CV (Fig. 3.6) is more accentuated than in the 4:1 case. This means that there was more MoS$_3$ to be converted in the 5:1 case, thus confirming our assumption that introducing more S in the synthesis procedure does increase the yield to MoS$_3$.

The charge-transfer resistance and the potential at -10 mA/cm$^2$ are decreased with respect to 4:1 case and no anomalies are observed (Fig. 3.7 and Tab. 3.3). Overall, the activity was improved.
7:1 S:Mo ratio → Weight obtained: 105.3 mg from:

- 0.068 g \((\text{NH}_4)_2\text{MoS}_4\)
- 0.188 g \(\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}\)
- 0.05 g GNP (GNP:MoS\(_3\) = 1:1)
- 10 ml 0.5 M H\(_2\)SO\(_4\)
- 150 ml water

\(\text{Fig. 3.9 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS}_3/\text{GNP, S:Mo = 7:1.}\)

The polarization curves from LSV (Fig. 3.9) show a trend similar to the previous catalysts. Again, the curves tell us that the catalyst is stable.
The reduction peak of MoS₃ to MoS₂ in the CV (Fig. 3.10) is more accentuated and it is still visible at higher cycles of stability tests than in the previous cases. This means that there was more MoS₃ to be converted in the 7:1 case, in line with our assumption.

Fig. 3.10 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS₂/GNP, S:Mo = 7:1.
Fig. 3.11 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 7:1.

Fig. 3.12 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 7:1.
Tab. 3.4 Summary of results for MoS₂/GNP, S:Mo = 7:1 after 0 (before and after the 1ˢᵗ LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Rs (Ω)</th>
<th>Rct (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm²)</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.7</td>
<td>44.5</td>
<td>25.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>6.1</td>
<td>41.8</td>
<td>28.5</td>
<td>50</td>
<td>-2.8 x 10⁻³</td>
<td>-179</td>
</tr>
<tr>
<td>10</td>
<td>6.7</td>
<td>44.9</td>
<td>27.6</td>
<td>46</td>
<td>-1.4 x 10⁻³</td>
<td>-179</td>
</tr>
<tr>
<td>50</td>
<td>6.6</td>
<td>48.5</td>
<td>26.7</td>
<td>45</td>
<td>-9.5 x 10⁻⁴</td>
<td>-181</td>
</tr>
<tr>
<td>100</td>
<td>6.6</td>
<td>51.4</td>
<td>26.0</td>
<td>44</td>
<td>-6.9 x 10⁻⁴</td>
<td>-183</td>
</tr>
<tr>
<td>200</td>
<td>6.5</td>
<td>55.9</td>
<td>25.0</td>
<td>42</td>
<td>-4.4 x 10⁻⁴</td>
<td>-185</td>
</tr>
</tbody>
</table>

The charge-transfer resistance and the potential at -10 mA/cm² are decreased with respect to the 4:1 and 5:1 cases (Fig. 3.11 and Tab. 3.4). The exchange current is increased and performances look definitely better. The extra sulfur is improving the activity without poisoning the catalyst. The catalyst’s weight is still close to 100 mg, thus confirming that no elemental sulfur is currently inside.

To investigate if we can push this trend further, hence improving the activity even more, we also tried the S:Mo initial ratio at 10:1.

10:1 S:Mo ratio → Weight obtained: 121.3 mg from:

- 0.068 g ((NH₄)₂MoS₄
- 0.377 g Na₂S·9H₂O
- 0.05 g GNP (GNP:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄
- 150 ml water
Fig. 3.13 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 10:1.

Fig. 3.14 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 10:1.
Fig. 3.15 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 10:1.

Fig. 3.16 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 10:1.
The increased weight (+21.3%), potential (+≈15 mV) and charge-transfer resistance tell us that we reached the limit for increasing the S:Mo ratio. The sulfur saturated all the Mo atoms and the extra S atoms remained as unbonded elemental S.

In order to have a better understanding of the differences that the change of the initial S:Mo ratio made, we now report a comparison plot of the first LSV data (at 0 cycles of CV stability tests) for all the different S:Mo ratio: at 0 cycles we always obtained the best activity (Fig. 3.17).

Pt data are generated on a platinum electrode with a flat and smooth surface.

Tab. 3.5 Summary of results for MoS\(_2\)/GNP, S:Mo = 10:1 after 0 (before and after the 1\(^{st}\) LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>(R_s) (Ω)</th>
<th>(R_{ct}) (Ω)</th>
<th>CPE/Area mF/cm(^2)</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm(^2))</th>
<th>Potential at -10 mA/cm(^2) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.3</td>
<td>97.4</td>
<td>11.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>6.5</td>
<td>72.7</td>
<td>14.7</td>
<td>48</td>
<td>-1.0 (× 10^{-3})</td>
<td>-193</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
<td>69.8</td>
<td>16.8</td>
<td>41</td>
<td>-2.9 (× 10^{-4})</td>
<td>-192</td>
</tr>
<tr>
<td>50</td>
<td>6.5</td>
<td>80.2</td>
<td>16.8</td>
<td>45</td>
<td>-6.3 (× 10^{-4})</td>
<td>-194</td>
</tr>
<tr>
<td>100</td>
<td>6.4</td>
<td>92.4</td>
<td>15.8</td>
<td>44</td>
<td>-3.9 (× 10^{-4})</td>
<td>-197</td>
</tr>
<tr>
<td>200</td>
<td>6.4</td>
<td>100.4</td>
<td>15.1</td>
<td>44</td>
<td>-3.5 (× 10^{-4})</td>
<td>-199</td>
</tr>
</tbody>
</table>
Fig. 3.17 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS\textsubscript{3}/GNP, at 4:1, 5:1, 7:1 and 10:1 S:Mo ratio. Pt data are also reported.

The plot shows a trend in the data from which we can get that the extra sulfur enhances the activity by increasing the yield to MoS\textsubscript{3}. On the other side, too much sulfur poisons the catalyst and decreases the performances in several aspects. As we clearly see in the 7:1 ratio, at higher potential the extra S increases also the initial current density, which quickly decreases with a slope higher than in the 5:1 ratio. The four samples at different S:Mo ratio have been analyzed with the ICP and CHN/S techniques (See Appendices A-B) to get the real composition and we report a summary (Tab. 3.6) of the electrochemical and physical data.
Tab. 3.6 Summary data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm² for MoS₃/GNP, S:Mo = 4/5/7/10:1 after 0 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% C</th>
<th>wt% H</th>
<th>wt% N</th>
<th>wt% S</th>
<th>wt% Sum</th>
<th>S:Mo ratio</th>
<th>wt% S+Mo</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current mA/cm²</th>
<th>Potential at -10 mA/cm² (mv)</th>
<th>R&lt;sub&gt;ct&lt;/sub&gt; (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4:1</td>
<td>41.3</td>
<td>0.2</td>
<td>0.5</td>
<td>24.6</td>
<td>18.5</td>
<td>85.0</td>
<td>4.0</td>
<td>43.1</td>
<td>21.5</td>
<td>43</td>
<td>-5.6 x 10⁻⁴</td>
<td>-184</td>
</tr>
<tr>
<td>5:1</td>
<td>39.9</td>
<td>0.5</td>
<td>0.5</td>
<td>28.7</td>
<td>18.1</td>
<td>87.8</td>
<td>4.7</td>
<td>46.8</td>
<td>20.6</td>
<td>42</td>
<td>-5.5 x 10⁻⁴</td>
<td>-180</td>
</tr>
<tr>
<td>7:1</td>
<td>34.5</td>
<td>0.7</td>
<td>0.3</td>
<td>29.3</td>
<td>16.5</td>
<td>81.4</td>
<td>5.3</td>
<td>45.8</td>
<td>28.5</td>
<td>50</td>
<td>-2.8 x 10⁻³</td>
<td>-179</td>
</tr>
<tr>
<td>10:1</td>
<td>31.9</td>
<td>0.2</td>
<td>0.3</td>
<td>40.5</td>
<td>16.8</td>
<td>89.6</td>
<td>7.2</td>
<td>57.3</td>
<td>14.7</td>
<td>48</td>
<td>-1.0 x 10⁻³</td>
<td>-193</td>
</tr>
</tbody>
</table>
The first problem I had with the real composition of the samples was that the percentages of the elements are far from being summing up to 100%. Since there are almost no contaminations, we investigated the problem and we found out that we had to calibrate the CHN/S analyzer on our carbon. This re-calibration worked with Ketjenblack and Vulcan, but not with GNP. As a consequence, we decided to consider the sum S + Mo more reliable than the % C.

The catalyst real weight percentage is ~ 57% for 10:1 and ~ 45% for all the other ones. The real S:Mo ratio is higher than three, meaning that we have other different molybdenum sulfides or unbonded elemental sulfur. This extra sulfur is probably washed away in part during the electrochemical tests: as for the 7:1 and the 10:1 ratio, the idea is that not all the extra sulfur can be washed away and the residuals poisons the catalyst. Fig. 3.17 and Tab. 3.6 clearly show a trend in which the 5:1 results the best S:Mo ratio for enhancing the activity of MoS$_3$ nanoparticles toward the HER.

3.1.2 Thermogravimetric analysis results

The decision of changing solvent for the synthesis procedure came from the problem of dissolving the Mo-precursor. This gave rise to new questions about the behavior of the main reactant at different temperatures. When water was used as synthesis solvent, the temperature was kept at ~ 100°C; however, use of ethylene glycol looked like a more suitable way out of the dissolution problem and its boiling temperature is ~ 200°C. The questions were if the catalyst would change behavior by being synthesized at higher T, and, if yes, which change we would see at different temperatures.
In order to answer to these questions, we performed a ThermoGravimetric Analysis (TGA) on the two Mo-precursors and on just the Ketjenblack carbon (Fig. 3.18 and 3.19).

As we can see in the plots, \((\text{NH}_4)_2\text{MoS}_4\) starts to decompose at \(\sim 165^\circ\text{C}\) and loses \(\sim 20\%\) of its weight in the following \(20^\circ\text{C}\). On the other side, \(\text{Mo}_7\text{O}_{24}(\text{NH}_4)_6\cdot4\text{H}_2\text{O}\) slowly decomposes with temperature increasing without any big and quick change in its weight. We can see the same difference when we hold the temperature at \(250^\circ\text{C}\): the old precursor has a slope of decomposition smaller than the new one, which has a big change in weight after \(\sim 30\) minutes.

As for the TGA of the molybdenum trisulfide, the latter shows a \(20\%\) weight loss after 90 minutes of ramping temperature up to \(500^\circ\text{C}\). This gives rise to a new interesting idea for future work: a heat treatment on \(\text{MoS}_3\) leading partially to \(\text{MoS}_2\) could improve the activity of the catalyst (see ch. 5).
Fig. 3.18 TGA of Thiomolybdate and Molybdate run in air from room T to 250°C at 5°C/min (a), with 1 hour hold at 250°C (b).
Fig. 3. TGA run in nitrogen from room T to 500°C at 5°C/min and hold at 500°C for 2 hours of Ammonium Tetrathiomolybdate (a) and MoS₂/Ketjenblack carbon (b).
3.1.3 Electrochemical results: GNP support at different S:Mo ratio in ethylene glycol

Let’s have a look at the behavior of the catalysts made in ethylene glycol. Since some experiments have been done by other members of the group I just report the LSV plot for better understanding my work.

4:1 S:Mo ratio:

- 0.068 g (NH₄)₂MoS₄
- 0 g Na₂S·9H₂O
- 0.05 g GNP (GNP:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml ethylene glycol

![LSV plot](image)

Fig. 3.20 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS₂/GNP, S:Mo = 4:1 in ethylene glycol.
Tab. 3.7 Summary of results for MoS$_2$/GNP, S:Mo = 4:1 in EG after 0 (before and after the 1$^\text{st}$ LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_S$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area mF/cm$^2$</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - before</td>
<td>8.0</td>
<td>18.3</td>
<td>21.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0 - after</td>
<td>4.5</td>
<td>20.6</td>
<td>23.8</td>
<td>41</td>
<td>-9.3 $\times$ 10$^{-4}$</td>
<td>-166</td>
</tr>
<tr>
<td>10</td>
<td>6.7</td>
<td>20.4</td>
<td>22.9</td>
<td>40</td>
<td>-6.7 $\times$ 10$^{-4}$</td>
<td>-168</td>
</tr>
<tr>
<td>50</td>
<td>6.7</td>
<td>22.5</td>
<td>22.2</td>
<td>46</td>
<td>-1.6 $\times$ 10$^{-3}$</td>
<td>-176</td>
</tr>
<tr>
<td>100</td>
<td>6.7</td>
<td>24.3</td>
<td>21.7</td>
<td>38</td>
<td>-3.1 $\times$ 10$^{-4}$</td>
<td>-171</td>
</tr>
<tr>
<td>200</td>
<td>6.5</td>
<td>25.8</td>
<td>21.1</td>
<td>39</td>
<td>-3.7 $\times$ 10$^{-4}$</td>
<td>-174</td>
</tr>
</tbody>
</table>

The first impression of these data is that the activity looks considerably improved. The charge-transfer resistance is low and the potential at -10 mA/cm$^2$ is on average ~ 20 mV higher than the catalysts made in water. The other parameters were constantly stable. However, the LSV plot (Fig. 3.20) shows some instability in the catalyst after the stability tests.

5:1 S:Mo ratio → Weight obtained: 75.5 mg from:

- 0.068 g (NH$_4$)$_2$MoS$_4$
- 0.063 g Na$_2$S·9H$_2$O
- 0.05 g GNP (GNP:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml ethylene glycol
Fig. 3.21 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1 in ethylene glycol.

Fig. 3.22 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/GNP, S:Mo = 5:1 in ethylene glycol.
Fig. 3.23 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 5:1 in ethylene glycol.

Fig. 3.24 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/GNP, S:Mo = 5:1 in ethylene glycol.
Tab. 3.8 Summary of results for MoS$_3$/GNP, S:Mo = 5:1 in ethylene glycol after 0 (before and after the 1st LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.5</td>
<td>37.8</td>
<td>16.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.5</td>
<td>32.8</td>
<td>19.5</td>
<td>42</td>
<td>$-5.2 \times 10^{-4}$</td>
<td>-183</td>
</tr>
<tr>
<td>10</td>
<td>5.6</td>
<td>35.5</td>
<td>19.2</td>
<td>40</td>
<td>$-3.6 \times 10^{-4}$</td>
<td>-179</td>
</tr>
<tr>
<td>50</td>
<td>5.5</td>
<td>40.5</td>
<td>18.3</td>
<td>38</td>
<td>$-1.8 \times 10^{-4}$</td>
<td>-182</td>
</tr>
<tr>
<td>100</td>
<td>5.6</td>
<td>51.2</td>
<td>17.3</td>
<td>40</td>
<td>$-2.7 \times 10^{-4}$</td>
<td>-185</td>
</tr>
<tr>
<td>200</td>
<td>5.5</td>
<td>61.2</td>
<td>15.9</td>
<td>41</td>
<td>$-2.6 \times 10^{-4}$</td>
<td>-187</td>
</tr>
</tbody>
</table>

The weight of this catalyst is 25 % lower than the expected one, yet the catalyst exhibits a better activity than its corresponding one in water. This is a great result, ethylene glycol is still showing a significant improvement in the activity of the catalyst. As in the 4:1 ratio, all the previous plots for the 5:1 ratio show a bit of instability and the curves after the stability tests go always worse. In particular we see a small change in the potential at -10 mA/cm$^2$ and in the exchange current, while a big change occurs in the charge-transfer resistance. This is probably due to the deterioration of the catalyst caused by the electrochemical tests.

At this point, since the MoS$_3$/GNP, S:Mo = 5:1 catalyst made in ethylene glycol looks already worse than the 4:1, we can say that in this case the extra sulfur poisons the catalyst at lower concentration than in the ones made with water. For this reason, we didn’t do further experiments at higher S:Mo ratio with GNP and ethylene glycol.

In conclusion of the work with the GNP, a plot with the LSVs at 0 cycles for 4:1 and 5:1 in water and ethylene glycol is reported (Fig. 3.25).
3.1.4 Electrochemical results: KETJENBLACK support at different S:Mo ratio in water

Another important change we made in the old recipe was to change the carbon support. In this section we report some experiments similar to the ones done on GNP, but this time using KETJENBLACK EC-300J Highly Electro-Conductive Carbon Black as support.
4:1 S:Mo ratio:

- 0.068 g (NH₄)₂MoS₄
- 0 g Na₂S·9H₂O
- 0.05 g KETJENBLACK (KETJEN:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml water

Fig. 3.26 Current density-potential curves from LSV after 0, 10, 50, 100 cycles of CV stability tests for MoS₃/KETJEN, S:Mo = 4:1.
Tab. 3.9 Summary of results for MoS$_3$/KETJEN, S:Mo = 4:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.3</td>
<td>190.0</td>
<td>11.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.9</td>
<td>169.5</td>
<td>12.4</td>
<td>56</td>
<td>-2.0 x 10$^{-3}$</td>
<td>-208</td>
</tr>
<tr>
<td>10</td>
<td>7.2</td>
<td>160.8</td>
<td>13.1</td>
<td>56</td>
<td>-2.0 x 10$^{-3}$</td>
<td>-207</td>
</tr>
<tr>
<td>50</td>
<td>6.3</td>
<td>156.7</td>
<td>13.6</td>
<td>54</td>
<td>-1.4 x 10$^{-3}$</td>
<td>-208</td>
</tr>
<tr>
<td>100</td>
<td>6.0</td>
<td>154.3</td>
<td>13.8</td>
<td>54</td>
<td>-1.3 x 10$^{-3}$</td>
<td>-208</td>
</tr>
</tbody>
</table>

The main problem in using Ketjenblack in water is that the carbon does not disperse well. Indeed, in every experiment with Ketjenblack and water, after the mixing, we could always see large agglomerated particles floating in the solvent even after many hours of sonication. Thus, this is definitely one of the main reasons for the previous bad results.

5:1 S:Mo ratio → Weight obtained: 107.71 mg from:

- 0.068 g (NH$_4$)$_2$MoS$_4$
- 0.063 g Na$_2$S·9H$_2$O
- 0.05 g KETJENBLACK (KETJEN:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml water
Fig. 3.27 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS\textsubscript{2}/KETJEN, S:Mo = 5:1.

Fig. 3.28 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS\textsubscript{2}/KETJEN, S:Mo = 5:1.
Fig. 3.29 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.30 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1.
Tab. 3.10 Summary of results for MoS\textsubscript{3}/KETJEN, S:Mo = 5:1 after 0 (before and after the 1\textsuperscript{st} LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Rs (Ω)</th>
<th>R\textsubscript{ct} (Ω)</th>
<th>CPE/Area mF/cm\textsuperscript{2}</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm\textsuperscript{2})</th>
<th>Potential at -10 mA/cm\textsuperscript{2} (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.3</td>
<td>30.4</td>
<td>17.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.2</td>
<td>29.5</td>
<td>18.8</td>
<td>43</td>
<td>-8.1 x 10\textsuperscript{-4}</td>
<td>-176</td>
</tr>
<tr>
<td>10</td>
<td>5.2</td>
<td>32.0</td>
<td>18.9</td>
<td>39</td>
<td>-2.9 x 10\textsuperscript{-4}</td>
<td>-178</td>
</tr>
<tr>
<td>50</td>
<td>5.2</td>
<td>34.7</td>
<td>19.7</td>
<td>40</td>
<td>-3.8 x 10\textsuperscript{-4}</td>
<td>-178</td>
</tr>
<tr>
<td>100</td>
<td>5.2</td>
<td>42.6</td>
<td>18.3</td>
<td>40</td>
<td>-3.0 x 10\textsuperscript{-4}</td>
<td>-181</td>
</tr>
<tr>
<td>200</td>
<td>5.1</td>
<td>49.9</td>
<td>17.6</td>
<td>38</td>
<td>-1.5 x 10\textsuperscript{-4}</td>
<td>-184</td>
</tr>
</tbody>
</table>

As in the GNP case with water, also the activity of MoS\textsubscript{3} on Ketjenblack in water in significantly improved thanks to the initial extra sulfur. Indeed, the potential at -10 mA/cm\textsuperscript{2} is increased by ~ 30 mV and the Tafel slope is reduced by ~ 15 mV/dec. The charge-transfer resistance is an indicator of the difficulty of the process. We usually got the best activity at an R\textsubscript{ct} lower than 30 ohm. The previous results were so encouraging that we went further with the experiments up to the S:Mo = 7:1. However, since we are usually comparing the results before the stability test, we didn’t perform the CV stability on this catalyst, but we tried to have higher loading on the electrode. Theoretically, all the layers of MoS\textsubscript{3} should be active until the thickness of the film reaches a plateau value that does not allow the catalyst to be in contact with the electrolyte.

The MoS\textsubscript{3}/Ketjenblack 7:1 ratio has been loaded at 250/350/500 μg/cm\textsuperscript{2}. This process is done by just adding more droplets in the ink deposition procedure. In particular, 350 μg/cm\textsuperscript{2} is reached with 7 ink droplets and 500 μg/cm\textsuperscript{2} with 10 ink droplets.
7:1 S:Mo ratio → Weight obtained: 99.19 mg from:

- 0.068 g (NH$_4$)$_2$MoS$_4$
- 0.188 g Na$_2$S·9H$_2$O
- 0.05 g KETJENBLACK (KETJEN:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml water

![Current density-potential curves from LSV at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.](image)

Fig. 3.31 Current density-potential curves from LSV at 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 7:1.
Fig. 3.32 Current density vs Potential curves from CV at 250, 350 and 500 μg/cm² loading for MoS₂/KETJEN, S:Mo = 7:1.

Fig. 3.33 Impedance curves from EIS at 250, 350 and 500 μg/cm² loading for MoS₂/KETJEN, S:Mo = 7:1.
Fig. 3.34 Tafel plot from LSV at 250, 350 and 500 μg/cm² loading for MoS₃/KETJEN, S:Mo = 7:1.

Tab. 3.11 Summary of results for MoS₃/KETJEN, S:Mo = 7:1 at 250, 350 and 500 μg/cm² loading.

<table>
<thead>
<tr>
<th>Loading μg/cm²</th>
<th>Rₛ (Ω)</th>
<th>Rₓₜ (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm²)</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>5.3</td>
<td>22.8</td>
<td>23.4</td>
<td>50</td>
<td>4.4 x 10⁻³</td>
<td>-168</td>
</tr>
<tr>
<td>350</td>
<td>5.4</td>
<td>18.9</td>
<td>28.8</td>
<td>46</td>
<td>2.9 x 10⁻³</td>
<td>-163</td>
</tr>
<tr>
<td>500</td>
<td>5.3</td>
<td>16.6</td>
<td>44.5</td>
<td>49</td>
<td>5.4 x 10⁻³</td>
<td>-160</td>
</tr>
</tbody>
</table>

The previous data show first that the MoS₃/Ketjenblack 7:1 in water is in some way better than the lower S:Mo ratios, e.g. the potential at -10 mA/cm² and the exchange current are higher and the charge-transfer resistance is lower. On the contrary, the Tafel slope is too
high, meaning that the mechanism is a bit changed. We believe that the extra sulfur modified the local charge density distribution, thus allowing the reaction to occur more with a Volmer-Tafel mechanism. The CV plot shows bigger currents and a more accentuated reduction peak of MoS$_3$ at higher loading, as expected.

The results at higher loading were predictable. The charge-transfer resistance is reduced, the capacitance, the exchange current and the potential are increased. The higher amount of carbon is mostly responsible of the increased capacitance, but as for the other parameters, they are improved thanks to the higher amount of MoS$_3$, which seems to be active in all its layers. A summary of the loading trend is showed in fig. 3.35.

![Graph showing potential and capacitance vs. loading for MoS$_3$/Ketjenblack at S:Mo = 7:1](image)

*Fig. 3.35 Curves for potential at -10 mA/cm$^2$ and capacitance at different loadings for MoS$_3$/Ketjenblack at S:Mo = 7:1*
In order to have a better understanding of the differences that the change of the initial S:Mo ratio made, we now report a comparison plot of the first LSV data (at 0 cycles of CV stability tests) for all the different ratio: at 0 cycles we almost always obtained the best activity (Fig. 3.36).

![Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS₃/KETJENBLACK, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported.](image)

**Fig. 3.36** Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS₃/KETJENBLACK, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported.

The plot shows a trend in the data from which we can get that the extra sulfur enhances the activity by increasing the yield to MoS₃. As in the GNP case in water, more sulfur keeps increasing the activity, even though I already underlined that not all the parameters are improved. As we clearly see in the 7:1 ratio, at higher potential the extra S gives more current density. We would probably need to correct the higher S:Mo ratio in order to fairly
take into account this extra current coming from the sulfur, which is probably responsible of the apparently better performances.

3.1.5 Electrochemical results: KETJENBLACK support at different S:Mo ratio in ethylene glycol

As was previously done with the catalysts on GNP support, ethylene glycol is used as solvent for dispersing the reactants. Ketjenblack has a poor solubility in water, however the ethylene glycol worked perfectly for this purpose. The particles of Ketjenblack were significantly reduced in size few minutes after the flask was put in the sonicator. The solution became homogeneous and black, and there were not visible particles.

The results we obtained with Ketjenblack in ethylene glycol made us believe that the catalysts synthesized in this way were the best ones we could make. In this paragraph, we show the data obtained from MoS$_3$/Ketjenblack at S: Mo = 4/5/7:1 in ethylene glycol.

4:1 S:Mo ratio:

- 0.068 g (NH$_4)_2$MoS$_4$
- 0 g Na$_2$S·9H$_2$O
- 0.05 g KETJENBLACK (KETJEN:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml ethylene glycol
Fig. 3.37 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/KETJEN, S:Mo = 4:1 in ethylene glycol.

Tab. 3.12 Summary of results for MoS$_2$/KETJEN, S:Mo = 4:1 in ethylene glycol after 0 (before and after the 1st LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.4</td>
<td>159.3</td>
<td>10.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>7.5</td>
<td>103.7</td>
<td>11.3</td>
<td>45</td>
<td>-4.8 x 10$^{-4}$</td>
<td>-193</td>
</tr>
<tr>
<td>10</td>
<td>6.8</td>
<td>100.7</td>
<td>12.1</td>
<td>45</td>
<td>-5.3 x 10$^{-4}$</td>
<td>-193</td>
</tr>
<tr>
<td>50</td>
<td>7.2</td>
<td>99.8</td>
<td>12.6</td>
<td>45</td>
<td>-5.0 x 10$^{-4}$</td>
<td>-192</td>
</tr>
<tr>
<td>100</td>
<td>8.1</td>
<td>100.6</td>
<td>12.6</td>
<td>43</td>
<td>-3.5 x 10$^{-4}$</td>
<td>-191</td>
</tr>
<tr>
<td>200</td>
<td>7.4</td>
<td>102.6</td>
<td>13.1</td>
<td>46</td>
<td>-6.1 x 10$^{-4}$</td>
<td>-194</td>
</tr>
</tbody>
</table>
As in the case with GNP, again the activity improved when ethylene glycol was used, even though the performance looks bad compared to other previous catalysts. The charge-transfer resistance in particular is significantly lower than the MoS$_3$/Ketjenblack 4:1 in water. This makes us confident that the MoS$_3$/Ketjenblack in ethylene glycol could be much better than the one made in water.

5:1 S:Mo ratio → Weight obtained: 93.54 mg from:

- 0.068 g (NH$_4$)$_2$MoS$_4$
- 0.063 g Na$_2$S·9H$_2$O
- 0.05 g KETJENBLACK (KETJEN:MoS$_3$ = 1:1)
- 10 ml 0.5 M H$_2$SO$_4$ (in H$_2$O)
- 150 ml ethylene glycol

Fig. 3.38 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.
Fig. 3.39 Current density vs Potential curves from CV after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Fig. 3.40 Impedance curves from EIS after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/KETJEN, S:Mo = 5:1 in ethylene glycol.
Fig. 3.41 Tafel plot from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol.

Tab. 3.13 Summary of results for MoS$_3$/KETJEN, S:Mo = 5:1 in ethylene glycol after 0 (before and after the 1st LSV), 10, 50, 100, 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_S$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area mF/cm$^2$</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.9</td>
<td>20.5</td>
<td>22.5</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.7</td>
<td>20.8</td>
<td>26.7</td>
<td>38</td>
<td>$-4.6 \times 10^{-4}$</td>
<td>-166</td>
</tr>
<tr>
<td>10</td>
<td>5.8</td>
<td>22.9</td>
<td>26.3</td>
<td>36</td>
<td>$-2.6 \times 10^{-4}$</td>
<td>-166</td>
</tr>
<tr>
<td>50</td>
<td>5.8</td>
<td>24.6</td>
<td>25.6</td>
<td>37</td>
<td>$-2.9 \times 10^{-4}$</td>
<td>-168</td>
</tr>
<tr>
<td>100</td>
<td>5.7</td>
<td>26.5</td>
<td>24.9</td>
<td>36</td>
<td>$-2.2 \times 10^{-4}$</td>
<td>-169</td>
</tr>
<tr>
<td>200</td>
<td>5.7</td>
<td>28.3</td>
<td>24.6</td>
<td>36</td>
<td>$-1.8 \times 10^{-4}$</td>
<td>-171</td>
</tr>
</tbody>
</table>
The surprising results of this catalyst make us consider it as the best one we made so far. The weight of the catalyst is close to 100 mg but lower (differently from the previous cases), meaning that we lost a small part of the catalyst. The charge-transfer process can easily occur thanks to a low resistance; the capacitance is increased by ~ 8-10 mF/cm² but the amount of carbon is still the same, meaning that our catalyst is able to store more charges than before. The exchange current is of the same order of magnitude as before while the potential at -10 mA/cm² is the one of the highest even in the literature. The catalyst looks very stable, as we can see from the LSV and Tafel plots (Fig. 3.38 and 3.41), from which we get surprising low Tafel slopes. The mechanism of reaction is in between the Volmer–Heyrovsky and the Volmer-Tafel. Finally, the CV plot (Fig. 3.39) tells us that the MoS₃ is completely converted in MoS₂ between 10 and 50 cycles of stability tests. The complete conversion to MoS₂ doesn’t necessarily mean a better activity, as we see from Tab. 3.13: the best values are reached between 0 and 10 cycles, although all the numbers are fairly close one another.

7:1 S:Mo ratio:

- 0.068 g (NH₄)₂MoS₄
- 0.188 g Na₂S·9H₂O
- 0.05 g KETJENBLACK (KETJEN:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml ethylene glycol
Fig. 3.42 Current density-potential curves from LSV after 0,10,50,100,200 cycles of CV stability tests for MoS$_2$/KETJEN, S:Mo = 7:1 in ethylene glycol.

Tab. 3.14 Summary of results for MoS$_2$/KETJEN, S:Mo = 7:1 in ethylene glycol after 0 (before and after the 1st LSV),10,50,100,200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area mF/cm$^2$</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.6</td>
<td>61.7</td>
<td>12.6</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>4.9</td>
<td>38.7</td>
<td>15.9</td>
<td>45</td>
<td>1.1 x 10$^{-3}$</td>
<td>-176</td>
</tr>
<tr>
<td>10</td>
<td>5.0</td>
<td>32.7</td>
<td>18.4</td>
<td>42</td>
<td>7.5 x 10$^{-4}$</td>
<td>-172</td>
</tr>
<tr>
<td>50</td>
<td>5.1</td>
<td>31.9</td>
<td>19.4</td>
<td>40</td>
<td>5.1 x 10$^{-4}$</td>
<td>-170</td>
</tr>
<tr>
<td>100</td>
<td>5.1</td>
<td>32.6</td>
<td>20.3</td>
<td>39</td>
<td>3.8 x 10$^{-4}$</td>
<td>-170</td>
</tr>
<tr>
<td>200</td>
<td>4.9</td>
<td>35.7</td>
<td>20.4</td>
<td>38</td>
<td>2.9 x 10$^{-4}$</td>
<td>-172</td>
</tr>
</tbody>
</table>
MoS$_3$/Ketjenblack 7:1 ratio in ethylene glycol shows worse performances than the 5:1 ratio. Even though the results are still good, I believe that the extra sulfur already started to poison the catalyst. It’s interesting to underline that the capacitance has been reduced a lot (~ 10 mF/cm$^2$), meaning that the catalyst has also half the ability to retain charges as a capacitor.

As before, we now compare the first LSV curve (at 0 cycles of CV stability tests) for all the different ratio of MoS$_3$ on Ketjenblack made in ethylene glycol (Fig. 3.43).

![Fig. 3.43 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/KETJENBLACK in ethylene glycol, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported.](image)

The trend in the data of the previous plot is clearly similar to the GNP one in ethylene glycol. The extra sulfur enhances the activity by increasing the yield to MoS$_3$, but at the same time it interferes with the atomic structure of the catalyst, thus blocking some active sites. When the
amount of sulfur reaches a critical value, the advantage of the increased yield is overtaken by the disadvantage of the reduced activity. In this way, we found that the best S:Mo ratio for MoS$_3$ on Ketjenblack in ethylene glycol is 5:1. It is important to note that, differently from the Ketjenblack in water, here the extra sulfur is strongly part of the MoS$_3$ structure and there is not elemental sulfur in the catalyst which gives more current density at higher potentials (see XPS data in sections 3.1.9 and 3.1.10).

To have a complete picture of the effect of the Ketjenblack carbon, we report the final comparison plot for Ketjenblack (Fig. 3.44).

![Graph showing current density-potential curves](image)

*Fig. 3.44 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/KETJEN, at 4:1, 5:1 and 7:1, made in water and ethylene glycol. Pt data are also reported.*
3.1.6 Electrochemical results: VULCAN support at different S:Mo ratio in water

The last type of carbon we analyzed in this project is the VULCAN® XC72R, a soft carbon delivering high conductivity at relatively low loading levels. The experiments are the same performed on the Ketjenblack carbon, with the only difference that we didn’t test the S:Mo = 7:1 ratio in ethylene glycol.

4:1 S:Mo ratio:

- 0.068 g \((\text{NH}_4)_2\text{MoS}_4\)
- 0 g Na\(_2\)S·9H\(_2\)O
- 0.05 g VULCAN (VULCAN:MoS\(_3\) = 1:1)
- 10 ml 0.5 M H\(_2\)SO\(_4\) (in H\(_2\)O)
- 150 ml water

![Current density-potential curve](image)

*Fig. 3.45 Current density-potential curves from LSV after 0, 10, 50, 100 cycles of CV stability tests for MoS\(_3\)/VULCAN, S:Mo = 4:1.*
Tab. 3.15 Summary of results for MoS₃/VULCAN, S:Mo = 4:1 after 0 (before and after the 1st LSV), 10, 50, 100 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Rₛ (Ω)</th>
<th>Rₑ (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm²)</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.2</td>
<td>39.6</td>
<td>10.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.4</td>
<td>57.7</td>
<td>8.7</td>
<td>49</td>
<td>1.5 x 10⁻³</td>
<td>-188</td>
</tr>
<tr>
<td>10</td>
<td>5.3</td>
<td>132.6</td>
<td>6.0</td>
<td>51</td>
<td>8.2 x 10⁻⁴</td>
<td>-210</td>
</tr>
<tr>
<td>50</td>
<td>5.4</td>
<td>133.0</td>
<td>5.9</td>
<td>48</td>
<td>5.2 x 10⁻⁴</td>
<td>-208</td>
</tr>
<tr>
<td>100</td>
<td>5.5</td>
<td>233.6</td>
<td>4.0</td>
<td>63</td>
<td>1.9 x 10⁻³</td>
<td>-233</td>
</tr>
</tbody>
</table>

Like Ketjenblack carbon, Vulcan is not very soluble in water and I encountered a behavior similar to the Ketjenblack after the mixing with water. As we can get from the previous results, this is probably the reason of the bad performance of this carbon. Fig. 3.45 and the diversified results of Tab. 3.15 show that the catalyst loses its properties after the stability tests, hence we can say that it is not stable. However, in order to have a clear idea that the extra sulfur is always improving the activity, even in the worst cases, we made MoS₃/Vulcan at 5:1 ratio, but we stopped the tests after 50 cycles.

5:1 S:Mo ratio → Weight obtained: 106.12 mg from:

- 0.068 g (NH₄)₂MoS₄
- 0.063 g Na₂S·9H₂O
- 0.05 g VULCAN (VULCAN:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml water
Fig. 3.46 Current density-potential curves from LSV after 0, 10, 50 cycles of CV stability tests for MoS$_2$/VULCAN, S:Mo = 5:1.

Fig. 3.47 Current density vs Potential curves from CV after 0, 10, 50 cycles of CV stability tests for MoS$_2$/VULCAN, S:Mo = 5:1.
Fig. 3.48 Impedance curves from EIS after 0, 10, 50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1.

Fig. 3.49 Tafel plot from LSV after 0, 10, 50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 5:1.
Tab. 3.16 Summary of results for MoS3/VULCAN, S:Mo = 5:1 after 0 (before and after the 1st LSV), 10, 50 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>Rs (Ω)</th>
<th>Rct (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current mA/cm²</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.6</td>
<td>62.7</td>
<td>6.9</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.4</td>
<td>44.0</td>
<td>9.6</td>
<td>43</td>
<td>4.7 x 10⁻⁴</td>
<td>-187</td>
</tr>
<tr>
<td>10</td>
<td>6.0</td>
<td>62.1</td>
<td>9.4</td>
<td>39</td>
<td>1.4 x 10⁻⁴</td>
<td>-191</td>
</tr>
<tr>
<td>50</td>
<td>5.7</td>
<td>82.0</td>
<td>8.0</td>
<td>39</td>
<td>1.1 x 10⁻⁴</td>
<td>-195</td>
</tr>
</tbody>
</table>

As we expected, the activity is increased with respect to the 4:1 ratio, but the overall results are still poor. The extra sulfur made the catalyst more stable than in the 4:1 S:Mo case, thus we believe that the S-precursor decreases the repulsion forces between carbon and water. In this way the Vulcan can play its natural role as support, by increasing its electronic coupling with the catalyst.

Since the results obtained with water remain worse than the ones with ethylene glycol, I chose to keep going just with the latter, neglecting the use of water. In the next paragraph the results obtained with Vulcan in ethylene glycol will confirm the theory that the ethylene glycol has indeed many more advantages than water. As for now, I just report the last catalyst made in water, MoS3/Vulcan at S:Mo = 7:1 ratio, which we tested up to 50 cycles of CV stability tests.
7:1 S:Mo ratio → Weight obtained: 97.28 mg from:

- 0.068 g \((\text{NH}_4)_2\text{MoS}_4\)
- 0.188 g \(\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}\)
- 0.05 g VULCAN (VULCAN:MoS\(_3\) = 1:1)
- 10 ml 0.5 M H\(_2\)SO\(_4\) (in H\(_2\)O)
- 150 ml water

**Fig. 3.50** Current density-potential curves from LSV after 0, 10, 50 cycles of CV stability tests for MoS\(_3\)/VULCAN, S:Mo = 7:1.

It is interesting to underline that in this case the CV stability tests in some way activated the catalyst and the activity increased after each cycles series.
Fig. 3.51 Current density vs Potential curves from CV after 0, 10, 50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1.

Fig. 3.52 Impedance curves from EIS after 0, 10, 50 cycles of CV stability tests for MoS$_3$/VULCAN, S:Mo = 7:1.
Fig. 3.53 Tafel plot from LSV after 0, 10, 50 cycles of CV stability tests for MoS$_2$/VULCAN, S:Mo = 7:1.

Tab. 3.17 Summary of results for MoS$_2$/VULCAN, S:Mo = 7:1 after 0 (before and after the 1st LSV), 10, 50 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.7</td>
<td>66.2</td>
<td>8.7</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.0</td>
<td>34.9</td>
<td>14.8</td>
<td>47</td>
<td>$1.5 \times 10^{-3}$</td>
<td>-180</td>
</tr>
<tr>
<td>10</td>
<td>5.5</td>
<td>23.8</td>
<td>20.1</td>
<td>43</td>
<td>$1.0 \times 10^{-3}$</td>
<td>-172</td>
</tr>
<tr>
<td>50</td>
<td>5.4</td>
<td>23.2</td>
<td>22.6</td>
<td>38</td>
<td>$4.0 \times 10^{-4}$</td>
<td>-168</td>
</tr>
</tbody>
</table>
The CV plot (Fig. 3.51) does not show any improvement in the reduction peak of MoS$_3$ but for the first cycle, in which all the catalyst has been converted in MoS$_2$. This is even stranger if we look at the other plots, because there is a clear improvement in the performances. My suggestion is that there was elemental sulfur inside at the begin of the tests. The electrochemical analysis in an aqueous sulfuric acid solution is usually able to wash away the elemental sulfur, who is blocking some active sites. After 50 cycles the catalyst activity resulted in one of the best ever obtained. However, this big change in the parameters makes us believe that the instability is such that we can’t say that this is a very good catalyst.

As usual, a comparison plot at the end of this paragraph shows the trend in the catalyst on Vulcan support made in water (Fig. 3.54).

*Fig. 3.54 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/VULCAN, at 4:1, 5:1 and 7:1 S:Mo ratio. Pt data are also reported.*
Again, we notice that the trend is in agreement with the other carbon supports in water. The highest S:Mo ratio looks better than the other ones, but it is more unstable, as the one at 4:1 ratio. The dispersion problem for the carbon is probably the main reason of this instability and it can be solved by using ethylene glycol, as we already saw with GNP and KETJENBLACK. As for the 7:1 ratio, the plot shows that the elemental sulfur is interfering a bit with the test, by giving us more current density at higher potential. As already underlined, this can give us apparently good results, which in fact are just coming from this disturbance.

3.1.7 Electrochemical results: VULCAN support at different S:Mo ratio in ethylene glycol

The final experiments we performed to decide which support, at which S:Mo ratio, and which solvent is better for MoS₃ activity are done on the catalysts made on Vulcan in ethylene glycol. Since the behavior of Vulcan both in water and ethylene glycol resulted very similar to the Ketjenlack one, we synthesized them just at 4:1 and 5:1 ratio. They were enough to confirm the hypothesis that, although Ketjenblack and Vulcan have different surface area, for our synthesis procedure it does not make essentially any difference to use one or the other.

4:1 S:Mo ratio:

- 0.068 g (NH₄)₂MoS₄
- 0 g Na₂S·9H₂O
- 0.05 g VULCAN (VULCAN:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml ethylene glycol
Fig. 3.55 Current density-potential curves from LSV after 0,10,50,100 cycles of CV stability tests for MoS$_2$/VULCAN in ethylene glycol, S:Mo = 4:1.

Tab. 3.18 Summary of results for MoS$_2$/VULCAN, S:Mo = 4:1 in ethylene glycol after 0 (before and after the 1$^{st}$ LSV),10,50,100 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>6.2</td>
<td>51.5</td>
<td>8.1</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>6.4</td>
<td>49.6</td>
<td>8.8</td>
<td>41</td>
<td>-3.9 x 10$^{-4}$</td>
<td>-180</td>
</tr>
<tr>
<td>10</td>
<td>7.1</td>
<td>54.3</td>
<td>8.8</td>
<td>38</td>
<td>-1.9 x 10$^{-5}$</td>
<td>-217</td>
</tr>
<tr>
<td>50</td>
<td>7.2</td>
<td>59.8</td>
<td>8.7</td>
<td>38</td>
<td>-1.8 x 10$^{-5}$</td>
<td>-218</td>
</tr>
<tr>
<td>100</td>
<td>6.2</td>
<td>64.6</td>
<td>8.4</td>
<td>40</td>
<td>-2.5 x 10$^{-5}$</td>
<td>-222</td>
</tr>
</tbody>
</table>
Despite the activity, which is not very good, it is remarkable to say that this catalyst confirm the idea that using ethylene glycol improves the stability of the catalyst. This means that, even after many cycles of CV stability tests, all the parameters do not have big changes. Usually good stability means also that the Tafel slope is low enough that the reaction does not change mechanism during the tests, which is the case of the previous catalyst.

5:1 S:Mo ratio → Weight obtained: 91.3 mg from:

- 0.068 g (NH₄)₂MoS₄
- 0.063 g Na₂S·9H₂O
- 0.05 g VULCAN (VULCAN:MoS₃ = 1:1)
- 10 ml 0.5 M H₂SO₄ (in H₂O)
- 150 ml ethylene glycol

Fig. 3.56 Current density-potential curves from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS₃/VULCAN in ethylene glycol, S:Mo = 5:1.
Fig. 3.57 Current density vs Potential curves from CV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/VULCAN in ethylene glycol, S:Mo = 5:1.

Fig. 3.58 Impedance curves from EIS after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_2$/VULCAN in ethylene glycol, S:Mo = 5:1.
Fig. 3.59 Tafel plot from LSV after 0, 10, 50, 100, 200 cycles of CV stability tests for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1.

Tab. 3.19 Summary of results for MoS$_3$/VULCAN in ethylene glycol, S:Mo = 5:1 after 0 (before and after the 1$^{st}$ LSV), 10, 50, 100 and 200 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>$R_s$ ($\Omega$)</th>
<th>$R_{ct}$ ($\Omega$)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-before</td>
<td>5.5</td>
<td>26.0</td>
<td>16.8</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0-after</td>
<td>5.8</td>
<td>21.7</td>
<td>22.0</td>
<td>41</td>
<td>8.9 x 10^{-4}</td>
<td>-167</td>
</tr>
<tr>
<td>10</td>
<td>5.8</td>
<td>21.1</td>
<td>24.3</td>
<td>38</td>
<td>4.6 x 10^{-4}</td>
<td>-165</td>
</tr>
<tr>
<td>50</td>
<td>5.6</td>
<td>24.7</td>
<td>24.4</td>
<td>37</td>
<td>3.1 x 10^{-4}</td>
<td>-168</td>
</tr>
<tr>
<td>100</td>
<td>5.3</td>
<td>28.1</td>
<td>22.0</td>
<td>37</td>
<td>2.5 x 10^{-4}</td>
<td>-171</td>
</tr>
<tr>
<td>200</td>
<td>5.8</td>
<td>30.2</td>
<td>21.8</td>
<td>36</td>
<td>1.8 x 10^{-4}</td>
<td>-172</td>
</tr>
</tbody>
</table>

Table 3.19 shows some surprising results. Not only MoS$_3$/Vulcan 5:1 is better than the 4:1 one and the corresponding catalyst made in water, but it also looks to have a behavior similar
to the MoS$_3$/Ketjenblack 5:1 in ethylene glycol. Indeed the activities of these two catalysts resulted the best ones and they both look stable.

Since Ketjenblack and Vulcan gave us very similar results, we decided not to proceed with Vulcan at 7:1 ratio and keep using just Ketjenblack as catalyst support. The reason of this decision came from another series of experiments, which will be showed later in this chapter (section 3.1.8): we explored the effects of lower and higher loading and Ketjenblack resulted in a best performance.

As usual, a summary plot of the first LSVs of the catalysts made on Vulcan carbon is reported (Fig. 3.60).

![Fig. 3.60 Current density-potential curves from LSV after 0 cycles of CV stability tests for MoS$_3$/VULCAN, at 4:1, 5:1 and 7:1, made in water and ethylene glycol. Pt data are also reported.](image-url)
3.1.8 Loading effect: GNP, KETJENBLACK and VULCAN supports

In the last paragraph we pointed out that Ketjenblack and Vulcan showed a similar behavior at 250 μg/cm², by giving the same values of activity at the corresponding different S:Mo ratio and with different solvents. One way to better understand the role of these carbon supports is to test the activity of the catalyst at different loadings on the electrode. This was done easily by just changing the number of ink droplets which were deposited on the electrode. Knowing that one droplet corresponds to 50 μg/cm², the electrode was loaded with 50, 150, 250, 350 and 500 μg/cm², by drop casting respectively 1, 3, 5, 7 and 10 ink droplets on the electrode. The tests were carried on MoS₃ on GNP, Ketjenblack and Vulcan at 5:1 ratio. For sake of simplicity just the LSV and summary plots are reported. Since the Ketjenblack showed the best results, we tried to go further by loading the electrode at 1 mg/cm², by using 10 droplets of an ink which had double the concentration of the usual ink.
MoS$_2$/GNP

Fig. 3.61 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 $\mu$g/cm$^2$ loading for MoS$_2$/GNP, S:Mo = 5:1.

Fig. 3.62 Summary of capacitance and potential at -10 mA/cm$^2$ vs loading for MoS$_2$/GNP, S:Mo = 5:1.
MoS$_3$/KETJEN

Fig. 3.63 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 μg/cm$^2$ loading for MoS$_3$/KETJEN, S:Mo = 5:1.

Fig. 3.64 Summary of capacitance and potential at -10 mA/cm$^2$ vs loading for MoS$_3$/KETJEN, S:Mo = 5:1.
Fig. 3.65 Current density-potential curves from LSV after 0 cycles of CV stability tests at 50, 150, 250, 350 and 500 μg/cm² loading for MoS₃/VULCAN, S:Mo = 5:1.

Fig. 3.66 Summary of capacitance and potential at -10 mA/cm² vs loading for MoS₃/VULCAN, S:Mo = 5:1.
As we expected, the trend in the data shows the capacitance and the potential at -10 mA/cm\(^2\) increase when the loading increases. GNP supported catalysts are weak at higher loadings (they detached from the electrode) and the reason of the bad results could be that the catalyst popped off because the layers were weakly bonded. Vulcan supported catalysts showed better results but still they don’t show a behavior as good as the Ketjenblack supported ones. This confirms the hypothesis that Ketjenblack is a more suitable support for this purpose. The highest loading we reached with MoS\(_3\)/Ketjenblack demonstrates that the assumption that the thickness of the film blocks part of the active sites is correct. We see a plateau in the plot and the activity didn’t increase at the same rate as before.

### 3.1.9 Material characterization: GNP, KETJENBLACK and VULCAN supports

(1) ICP and CHNS

As we already did before, the real composition of the catalysts have been detected by ICP-CHNS analysis. Table 3.20 reports a summary of the electrochemical and real composition parameters for MoS\(_3\) on GNP, Ketjenblack and Vulcan at 5:1 S:Mo ratio in ethylene glycol.
Tab. 3.20 Summary data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm² for MoS₃ on GNP, Ketjenblack and Vulcan, S:Mo = 5:1 in ethylene glycol after 0 cycles of CV stability tests

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% C</th>
<th>wt% H+N</th>
<th>wt% S</th>
<th>wt% Mo</th>
<th>wt% Sum</th>
<th>S:M o ratio</th>
<th>wt% S+Mo</th>
<th>R_{ct} (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current mA/cm²</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
<td>54.3</td>
<td>1.5</td>
<td>23.2</td>
<td>14.1</td>
<td>93.0</td>
<td>4.9</td>
<td>37.2</td>
<td>32.8</td>
<td>19.5</td>
<td>42</td>
<td>5.2 x 10^{-4}</td>
<td>-183</td>
</tr>
<tr>
<td>KETJEN</td>
<td>47.3</td>
<td>0.7</td>
<td>24.3</td>
<td>17.3</td>
<td>89.7</td>
<td>4.2</td>
<td>41.7</td>
<td>20.8</td>
<td>26.7</td>
<td>38</td>
<td>4.6 x 10^{-4}</td>
<td>-166</td>
</tr>
<tr>
<td>VULCAN</td>
<td>41.7</td>
<td>0.9</td>
<td>24.6</td>
<td>17.1</td>
<td>84.3</td>
<td>4.3</td>
<td>41.7</td>
<td>1.7</td>
<td>22</td>
<td>41</td>
<td>8.9 x 10^{-4}</td>
<td>-167</td>
</tr>
</tbody>
</table>
(2) SEM

The loading experiments raised new questions about the integrity and functionality of the catalyst film on the electrode. The drop casting technique is repeated multiple times, which may be a way to give rise to a layered structure and not to the desired homogeneous one. The composition and support of the catalyst do affect the dispersion of nanoparticles on the electrode. We investigated this effect by drop casting the ink on a glassy carbon plate 5 mm x 5 mm by using the same catalyst per unit area as before (50 μg/cm² per droplet, 250 μg/cm² in total).

Fig. 3.67 SEM images of MoS₃ on GNP in water S:Mo ratio 4:1 (a), 5:1 (b), 7:1 (c), 10:1 (d) Location: center of the plate; Zoom: x50
Fig. 3.68 SEM images of MoS$_3$ on GNP: S:Mo 4:1 ratio in water (a) and Ethylene Glycol (b), S:Mo ratio 5:1 in water (c) and Ethylene Glycol (d). Location: center of the plate; Zoom: x50

Fig. 3.69 SEM images of MoS$_3$ in Ethylene Glycol, S:Mo ratio 5:1 on GNP (a), KETJENBLACK (b) and VULCAN (c). Location: center of the plate; Zoom: x50
We used a profilometer to analyze a glassy carbon plate with 250 μg/cm² loading of MoS₃ on Ketjenblack carbon, synthesized with 5:1 S:Mo ratio in ethylene glycol. The tests showed the following results for the catalyst film:

- Roughness: 20-25 μm;
- Thickness: 10-12 μm;

In order to have a calibration for the profilometer we had to scratch out 20% - 30% of the film, so to have a baseline to measure the thickness.

The profilometer had the following set-up:

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Scan Type</strong></td>
<td>Standard Scan</td>
</tr>
<tr>
<td><strong>Stylus</strong></td>
<td>Radius: 12.5 μm</td>
</tr>
<tr>
<td><strong>Length</strong></td>
<td>4061.0 μm</td>
</tr>
<tr>
<td><strong>Duration</strong></td>
<td>180 sec</td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>0.075 μm/sample</td>
</tr>
<tr>
<td><strong>Force</strong></td>
<td>5.00 mg</td>
</tr>
<tr>
<td><strong>Measurement Range</strong></td>
<td>65.5 μm</td>
</tr>
</tbody>
</table>
Fig. 3.70 Profile of MoS$_3$/Ketjenblack film 5:1 in ethylene glycol deposited on a glassy carbon plate.

(4) TEM

In order to have a deeper look to the structure of the carbon support and of the catalyst, we took TEM pictures of GNP, Ketjenblack, Vulcan and MoS$_3$/Ketjenblack 5:1 in ethylene glycol (Fig. 3.71).
Fig. 3.71 TEM images at two different spots for each sample of xGNP (a) and (b), Ketjenblack (c) and (d), Vulcan (e) and (f), MoS$_3$/Ketjenblack in ethylene glycol, S:Mo ratio 5:1 (g) and (h).

We can see that Ketjenblack and Vulcan have almost the same nanostructure, while GNP looks different and unsuitable to host catalyst nanoparticles. The black spots on Fig. 3.71 (g) and (h) are the MoS$_3$ nanoparticles, which give us an idea of the dispersion of the catalyst on the carbon support.

(5) XPS

We performed the XPS tests and fitting of MoS$_3$ on GNP, Ketjenblack and Vulcan carbon supports made in ethylene glycol and we compared the results with the ICP analysis. Unfortunately the catalyst on GNP showed a very weak signal even after several tries and the result is not reliable.
Tab. 3.21 Compositions analysis of MoS\(_x\) electrocatalysts from XPS (top) and ICP-CHNS (bottom) made on GNP, Ketjen, Vulcan at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>composition from XPS (wt %)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>GNP</td>
<td>68.1</td>
<td>17.3</td>
</tr>
<tr>
<td>Ketjen</td>
<td>39.8</td>
<td>26.7</td>
</tr>
<tr>
<td>Vulcan</td>
<td>25.3</td>
<td>34.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition from ICP-CHNS (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GNP</td>
</tr>
<tr>
<td>Ketjen</td>
</tr>
<tr>
<td>Vulcan</td>
</tr>
</tbody>
</table>

XPS is a surface analysis. By comparing the two results we can see that in Ketjenblack the surface and inner composition are similar while in Vulcan the catalyst particles are more spread on the surface, so we have a less percentage of carbon in XPS analysis.

Tab. 3.22 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoS\(_x\) electrocatalysts pure from Sigma-Aldrich, supported on GNP, KetjenBlack and Vulcan, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo(^{3+}) (eV)</th>
<th>Mo(^{5+}) (eV)</th>
<th>Mo(^{6+}) (eV)</th>
<th>S(^{2-}) (eV)</th>
<th>S(^{2-}/S^{3-}) (eV)</th>
<th>S(^0) (eV)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS(_2)-Aldrich</td>
<td>229.8</td>
<td>-</td>
<td>232.9</td>
<td>162.7</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>GNP-EG(1:5)</td>
<td>230.0</td>
<td>-</td>
<td>233.9</td>
<td>162.7</td>
<td>163.7</td>
<td>164.3</td>
<td>8.8</td>
</tr>
<tr>
<td>KB-EG(1:5)</td>
<td>230.2</td>
<td>-</td>
<td>233.0</td>
<td>162.9</td>
<td>164.1</td>
<td>-</td>
<td>3.1</td>
</tr>
<tr>
<td>Vulcan-EG(1:5)</td>
<td>230.1</td>
<td>-</td>
<td>234.2</td>
<td>162.8</td>
<td>164.0</td>
<td>-</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Tab. 3.23 Chemical states and peak area ratios of MoS₃ electrocatalysts pure from Sigma-Aldrich, supported on GNP, KetjenBlack and Vulcan, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Chemical state</th>
<th>MoS₂-aldrich</th>
<th>GNP-EG(1:5)</th>
<th>KB-EG(1:5)</th>
<th>Vulcan-EG(1:5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo⁴⁺</td>
<td>94.0</td>
<td>95.7</td>
<td>99.2</td>
<td>99.8</td>
</tr>
<tr>
<td>Mo⁵⁺</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo⁶⁺</td>
<td>6.0</td>
<td>4.3</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>S²⁻ (basal)</td>
<td>100</td>
<td>13.4</td>
<td>28.3</td>
<td>31.5</td>
</tr>
<tr>
<td>S₂⁻/S³⁻*</td>
<td>0</td>
<td>33.1</td>
<td>71.7</td>
<td>68.5</td>
</tr>
<tr>
<td>S⁰</td>
<td>0</td>
<td>53.5</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Basal S²⁻; ** bridging S₂⁻ and/or apical S³⁻.

We can understand from the previous tables that our catalyst are pure MoS₃ without any oxides (which are related to Mo⁶⁺). Also, there is a relevant higher amount of bridging/apical S than basal S, which means that there are more active sites than in the commercial catalyst from Aldrich-Sigma Company. No elemental S was found in Ketjenblack nor in Vulcan: the idea that more S (5:1 ratio in this case) would have increased the yield to MoS₃ without poisoning it with elemental S was right.

We report also the x-ray photoelectron spectra for the three catalysts synthesized:
Fig. 3.72 X-ray photoelectron spectra of MoS$_3$/GNP 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV.

Fig. 3.73 X-ray photoelectron spectra of MoS$_3$/Ketjenblack 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV.
Fig. 3.74 X-ray photoelectron spectra of MoS$_3$/Vulcan 5:1 in ethylene glycol from (a) S(2p) and (b) Mo(3d). C1s 285.0 eV.

3.1.10 Discussion

By varying a variable at time, we presented a study on the several outcomes in the activity and morphology of MoS$_3$ nanoparticles on carbon support depending on carbon, initial S:Mo atomic ratio and solvent. Even though there have been studies on MoS$_3$ supported by different carbon, this is the first project involving the effect of changing S:Mo ratio and solvent in the solvothermal reaction. Previous studies dealt with ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$) as the only Mo-precursor$^{1,2,3}$. This means to have a

---


constant S:Mo ratio equal to 4:1. Other ones used ammonium molybdate tetrahydrate (Mo₇O₂₄(NH₄)₆·4H₂O) and sodium sulfide (Na₂S) with constant ratio of 2:1.

With all three carbon supports, the extra sulfur generated the same results, depending on if the synthesis has occurred in water or ethylene glycol. In each case, the extra sulfur at the begin of the synthesis enhances the activity by increasing the yield to MoS₃. However, when the S:Mo ratio is above 5, the sulfur atoms are not able to be integrated in the catalyst structure. Thus, the mechanism of reaction slightly changes (Tafel slope increases) and the catalyst’s activity starts to decrease. As we clearly see in Fig. 3.17 (GNP), Fig. 3.36 (Ketjen) and Fig. 3.54 (Vulcan), the 7:1 ratio curve has an initial slope higher than the ones at lower S:Mo ratio: at higher potential the extra S increases also the initial current density, which quickly decreases with a slope higher than in the 5:1 ratio. Surprisingly, the 10:1 ratio looked always more stable than the 7:1, but the activity decreased enormously. Indeed, the weight of the 10:1 catalyst is 20-30% higher than expected, so we believe that the high amount of extra sulfur stabilizes at some point the catalyst.

We found extremely important to cap the flask during the synthesis procedure. Few experiments on uncapped flask showed that keeping the H₂S formed in the gas phase inside the flask is necessary to maintain the same sulfur atoms concentration. In the uncapped flask experiments, the sulfur was allowed to leave the flask and the yield to MoS₃ resulted very low.

The XPS data demonstrated that the surface of MoS₃ on GNP has more than 50% of elemental sulfur, which is probably the reason of its poor activity. However, not only the

---

elemental sulfur was completely absent on the surface of catalysts made on Ketjenblack and Vulcan, but 70% of the sulfur atoms in the lattice were bridging or apical, meaning that there were more active sites than in catalysts on GNP (Tab. 3.23, Fig. 3.72). XPS gave a ratio S:Mo around 3 for Ketjenblack and Vulcan, confirming the absence of elemental S, while the signal was so weak for GNP that the ratio of more than 8 can’t be considered reliable (Tab. 3.21, Fig. 3.73, Fig. 3.74). In fact, by cross-referencing the results with the ICP we see that the latter have higher S:Mo ratio than the XPS ones. However, as stated in Appendix B, the ICP technique has 5-10% error. Based on our experience and calculation, we believe that the results obtained with the ICP technique show a molybdenum content ~6-7% lower than the real one. This means that the real S:Mo is ~ 3, suggesting that the assumption made thanks to the XPS data (MoS$_3$ is pure and no elemental sulfur is trapped inside) is not confined to the surface of the catalysts, but can be expanded also to the bulk (Tab. 3.20).

One last data showed in the XPS tables is Mo$^{6+}$, which is an index of the amount of molybdenum oxide. The commercial MoS$_2$ shows 6% of Mo$^{6+}$, while our MoS$_3$/GNP shows ~4% and Ketjenblack and Vulcan even lower than 1%. This confirms again the hypothesis of high purity for our catalysts.

We didn’t find any studies dealing with the effects of the solvents. The majority of the papers in literature use dimethylformamide (DMF) as a solvent for the solvothermal reaction. In section 3.3 we analyze the effect of DMF on our best catalyst. As for now, we know that neither water nor ethylene glycol are able to completely dissolve the Mo-precursor. However, since the carbon does disperse in different ways in water and ethylene glycol, the latter showed better results with all the three carbon tested (Fig. 3.17, 3.36, 3.60). The main
problem in using Ketjenblack and Vulcan in water is that the carbons do not disperse well. Indeed, in every experiments with Ketjen/Vulcan and water, after the mixing, we could always visually see particles floating in the solvent even after many hours of sonication. Thus, this is definitely one of the main reasons for better results of ethylene glycol, which instead is able to completely disperse both Ketjenblack and Vulcan. It’s a matter of fact that the best catalyst obtained were synthesized in ethylene glycol.

Since the main reactant is not completely dissolved, but rather stays in a suspension of tiny particles, the amount of solvent was not an important factor and we used 150 ml instead of the initial 200 ml.

As far as the electrochemical activity is concerned, we are now able to tell which condition is better to improve the catalyst performances. The 7:1 and 10:1 ratio showed an initial good response in terms of potential at -10 mA/cm², but the Tafel slopes were usually ~50-55 mV/dec, 10 mV/dec higher than the catalysts at lower ratio (Tab. 3.6, 3.11, 3.14). Chang et al.¹ obtained the same Tafel slopes for their MoSₓ grown on graphene, but the potential at -10 mA/cm² for these catalyst was ~ -150 mV, much better than our catalysts in that range of Tafel slope (for ours the potential was ~ -190 mV). The catalysts made on GNP are relatively worse than the ones on the other two carbons. This is probably due to a lack of good porosity for GNP. This was surprising, since there have been studies showing that graphene was a very good support for MoS₃. Indeed, Li et al. obtained -10 mA/cm² at ~ -165 mV with MoS₂ nanoparticles on reduced graphene oxide (RGO)⁵. The Tafel slope for their catalyst was 41

---


mV/dec and it was stable after several stability tests, even though the charge-transfer resistance was above 200 Ω (ours was ~ 50 Ω).

MoS$_3$ on Ketjenblack carbon at 5:1 S:Mo ratio in ethylene glycol can be considered our best catalyst. The dispersion on the electrode was improved and the catalyst formed a uniform layer (Fig. 3.69). The potential at -10 mA/cm$^2$ was -166 mV, the Tafel slope 38 mV/dec and $R_{ct}$ was 20 Ω. One reason for these good results is certainly the absence of unbonded sulfur. Yan et al. reported MoS$_3$ on CNTs, which gave -10 mA/cm$^2$ at -200 mV and $R_{ct}$ ~ 90 Ω: the reason was mostly the presence of unsaturated sulfur atoms$^6$. MoS$_3$ on CNTs was reported by Bian et al. too$^3$. They were able to reach -7 mA/cm$^2$ with ~ -155 mV, while we did that with -160 mV using Ketjenblack and Vulcan, and with -174 mV using GNP (all in ethylene glycol). The literature of MoS$_x$ on carbon supports shows a value of capacitance around 7-10 mF/cm$^2$, while we could get ~ 26 mF/cm$^2$ for the best catalysts. Zheng et al. reported MoS$_2$ on Reduced Graphene Oxide$^7$ with a capacitance of 2 mF/cm$^2$, an $R_{ct}$ above 200 Ω and they could get -23 mA/cm$^2$ at -200 mV (our best catalyst did that at -183 mV). Liao et al. used mesoporous graphene as support and despite the incredibly low capacitance (10 mF/cm$^2$) their potential at -10 mA/cm$^2$ was ~-140 mV$^8$.

Ketjenblack and Vulcan showed always better results than GNP, suggesting that their various-sized porosity is more suitable to deposit MoS$_3$ nanoparticles. However, the loading

---


experiments pointed out a bit of weakness in Vulcan carbon bonding on the electrode (Fig. 3.65 and 3.66), hence we can essentially say that Ketjenblack is the best carbon support tested. Also, the increased loading improved even more the activity of the best catalyst. Indeed the results at 1 mg/cm$^2$ indicated a potential at -10 mA/cm$^2$ equal to -152 mV (14 mV better than 250 μg/cm$^2$) and capacitance ~ 62 mF/cm$^2$. Despite the increased loading, the catalyst film wasn’t thick enough to block the active sites, but a plateau value was clearly reached (Fig. 3.63 and 3.64).

The thickness of the film at 250 μg/cm$^2$ was calculated with a profilometer and resulted to be 10-12 μm. The roughness, which is an integral average of the height of the film over the length, is ~ 20-25 μm (Fig. 3.70).

To conclude, the size of MoS$_3$ nanoparticles is usually less than 10 nm. However, the wide range of sizes makes it difficult to establish which is the average value. Even if the distribution was good, this big assortment of sizes made us believe that the dispersion could be improved to have a homogenous and small range of particles (Fig. 3.71).

### 3.2 EFFECTS OF IRON AND COBALT AS DOPANTS FOR MOS$_3$/KETJENBLACK

The second section of this thesis deal with the effect of two transition metals (Co and Fe) added to the catalyst to improve the activity. The idea is that the dopant atoms may increase the performance of the catalyst by being inserted in the vacancies of MoS$_3$ lattice. Since they should be part of the catalyst and not of the carbon support, we kept the weight percentage of carbon fixed and we decreased the amount of catalyst when we added the dopants. The addition of Co/Fe has been done by adding to the initial solution different amounts of Co/Fe-
acetate together with the other reactants. We also studied the effect of varying the S:Mo ratio from 5:1 to 7:1 while doping the catalyst.

Again we developed a table to summarize the pathway chosen (Tab. 3.24).

Tab. 3.24 Matrix of the second series of experiments.

<table>
<thead>
<tr>
<th>Dopant %</th>
<th>2%</th>
<th>5%</th>
<th>10%</th>
</tr>
</thead>
<tbody>
<tr>
<td>S:Mo Dopant</td>
<td>5:1</td>
<td>7:1</td>
<td>5:1</td>
</tr>
<tr>
<td>Co</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fe</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

3.2.1 Electrochemical results: Co-doped MoS$_2$/Ketjenblack

Differently from before, we are now interested in just improving the activity. This means that we performed less stability tests than before (usually 50 cycles), mostly because the performances of the catalyst could be understood without them. In this framework we avoid to report the plots showing the tests for each catalyst and we decide to report just comparison plots at 0 cycles of stability tests.

Tables 3.25 and 3.26 report the amount of reactants to obtain the desired weight percentages of products respectively at S:Mo 5:1 and 7:1.
Table 3.25 Reactants needed to obtain the desired doped products at S:Mo 5:1.

<table>
<thead>
<tr>
<th>Products (wt%)</th>
<th>Reactant (mg)</th>
<th>2%Co - 48%MoS₃</th>
<th>5%Co - 45%MoS₃</th>
<th>10%Co - 40%MoS₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50% Ketjen</td>
<td>50% Ketjen</td>
<td>50% Ketjen</td>
</tr>
<tr>
<td>(NH₄)₂MoS₄</td>
<td>65</td>
<td>61</td>
<td>61</td>
<td>54</td>
</tr>
<tr>
<td>Na₂S·9H₂O</td>
<td>60</td>
<td>57</td>
<td>57</td>
<td>50</td>
</tr>
<tr>
<td>Co(acetate)</td>
<td>6</td>
<td>15</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Ketjenblack</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.26 Reactants needed to obtain the desired doped products at S:Mo 7:1.

<table>
<thead>
<tr>
<th>Products (wt%)</th>
<th>Reactant (mg)</th>
<th>2%Co - 48%MoS₃</th>
<th>5%Co - 45%MoS₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50% Ketjen</td>
<td>50% Ketjen</td>
</tr>
<tr>
<td>(NH₄)₂MoS₄</td>
<td>60</td>
<td>61</td>
<td>169</td>
</tr>
<tr>
<td>Na₂S·9H₂O</td>
<td>180</td>
<td>169</td>
<td>169</td>
</tr>
<tr>
<td>Co(acetate)</td>
<td>6</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Ketjenblack</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Since we didn’t want to strongly modify our catalyst, the dopants amount added never exceeded 10% by weight. However, the results tell us that it was not worth to increase the percentage of cobalt and iron in the catalyst, as shown in Fig. 3.75 and 3.76.
Fig. 3.75 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt%, 5 wt% and 10 wt% cobalt., at 5:1 S:Mo ratio. Pt data are also reported.

Fig. 3.76 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt% and 5 wt% cobalt., at 7:1 S:Mo ratio. Pt data are also reported.
Fig. 3.77 Tafel plot from LSV after 0 of CV stability tests for Co-doped MoS$_2$/Ketjenblack at 5:1 and 7:1 S:Mo ratio.

Fig. 3.78 Current density vs Potential curves from CV after 0 cycles of CV stability tests Co-doped MoS$_2$/Ketjenblack at 5:1 and 7:1 S:Mo ratio.
Tab. 3.27 Summary of results for Co-doped MoS₂/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 after 0 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R_{ct} (Ω)</th>
<th>CPE/Area mF/cm²</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm²)</th>
<th>Potential at -10 mA/cm² (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Co - 5:1</td>
<td>39.7</td>
<td>17.0</td>
<td>38</td>
<td>-2.2 x10⁻⁴</td>
<td>-177</td>
</tr>
<tr>
<td>5%Co - 5:1</td>
<td>56.0</td>
<td>18.2</td>
<td>43</td>
<td>-5.6 x10⁻⁴</td>
<td>-184</td>
</tr>
<tr>
<td>10%Co - 5:1</td>
<td>124.5</td>
<td>17.8</td>
<td>71</td>
<td>-9.1 x10⁻³</td>
<td>-218</td>
</tr>
<tr>
<td>2%Co - 7:1</td>
<td>31.4</td>
<td>21.8</td>
<td>56</td>
<td>-4.4 x10⁻⁴</td>
<td>-193</td>
</tr>
<tr>
<td>5%Co - 7:1</td>
<td>36.3</td>
<td>26.2</td>
<td>49</td>
<td>-2.1 x10⁻⁴</td>
<td>-179</td>
</tr>
</tbody>
</table>

Although the data just presented show a trend in the activity of the doped catalysts, none of them was equal or better than the original undoped one. The parameters in Tab. 3.27 suggest that we probably lost a lot of the dopant ions, who were washed out in the filtrate solution. This doesn’t mean that their presence during the reaction didn’t modify the catalysts. Unfortunately, it looks like this modification went toward a worse activity. At 2%Co the increase in the S:Mo greatly decreases the activity, while at 5%Co 7:1 S:Mo we obtain -10 mA/cm² with higher potential and R_{ct} is lower than at 5:1 ratio.

The wide range of different results tells us that, without knowing the real weight percentage of dopant inside, just its presence in the reaction changes significantly the activity of the catalyst and in many different ways.
3.2.2 Materials characterization: Co-doped MoS$_3$/Ketjenblack

The real composition of the catalysts have been detected by ICP-CHNS analysis. Table 3.28 reports a summary of the real composition parameters for MoS$_3$/Ketjenblack doped with cobalt.

(1) ICP and CHNS

Tab. 3.28 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm$^2$ for Co-doped MoS$_3$/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt% C</th>
<th>wt% Mo</th>
<th>wt% S</th>
<th>wt% Co</th>
<th>wt% Sum</th>
<th>wt% S+Mo</th>
<th>S:Mo ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Co - 5:1</td>
<td>51.7</td>
<td>12.3</td>
<td>21.0</td>
<td>0.1</td>
<td>85.0</td>
<td>33.3</td>
<td>5.1</td>
</tr>
<tr>
<td>5%Co - 5:1</td>
<td>58.0</td>
<td>9.4</td>
<td>18.6</td>
<td>0.1</td>
<td>86.2</td>
<td>28.0</td>
<td>5.9</td>
</tr>
<tr>
<td>2%Co - 7:1</td>
<td>55.9</td>
<td>9.2</td>
<td>22.1</td>
<td>0.0</td>
<td>87.1</td>
<td>31.3</td>
<td>7.2</td>
</tr>
<tr>
<td>5%Co - 7:1</td>
<td>42.8</td>
<td>8.6</td>
<td>17.9</td>
<td>0.3</td>
<td>69.6</td>
<td>26.5</td>
<td>6.2</td>
</tr>
</tbody>
</table>

It is surprising to find out that in most cases the weight percentage of cobalt is ~ 0.1%. This confirms the hypothesis that cobalt is washed away during the filtration step and it does not go into the molybdenum sulfide structure. It is also remarkable that the Mo % is 3-6 % lower on average than the original catalyst and so the S:Mo ratio is increased. The carbon percent and the S:Mo ratio are generally higher.

The proof for knowing if there actually is cobalt in the catalyst is to perform elemental mapping on it (Fig. 3.79).

(2) TEM

Co-doped MoS$_3$/Ketjenblack have been analyzed at the TITAN and Fig. 3.79 shows an elemental survey, a TEM image and an elemental mapping of the elements in it.
Fig. 3.79 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_2$/Ketjenblack 5:1 ratio with 2% Co (top) and 5% Co (bottom).
It is clear that the catalysts have an anomalous distribution. Not only in the 5%Co just few spots of cobalt agglomerates can be seen, but in the 2%Co the dopant is completely absent and the background noise is the only reason of the light blue dots indicating the cobalt.

(3) **XPS**

We performed the XPS tests and fitting of Co-doped MoS$_3$ on Ketjenblack 5:1 in ethylene glycol and we compared the results with the ICP analysis (Tab 3.21).

*Tab. 3.29 Compositions analysis of MoS$_x$ electrocatalysts from XPS (top) and ICP-CHNS (bottom) doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol.*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition from XPS (wt %)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>2Co-MoS$_3$/KB</td>
<td>58.5</td>
<td>19.0</td>
</tr>
<tr>
<td>5Co-MoS$_3$/KB</td>
<td>63.4</td>
<td>15.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Composition from ICP-CHNS (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Co-MoS$_3$/KB</td>
</tr>
<tr>
<td>5Co-MoS$_3$/KB</td>
</tr>
</tbody>
</table>

XPS is a surface analysis. By comparing the two results we can see that they are different for 6-8% mostly in carbon and molybdenum. We can say that the surface has a higher concentration of Mo, carbon and Co than the bulk. The S:Mo ratio in the 5%Co in 2.3, which is lower than the expected 3: we can hypothesize than a mixture of MoS$_2$ and MoS$_3$ in present on the catalyst surface.
Tab. 3.30 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoSx electrocatalysts pure from Sigma-Aldrich, and doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo⁴⁺ (eV)</th>
<th>Mo⁵⁺ (eV)</th>
<th>Mo⁶⁺ (eV)</th>
<th>S²⁻ (eV)</th>
<th>S₂⁻/S²⁺ (eV)</th>
<th>CoSO₃ (or CoS₂O₄) (eV)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoSₓ-Aldrich</td>
<td>229.8</td>
<td>-</td>
<td>232.9</td>
<td>162.7</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>5Co-MoSₓ/KB</td>
<td>230.5</td>
<td>231.5</td>
<td>233.2</td>
<td>162.9</td>
<td>164.2</td>
<td>169.3</td>
<td>2.3</td>
</tr>
<tr>
<td>2Co-MoSₓ/KB</td>
<td>230.2</td>
<td>-</td>
<td>233.0</td>
<td>162.9</td>
<td>164.1</td>
<td>169.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Tab. 3.31 Chemical states and peak area ratios of MoSₓ electrocatalysts pure from Sigma-Aldrich, and doped with 2%Co and 5%Co on Ketjenblack, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Chemical state</th>
<th>XPS area ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MoSₓ-Aldrich</td>
</tr>
<tr>
<td>Mo⁴⁺</td>
<td>94.0</td>
</tr>
<tr>
<td>Mo⁵⁺</td>
<td>0</td>
</tr>
<tr>
<td>Mo⁶⁺</td>
<td>6.0</td>
</tr>
<tr>
<td>S²⁻ (basal)</td>
<td>100</td>
</tr>
<tr>
<td>S₂⁻/S²⁺</td>
<td>0</td>
</tr>
<tr>
<td>CoSO₃ (or CoS₂O₄)</td>
<td>0 (15.8)</td>
</tr>
</tbody>
</table>

* Basal S²⁻; ** bridging S₂⁻ and/or apical S²⁻.

We can understand from the previous tables that our catalyst is not pure. We tried to fit the curves with the binding energy of cobalt sulfite and cobalt sulfate and we found out that actually during the reaction cobalt sulfate has been formed, which probably is responsible of the lower activity. This is because the sulfur inside the cobalt sulfate is not able to catalyze the HER, hence we have less active sites.

We report also the x-ray photoelectron spectra for the two compounds in the previous table:
3.2.3 Electrochemical results: Fe-doped MoS3/Ketjenblack

As far as the iron doped catalysts are concerned, we now present two tables with the amount of reactants to obtain the desired weight percentages of products respectively at S:Mo 5:1 and 7:1.
Tab. 3.32 Reactants needed to obtain the desired doped products at S:Mo 5:1.

<table>
<thead>
<tr>
<th>Products (wt%)</th>
<th>2%Fe - 48%MoS$_3$</th>
<th>5%Fe - 45%MoS$_3$</th>
<th>10%Fe - 40%MoS$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant (mg)</td>
<td>50% Ketjen</td>
<td>Ketjen</td>
<td>50% Ketjen</td>
</tr>
<tr>
<td>(NH$_4$)$_2$MoS$_4$</td>
<td>65</td>
<td>61</td>
<td>54</td>
</tr>
<tr>
<td>Na$_2$S-9H$_2$O</td>
<td>60</td>
<td>57</td>
<td>50</td>
</tr>
<tr>
<td>Fe(acetate)</td>
<td>6.5</td>
<td>15.5</td>
<td>31</td>
</tr>
<tr>
<td>Ketjenblack</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Tab. 3.33 Reactants needed to obtain the desired doped products at S:Mo 7:1.

<table>
<thead>
<tr>
<th>Products (wt%)</th>
<th>2%Fe - 48%MoS$_3$</th>
<th>5%Fe - 45%MoS$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactant (mg)</td>
<td>50% Ketjen</td>
<td>50% Ketjen</td>
</tr>
<tr>
<td>(NH$_4$)$_2$MoS$_4$</td>
<td>60</td>
<td>61</td>
</tr>
<tr>
<td>Na$_2$S-9H$_2$O</td>
<td>180</td>
<td>169</td>
</tr>
<tr>
<td>Fe(acetate)</td>
<td>6.5</td>
<td>15.5</td>
</tr>
<tr>
<td>Ketjenblack</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

Fig. 3.82 to 3.85 show the electrochemical results.
Fig. 3.82 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt%, 5 wt% and 10 wt% of iron, at 5:1 S:Mo ratio. Pt data are also reported.

Fig. 3.83 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack doped with 2 wt% and 5 wt% of iron, at 7:1 S:Mo ratio. Pt data are also reported.
Fig. 3.84 Tafel plot from LSV after 0 of CV stability tests for Fe-doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio.

Fig. 3.85 Current density vs Potential curves from CV after 0 cycles of CV stability tests Fe-doped MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio.
Tab. 3.34 Summary of results for Fe-doped MoS$_2$/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1 after 0 cycles of CV stability tests.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$R_{ct}$ ($\Omega$)</th>
<th>CPE/Area (mF/cm$^2$)</th>
<th>Tafel Slope (mV/dec)</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Fe - 5:1</td>
<td>21.1</td>
<td>20.9</td>
<td>39</td>
<td>-4.4 x10$^{-4}$</td>
<td>-171</td>
</tr>
<tr>
<td>5%Fe - 5:1</td>
<td>37.3</td>
<td>11.7</td>
<td>39</td>
<td>-2.6 x10$^{-4}$</td>
<td>-180</td>
</tr>
<tr>
<td>10%Fe - 5:1</td>
<td>181</td>
<td>12.1</td>
<td>57</td>
<td>-1.0 x10$^{-3}$</td>
<td>-231</td>
</tr>
<tr>
<td>2%Fe - 7:1</td>
<td>27.8</td>
<td>21.0</td>
<td>39</td>
<td>-4.2 x10$^{-4}$</td>
<td>-171</td>
</tr>
<tr>
<td>5%Fe - 7:1</td>
<td>113.5</td>
<td>11.8</td>
<td>49</td>
<td>-6.9 x10$^{-4}$</td>
<td>-205</td>
</tr>
</tbody>
</table>

Again, increasing the amount of dopant inside the catalyst decreases the overall activity. Indeed the 10%Fe catalyst is one of the worse we synthesized so far. The 2%Fe is fairly good with both S:Mo ratios, however the 2%Fe 7:1 is the only doped catalyst that showed improved performances with respect to the original undoped one, with increased potential at -10 mA/cm$^2$ and exchange current, and decreased $R_{ct}$ and Tafel slope.

Fig. 3.84 shows LSV results for all the doped catalysts together. Even though it’s confusing, it gives an idea of how the dopants changed the behavior of the original undoped catalysts.
Fig. 3.86 Current density vs potential from LSV after 0 cycles of CV stability for Co/Fe doped MoS$_2$/Ketjenblack at 5:1 and 7:1 S:Mo ratio. Pt data are also reported.

Fig. 3.87 Impedance curves from EIS after 0 cycles of CV stability tests for Co/Fe doped MoS$_2$/Ketjenblack at 5:1 and 7:1 S:Mo ratio.
3.2.4 Materials characterization: Fe-doped MoS$_3$/Ketjenblack

As before, the iron-doped catalysts have been analyzed with the ICP-CHNS technique to know the real composition. Table 3.32 reports a summary of the real composition parameters for MoS$_3$/Ketjenblack doped with iron.

(1) ICP and CHNS

Tab. 3.35 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm$^2$ for Fe-doped MoS$_3$/Ketjenblack in ethylene glycol, S:Mo = 5:1 and 7:1.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>wt% C</th>
<th>wt% Mo</th>
<th>wt% S</th>
<th>wt% Fe</th>
<th>wt% Sum</th>
<th>wt% S+Mo</th>
<th>S:Mo ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Fe - 5:1</td>
<td>46.2</td>
<td>7.9</td>
<td>21.2</td>
<td>0.0</td>
<td>75.3</td>
<td>29.1</td>
<td>8.0</td>
</tr>
<tr>
<td>5%Fe - 5:1</td>
<td>75.1</td>
<td>4.9</td>
<td>15.1</td>
<td>0.0</td>
<td>95.1</td>
<td>20.0</td>
<td>9.2</td>
</tr>
<tr>
<td>2%Fe - 7:1</td>
<td>55.4</td>
<td>11.7</td>
<td>24.7</td>
<td>0.0</td>
<td>91.8</td>
<td>36.4</td>
<td>6.3</td>
</tr>
<tr>
<td>5%Fe - 7:1</td>
<td>50.7</td>
<td>14.3</td>
<td>22.6</td>
<td>0.1</td>
<td>87.7</td>
<td>36.9</td>
<td>4.7</td>
</tr>
</tbody>
</table>

The weight percentage of iron is almost zero. The assumption that with this type of synthesis we are not able to insert correctly the dopants inside the catalyst is slowly becoming a certainty. While the sulfur content usually reflects the corresponding undoped catalyst, again the molybdenum weight percent is 4-6% lower than usual. It has to be pointed out that the 2% Fe 7:1 catalyst showed better performances than the original one but with a lower amount of MoS$_3$ and a real ratio of 6:1.

The proof for knowing if there actually is iron in the catalyst is to perform elemental mapping on it (Fig. 3.88).

(2) TEM

Fe-doped MoS$_3$/Ketjenblack have been analyzed at the TITAN and Fig. 3.88 shows an elemental survey, a TEM image and an elemental mapping of the elements in it.
Fig. 3.88 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_2$/Ketjenblack 5:1 ratio with 2% Fe (top) and 5% Fe (bottom).
XPS analysis and fitting has been carried out on Fe-doped MoS$_3$ on Ketjenblack and has been compared with the results from the ICP analysis (Tab. 3.36). With this last test we are now sure that no iron atoms went inside the catalyst structure, but instead they have been washed away.

*Tab. 3.36 Compositions analysis of MoS$_x$ electrocatalysts from XPS (top) and ICP-CHNS (bottom) doped with 2%Fe and 5%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol.*

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition from XPS (wt %)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>S</td>
</tr>
<tr>
<td>2Fe-MoS$_3$/KB</td>
<td>47.7</td>
<td>32.4</td>
</tr>
<tr>
<td>5Fe-MoS$_3$/KB</td>
<td>59.6</td>
<td>20.7</td>
</tr>
<tr>
<td></td>
<td>Composition from ICP-CHNS (wt %)</td>
<td></td>
</tr>
<tr>
<td>2Fe-MoS$_3$/KB</td>
<td>46.2</td>
<td>21.2</td>
</tr>
<tr>
<td>5Fe-MoS$_3$/KB</td>
<td>75.1</td>
<td>15.1</td>
</tr>
</tbody>
</table>

The sulfur and molybdenum content on the surface are greater, meaning that we have more catalyst than in the bulk. The weight percentage of S and Mo is surprisingly higher in the XPS analysis than in the ICP and the S:Mo ratio for the 5%Fe is almost 3.
Tab. 3.37 Binding energy and assignment of the characteristic peaks found in the XPS spectra (Mo 3d5/2 and S 2p3/2) of MoS₅ electrocatalysts pure from Sigma-Aldrich, and doped with 2%Fe and 5%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo⁴⁺ (eV)</th>
<th>Mo³⁺ (eV)</th>
<th>Mo²⁺ (eV)</th>
<th>S²⁻ (eV)</th>
<th>S²⁻/S²⁺⁺ (eV)</th>
<th>S⁰ (eV)</th>
<th>S/Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂-Aldrich</td>
<td>229.8</td>
<td>-</td>
<td>232.9</td>
<td>162.7</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>5Fe-MoS₂/KB</td>
<td>230.1</td>
<td>-</td>
<td>-</td>
<td>162.9</td>
<td>164.2</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>2Fe-MoS₂/KB</td>
<td>230.1</td>
<td>-</td>
<td>233.5</td>
<td>162.8</td>
<td>164.1</td>
<td>-</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Tab. 3.38 Chemical states and peak area ratios of MoS₅ electrocatalysts pure from Sigma-Aldrich, and doped with 2%Fe and 5%Fe on Ketjenblack, at S:Mo 5:1 in ethylene glycol.

<table>
<thead>
<tr>
<th>Chemical state</th>
<th>XPS area ratio (%)</th>
<th>MoS₂-Aldrich</th>
<th>5Fe-MoS₂/KB</th>
<th>2Fe-MoS₂/KB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo⁴⁺</td>
<td>94.0</td>
<td>100</td>
<td>98.5</td>
<td></td>
</tr>
<tr>
<td>Mo³⁺</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Mo²⁺</td>
<td>6.0</td>
<td>0</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>S²⁻ (basal)</td>
<td>100</td>
<td>31.5</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>S²⁻/S²⁺⁺</td>
<td>0</td>
<td>68.5</td>
<td>66.1</td>
<td></td>
</tr>
<tr>
<td>S⁰</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* Basal S²⁻; ** bridging S₂⁻ and/or apical S²⁻.

We didn’t find any peaks for an eventual iron sulfate, as in the cobalt case and the ratio between basal and bridging/apical sulfur is the same as in the original undoped catalyst. Thus we can conclude that the reason of the bad performances for these two catalyst relies on the amount of catalyst they had inside. We can assume that the MoS₃ percentage is lower than in the original catalyst, as the ICP data confirm.

We report also the x-ray photoelectron spectra for the two compounds in the previous table:
3.2.5 Discussion

By slightly modifying the synthesis procedure with the addition of transition metals acetates, we tried to incorporate cobalt and iron atoms into the molybdenum sulfide lattice. The idea came from recent studies which demonstrated that, not only the incorporation of cobalt and iron was possible, but also it was favorable because of the lower energy of doped MoS₃ with...
respect to the original one. However, most of these studies just showed the morphological change in the compound without any relation to the HER or any electrochemical test, or they were related to other reactions, such as hydrodesulfurization (to which MoS$_2$ was found active before to the HER, see ch. 1) or oxygen reduction.

The reason of lack of electrochemical studies on the effect of the dopants on MoS$_2$ for HER is probably related to the fact that there are still doubts on how much the dopants are improving the activity of molybdenum sulfides and toward which reaction they are actually more suitable. Also, the idea of exploiting transition metal dopants on MoS$_2$ in the hydrogen evolution reaction is relatively new and the synthesis procedures are still not well understood.

Indeed, in this study we were not able to dope our catalysts. The final composition we got from both the ICP and XPS analysis was different from the one by recipe (Tab. 3.25, 3.29, 3.32, 3.36). In a previous study this group showed how the Fe-doped MoS$_3$ was improving the activity by decreasing the weight percentage of iron from 25% to 10%. Thus we realized that a small percentage of dopants would have been enough to increase the activity: too much Fe/Co would have poisoned the catalyst. Since the results show that the percentage of dopants inside the catalysts are lower than 0.3%, we believe that they were not directly responsible of the activity change. More likely, the dopants, changed indirectly the number of active sites, by modifying the morphology of the MoS$_3$ nanoparticles.

---

As shown in Fig. 3.79 and 3.88, TEM results are indicating that the nanoparticles are bigger than before and the dispersion of Mo, S and C is worse. As for the dispersion of the dopants, just in the 5%Co catalyst we were able to detect the dopant in the TEM, but the results showed few big spots of high cobalt-concentrated material, whilst cobalt was absent in the rest of the catalyst. There are still doubts about the reason of the loss and bad dispersion of the cobalt and iron, however we believe that the undissolved Mo-precursor and the low temperature of the process (~ 165°C) are the main factors. The dissolution of the reactants can be an issue both for the chemical reaction to MoS$_3$ and for the deposition of the dopants on the catalyst: the bigger are the reactants particles, the worse is the final dopants dispersion. In sections 3.3 and 3.4 we will deal and solve the dissolution problem. The temperature might be another issue because we intend to insert the dopants in the catalyst vacancies. By increasing the temperature we increase the number of the vacancies too, and so we raise the probability that the dopants will be deposited into them.

As far as the electrochemical experiments are concerned, the Co-doped catalysts at S:Mo 7:1 have higher capacitance and Tafel slope, and lower charge-transfer resistance than the ones with the same cobalt percentage at 5:1. However, the exchange current and the potential at -10 mA/cm$^2$ look similar. As for the Fe-doped catalyst, we don’t see these differences; the 2%Fe shows almost the same parameters if synthesized at 5:1 or at 7:1 S:Mo ratio, while the 5%Fe looks definitely worse at 7:1 than at 5:1 S:Mo ratio, in particular for the charge-transfer resistance (> 100 Ω in the 7:1). Both the 10%-doped catalysts have the lowest activity measured so far. Their $R_{ct}$ is huge compared to the other doped catalysts, the Tafel
slope is above 55 mV/dec and the potential at -10 mA/cm² is at least 20-30 mV lower than the others.

However, our results are often better than the literature ones. Merki et al. synthesized Co/Fe-doped MoS₂. Their Co-promoted MoS₃ film was prepared by electropolymerization of (NH₄)₂[Co(MoS₄)₂], which can be prepared in situ immediately upon the mixing of CoCl₂ with (NH₄)₂[MoS₄]. The Co-MoS₃ film showed optimal catalytic activity when the initial Co:Mo ratio was about 1:3, in particular the R_{ct} was 62 Ω, the capacitance was 7.6 mF/cm², the Tafel slope 43 mV/dec and they could reach -10 mA/cm² with -185 mV (we did that with most of the doped catalysts in a range between -171 mV and -184 mV). Their Fe-doped catalysts showed similar response, but for the Tafel slope which was above 50 mV/dec.

Bonde et al. prepared a Co-promoted MoS₂ by co-impregnation of the Mo- and the Co-precursor. While they claim that the cobalt sulfide formed during the synthesis is responsible for a decrease in the activity, the cobalt looks improving the activity of the catalyst. However, their results can be considered negligible because they could reach -10 mA/cm² only with -350 mV, almost 180 mV lower than our catalyst’s performances.

In conclusion, we still believe that the transition metal ions can improve the activity of the molybdenum sulfide, as long as it is synthesized with a procedure that allows cobalt and iron ions to go inside the MoS₃ structure. Indeed, in 2015 Tsai et al. demonstrated with DFT and theoretical calculations that the transition metals are most likely inserted on the S-edge with

---

all the Mo atoms at the edge substituted by the metal dopant\textsuperscript{16}. By studying the HER on the
dge sites, they determined the role of the metal dopant in modifying the strength of sulfur
binding on the edge, which establishes hydrogen binding onto S atoms on the edge through a
negative linear scaling.

The theoretical studies are sometimes difficult to apply to practical problems. Wang \textit{et al.}
showed that difficulties in accurately engineering the desired atomic sites lead to challenges
in making direct comparisons between experimental and theoretical results\textsuperscript{17}. Even though
their transition metal-doped molybdenum sulfide shows improved electrochemical
parameters, the activity was still far from being competitive with the other recent studies on
molybdenum sulfides catalysts.

3.3 DIMETHYLFORMAMIDE AS A SOLVENT FOR MOS\textsubscript{3}/KETJENBLACK

We already saw in section 3.1 the extreme importance of the solvent in our synthesis
reaction. By changing the solvent (water and ethylene glycol in that case) we were able to
change the boiling temperature, the solubility of the molybdenum precursor, the interactions
and side reactions of the molecules in the flask, and the yield to MoS\textsubscript{3}. In this section we
presents some experiments with different solvents, mostly mixtures of N,N-
Dimethylformamide (DMF).

\textsuperscript{16} “Rational design of MoS\textsubscript{2} catalysts: tuning the structure and activity via transition metal doping” C. Tsai, K.

\textsuperscript{17} “Transition-metal doped edge sites in vertically aligned MoS\textsubscript{2} catalysts for enhanced hydrogen evolution” H.
Wang, C. Tsai, D. Kong, K. Chan, F. Abild-Pedersen, J. K. Nørskov, and Y. Cui, Nano Research 2015, 8(2),
566–575.
Tab. 3.39 reports all the different solvents used to try to completely dissolve the ammonium tetrathiomolybdate. The last column shows if they were successful or not.

**Tab. 3.39 Mixtures of solvents used in the attempt to completely dissolve (NH₄)₂MoS₄.**

<table>
<thead>
<tr>
<th>Solvent 1</th>
<th>Amount (ml)</th>
<th>Solvent 2</th>
<th>Amount (ml)</th>
<th>Total (ml)</th>
<th>Dissolved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene Glycol</td>
<td>Up to 500</td>
<td>-</td>
<td>-</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>150/300/400</td>
<td>Water</td>
<td>50/100/150</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>N-Methyl-2-pyrrolidone</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>No</td>
</tr>
<tr>
<td>Water</td>
<td>500</td>
<td>-</td>
<td>-</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>Up to 400</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td>No</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>400</td>
<td>Water</td>
<td>100</td>
<td>500</td>
<td>No</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>175</td>
<td>Water</td>
<td>125</td>
<td>300</td>
<td>Yes</td>
</tr>
<tr>
<td>N,N-Dimethylformamide</td>
<td>50</td>
<td>Ethylene Glycol</td>
<td>150</td>
<td>200</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Amongst all the solvents tested, just the mixtures 125 ml H₂O + 175 ml DMF and 150 ml EG + 50 ml DMF were able to completely dissolve the Mo-precursor. With the other solvents the solution (which actually was a suspension) had a brownish opaque color, while with working solvents the solution became shining orange.

### 3.3.1 Electrochemical results

The two DMF mixtures were able to dissolve the Mo-precursor, however DMF forms stable H-bonded complexes with Sulfuric Acid: (H₂SO₄)₂-DMF. Without the correct amount of free acid in solution, the acidification reaction occurs at a lower extent. Eventually, this leads

---

to unreacted Mo-precursor and so to a decreased yield to MoS\textsubscript{3}. We kept performing the test using the recipe of our best catalyst, MoS\textsubscript{3}/Ketjenblack at S:Mo 5:1. The synthesis failed several times before getting to the idea that increasing the amount of sulfuric acid in the reaction would have driven the reaction to the desired products. Tab. 3.40 reports a summary of the catalyst synthesized, where the first row show the usual parameters we measured when the synthesis failed.

*Tab. 3.40 Summary of solvents, amount of sulfuric acid and S:Mo ratio used in the DMF experiments. The final pH, color of the filtrate solution and weight of the catalysts are reported.*

<table>
<thead>
<tr>
<th>Solvents</th>
<th>S:Mo ratio</th>
<th>2.5M H\textsubscript{2}SO\textsubscript{4} (ml)</th>
<th>pH</th>
<th>color</th>
<th>Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMF(175ml)+H\textsubscript{2}O(125ml)</td>
<td>5:1</td>
<td>2*</td>
<td>3.6</td>
<td>Brown</td>
<td>n/a</td>
</tr>
<tr>
<td>DMF(175ml)+H\textsubscript{2}O(125ml)</td>
<td>5:1</td>
<td>20</td>
<td>2.6</td>
<td>Yellow/brown</td>
<td>68</td>
</tr>
<tr>
<td>DMF(175ml)+H\textsubscript{2}O(125ml)</td>
<td>7:1</td>
<td>30</td>
<td>2.7</td>
<td>Yellow</td>
<td>93</td>
</tr>
<tr>
<td>DMF(175ml)+H\textsubscript{2}O(125ml)</td>
<td>5:1</td>
<td>50</td>
<td>2.9</td>
<td>Yellow</td>
<td>92</td>
</tr>
<tr>
<td>DMF(50ml)+EG(150ml)</td>
<td>5:1</td>
<td>30</td>
<td>3.6</td>
<td>Light Yellow</td>
<td>88</td>
</tr>
</tbody>
</table>

* Equivalent volume of 2.5 M H\textsubscript{2}SO\textsubscript{4}. The actual solution used was 0.5 M H\textsubscript{2}SO\textsubscript{4}.

The molarity of the sulfuric acid was increased to avoid using a high volume of acidic solution, thus creating an error in calculating the concentration of the reactants. The similar values in the pH tell us that, although the amount of acid was increased, the amount of free protons in solution was constant, confirming the interactions between the DMF and the acids. As for the catalyst weight, when using the DMF we usually got lower yield (70-90%) than
the experiments done in water and ethylene glycol. Indeed, the colored solutions were always indicating a loss of unreacted Mo-precursor.

Fig. 3.91 Current density vs potential from LSV after 0 cycles of CV stability for MoS₃/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H₂O and DMF+EG. Pt data are also reported.
Fig. 3.92 Impedance curves from EIS after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG.

Fig. 3.93 Tafel plot from LSV after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG.
It’s surprising that, despite the different solvents and the different amount of sulfuric acid, all the catalysts synthesized and tested showed very similar results with all the parameters reported. It is also remarkable to say that the electrochemical results were essentially identical to the original best catalyst made in ethylene glycol with 10 ml 0.5 M H$_2$SO$_4$ and in some cases they were even better, such as for the exchange current always higher than the original catalyst. The Tafel slopes were stable around 40 mV/dec and the charge-transfer resistances were always lower than 30 Ω.

3.3.2 Materials characterization

The results of real composition from the ICP-CHNS analysis for the catalysts made in DMF are reported in this paragraph. Table 3.32 reports a summary of the real composition parameters for MoS$_2$/Ketjenblack doped with iron.

---

**Tab. 3.41 Summary of results for MoS$_2$/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H$_2$O and DMF+EG after 0 cycles of CV stability tests.**

<table>
<thead>
<tr>
<th>Solvents</th>
<th>2.5M H$_2$SO$_4$ (ml)</th>
<th>R$_{ct}$ (Ω)</th>
<th>CPE/Area mF/cm$^2$</th>
<th>Tafel Slope mV/dec</th>
<th>Exchange current (mA/cm$^2$)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>2</td>
<td>20.8</td>
<td>26.7</td>
<td>38</td>
<td>-4.6 x 10$^{-4}$</td>
<td>-166</td>
</tr>
<tr>
<td>DMF+H$_2$O</td>
<td>20</td>
<td>20.0</td>
<td>29.7</td>
<td>43</td>
<td>-1.2 x 10$^{-3}$</td>
<td>-169</td>
</tr>
<tr>
<td>DMF+H$_2$O</td>
<td>50</td>
<td>27.1</td>
<td>24.7</td>
<td>39</td>
<td>-4.6 x 10$^{-4}$</td>
<td>-169</td>
</tr>
<tr>
<td>DMF+EG</td>
<td>30</td>
<td>23.1</td>
<td>22.7</td>
<td>43</td>
<td>-1.1 x 10$^{-3}$</td>
<td>-171</td>
</tr>
<tr>
<td>DMF+H$_2$O</td>
<td>30</td>
<td>21.1</td>
<td>28.4</td>
<td>40</td>
<td>-6.3 x 10$^{-4}$</td>
<td>-169</td>
</tr>
</tbody>
</table>

---

It’s surprising that, despite the different solvents and the different amount of sulfuric acid, all the catalysts synthesized and tested showed very similar results with all the parameters reported. It is also remarkable to say that the electrochemical results were essentially identical to the original best catalyst made in ethylene glycol with 10 ml 0.5 M H$_2$SO$_4$ and in some cases they were even better, such as for the exchange current always higher than the original catalyst. The Tafel slopes were stable around 40 mV/dec and the charge-transfer resistances were always lower than 30 Ω.

3.3.2 Materials characterization

The results of real composition from the ICP-CHNS analysis for the catalysts made in DMF are reported in this paragraph. Table 3.32 reports a summary of the real composition parameters for MoS$_2$/Ketjenblack doped with iron.
(1) ICP and CHNS

Tab. 3.42 Data of real weight percentage of C, H, N, S, Mo, S:Mo ratio, charge-transfer resistance, capacitance per unit area, Tafel slope, exchange current, potential at -10 mA/cm² for MoS₃/Ketjenblack at 5:1 and 7:1 S:Mo ratio in DMF+H₂O and DMF+EG.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>2.5M H₂SO₄ (ml)</th>
<th>wt% C</th>
<th>wt% H</th>
<th>wt% N</th>
<th>wt% Mo</th>
<th>wt% S</th>
<th>wt% Sum</th>
<th>wt% S+Mo</th>
<th>S:Mo ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>5:1 S:Mo ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF+H₂O</td>
<td>20</td>
<td>63.3</td>
<td>0.7</td>
<td>0.6</td>
<td>11.3</td>
<td>13.4</td>
<td>89.4</td>
<td>24.7</td>
<td>3.6</td>
</tr>
<tr>
<td>DMF+H₂O</td>
<td>50</td>
<td>51.9</td>
<td>0.5</td>
<td>0.6</td>
<td>15.0</td>
<td>22.0</td>
<td>90.0</td>
<td>37.0</td>
<td>4.4</td>
</tr>
<tr>
<td>DMF+EG</td>
<td>30</td>
<td>53.6</td>
<td>0.5</td>
<td>0.6</td>
<td>14.3</td>
<td>22.2</td>
<td>91.1</td>
<td>36.5</td>
<td>4.6</td>
</tr>
<tr>
<td>7:1 S:Mo ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF+H₂O</td>
<td>30</td>
<td>50.6</td>
<td>0.5</td>
<td>0.5</td>
<td>15.1</td>
<td>23.0</td>
<td>89.6</td>
<td>38.1</td>
<td>4.6</td>
</tr>
</tbody>
</table>

In most cases we recognize the same weight percentage of the original best catalyst made in just ethylene glycol. Mo is around 15 wt%, S is around 22 wt%, carbon is ~ 50 wt% and the S:Mo ratio is around 4.5. The catalyst made in DMF + H₂O with 20 ml of acid looks different from the other ones and has less MoS₃ inside. However, it has the same electrochemical activity, meaning that it actually is more active toward the HER per every μg of catalyst than the other catalysts.

(2) TEM

The reason why we started thinking about the dissolution problem came from the idea that, since the nanoparticles of MoS₃ we were synthesizing so far were between 5 and 10 nm, we believed that smaller particles would have increased the number of active sites and the activity. The TEM analysis were necessary to know if the structure of our catalysts changed thanks to the complete dissolution of all the reactants.
Fig. 3.94 TEM images of MoS$_2$/Ketjenblack 5:1 made in DMF + EG at two different magnifications. Particle sizes: 1-2 nm.

Fig. 3.95 STEM FEI Titan 80-300 elemental mapping and survey of MoS$_2$/Ketjenblack 5:1 made in DMF + EG.
3.3.3 Discussion

To the best of our knowledge, there are no studies on the dissolution of Ammonium TetrathioMolybdate (ATM). Lin et al. claim to have obtained a homogenous dispersion with 160 g of ATM in 20% aqueous ethanol, when they synthesized MoS$_3$/carbon nanotube\textsuperscript{19}. Their particles size was 1-2 nm but they could reach -10 mA/cm$^2$ only at a potential below -200 mV. Morales et al. tried to dissolve ATM in water, claiming that they obtained [MoS$_4$]$^{2-}$ ions without problems in the attempt of synthesizing amorphous MoS$_3$ particles\textsuperscript{20}. Their particles size was 100 nm and above but the potential at -10 mA/cm$^2$ was 160 mV: a great result despite the extent of their particles. Water was also widely used to try to dissolve the Mo-precursor\textsuperscript{21,22,23}, but we tested that it is not possible to reach a complete dissolution. In most of the studies on the synthesis of MoS$_3$ nanoparticles that use (NH$_4$)$_2$MoS$_4$ as precursor, usually the latter is dissolved in DMF. However, none of them explores the solvothermal synthesis via the acidification reaction. Moreover, in part of those studies graphene or mesoporous carbon is used as support and is directly added to the solution together with the other reactants. Since the carbons are black, it’s almost impossible to distinguish if the mixtures are suspensions or solutions. Li et al. reported MoS$_2$ nanoparticles on graphene oxide and they claim to obtain a clear and homogeneous solution upon the addition of ATM in a DMF and graphene oxide solution\textsuperscript{5}. Clearly, it can’t be detectable.

Since the purpose of changing solvents was to have smaller nanoparticles, the TEM images (Fig. 3.94) tell us that we achieved our goal because we detected MoS\(_3\) nanoparticles of 1-2 nm. Also, the elemental mapping and survey of Fig. 3.95 on MoS\(_3\)/Ketjenblack made in DMF+EG give us an idea of the great potential of this technique on the catalysts. Indeed, a very good dispersion is visible, where all the nanoparticles are fairly spread on the carbon support.

The real composition of the catalysts showed in Tab. 3.42 is similar to the original MoS\(_3\)/Ketjenblack made in ethylene glycol, with an average of 55% by weight of carbon and 45% of molybdenum sulfide, but for the catalyst made with 20 ml of acid, which, despite the lower percentage of MoS\(_3\) (lower than 30 wt%), has still the same activity of the other ones. In most cases the real S:Mo ratio is 4.5, close to the expected one by recipe.

As far as the electrochemical experiments are concerned, we obtained results essentially identical to the original best catalyst made in ethylene glycol with 10 ml 0.5 M H\(_2\)SO\(_4\). This was unexpected mostly because of the important variables we changed. In fact, all the catalysts synthesized in DMF showed very similar results in terms of potential at -10 mA/cm\(^2\) (basically all around -169 mV), charge-transfer resistance and Tafel slope. The catalyst made with 20 ml of acid and the one at 7:1 S:Mo ratio had a capacitance closer to 30 mF/cm\(^2\), higher than the original one. The Tafel slopes were stable around 40 mV/dec and the charge-transfer resistances were always lower than 30 Ω. It’s important to underline that the exchange current was always higher than in the original catalyst in ethylene glycol, and in some cases (such as the catalyst made with 20 ml of acid and H\(_2\)O and the one made with 30 ml of acid in EG) it increased up to 1.2 x 10\(^{-3}\) mA/cm\(^2\). If we could get the same amount of
catalyst with the catalyst made with 20 ml of acid, we would probably see an even greater increase in the activity.

In chapter 5 we will explore the possible future work that could be done with this technique.

3.4 SODIUM HYDROXIDE: THE KEY COMPOUND FOR THE DISSOLUTION OF (NH₄)₂MOS₄

In the previous section we talked about the problem of dissolving ammonium tetrathiomolybdate (NH₄)₂MoS₄ and one of the possible solutions to go from a suspension of particles to a real solution, hence improving the activity. In this last section of the chapter we propose and analyze another recent solution to the same problem, which allows us to keep the same solvent (ethylene glycol) but with the addition of a new reactant: sodium hydroxide (NaOH 98.9%). The reaction between the Mo-precursor and NaOH leads to sodium thiomolybdate (Na₂MoS₄) which has high solubility in water and organic solvents:

\[
(NH₄)₂MoS₄ + 2NaOH \rightarrow Na₂MoS₄ + 2H₂O + 2NH₃
\]

We usually synthesized the same best catalyst obtained so far, which is MoS₃ on Ketjenblack at S:Mo 5:1 in ethylene glycol (although we tried the 4:1 ratio and water too). After the mixing of Mo-precursor with the solvent and a 30 minutes sonication, we added ~ 120 mg of NaOH (in pellet of ~ 120 mg each). The solution was sonicated for 2 hours at 40° C and the flask was left uncapped to allow the stripping of ammonia and speed up the reaction. After the sonication, the solution was shining orange and transparent and the pellet had completely reacted. At this point the sodium sulfide and the carbon were added and the procedure was

---

the same as before. The initial pH before the addition of the acid (in these experiments we used both H$_2$SO$_4$ and HCl) was ~ 11 and we varied the amount of acid by checking the final pH and not the volume of acid solution added. Most of the experiments differ one another just for the final pH (caused by a different amount of acid added). This is the reason why we always report the final pH. For the first two experiments we didn’t check the pH precisely because we thought that a rough estimate was sufficient. Later we found out that the final pH affects our reaction even if it varies by 0.1. All the experiments are carried out at 165°C, but for one, which has been done with the addition of a solution of 0.5 M H$_2$SO$_4$ in ethylene glycol, which allowed the solution to boil at higher temperature (200°C).

### 3.4.1 Electrochemical results

As we did in the previous section, since not all the catalyst went through the stability tests, we don’t report the single LSV, CV and EIS tests for each catalyst, but just the comparison plots.
Fig. 3.96 Current density vs potential from LSV after 0 cycles of CV stability for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs. Pt data are also reported.

Fig. 3.97 Tafel plot from LSV after 0 cycles of CV stability tests for MoS$_3$/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs.
Fig. 3.98 Current density vs potential from CV after 0 cycles of CV stability tests for MoS\textsubscript{3}/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs.

Fig. 3.99 Impedance curves from EIS after 0 cycles of CV stability tests for MoS\textsubscript{3}/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs.
Summary of results for MoS₃/Ketjenblack at 4:1 and 5:1 S:Mo ratio in ethylene glycol at different final pHs after 0 cycles of CV stability tests.

The 4:1 catalyst results were similar to the original, but for the capacitance, which was the lowest of the series. Almost all the catalysts have equal or higher activity, but for the one synthesized at 200°C, which showed worse parameters. Since the results show some differences even at small pH changes, we can understand how the latter does affect a lot the reaction products. We found out that the pH to obtain the best catalyst should be close to 2.65. At higher pH we have unreacted Mo-precursor and the filtrate solution in orange, at lower pH there probably are some side (or backward) reactions which still decrease the yield to MoS₃ and give a greenish more opaque filtrate solution (Fig. 3.100).
3.4.2 Materials characterization

(1) TEM

As in the DMF case, since the nanoparticles of MoS$_3$ we were synthesizing so far were between 5 and 10 nm, we wanted to see if we could get smaller particles and if they would have increased the number of active sites and the activity. The TEM analysis were performed just on the 4:1 catalyst at pH 4-5 and on the 5:1 one at pH 3-4.
Fig. 3.101 TEM images of MoS$_3$/Ketjenblack 5:1 made in EG + NaOH at two different magnifications. pH = 3-4 H$_2$SO$_4$. Particle size < 1 nm.
Fig. 3.102 TEM images of MoS$_3$/Ketjenblack 4:1 made in EG + 120 mg NaOH at two different magnifications. pH = 4-5 HCl. Particle size < 1 nm.

Our intent was to reduce the particle size to 1-2 nm, but we went even further. The particles detectable at the TEM are 1 nm or above, but we are not able to distinguish any particles in Fig. 3.101 and 3.102. This means that MoS$_3$ is now a thin film of nanoparticles smaller than 1 nm.
Fig. 3.103 STEM elemental mapping of MoS$_2$/Ketjenblack 5:1 in EG + NaOH. pH = 3-4 H$_2$SO$_4$.

Fig. 3.104 STEM elemental mapping of MoS$_2$/Ketjenblack 4:1 in EG + NaOH. pH = 4-5 HCl.
3.4.3 Discussion

One of the main problems we came across in this study was how to completely dissolve ammonium tetrathiomolybdate in water or ethylene glycol. As we have already seen in section 3.3, there are lots of studies in literature that uses the Mo-precursor by dissolving it in DMF\textsuperscript{20-23}, but none of them run the acidification reaction. The problem with DMF is that it forms stable H-bonded complexes with lots of strong acids, like \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \). This is the reason why we started thinking how to avoid the use of DMF but at the same time have the ATM completely dissolved in solution. The reaction between \((\text{NH}_4)_2\text{MoS}_4\) and \(\text{NaOH}\) illustrated by Laurie \textit{et al.} in 1984 looked suitable to our purpose, because the product, \(\text{Na}_2\text{MoS}_4\), is soluble both in water and organic solvents\textsuperscript{24}. Then, through reaction 6. (See section 2.2) \(\text{MoS}_3\) nanoparticles can still be formed in presence of acid. Whether or not the activity increases in this way has been showed by our experiments.

The TEM images in Fig. 3.101 and 3.102 show that not only the nanoparticles size is decreased, but particles are hardly or not visible even at high magnifications. The particles that could be seen at that zooming are as small as 1 nm, meaning that our \(\text{MoS}_3\) nanoparticles are smaller than 1 nm. Indeed a uniform and indistinct thin film is visible, denoting that we achieved the goal of decreasing the particles size.

In Fig. 3.103 and 3.104 we can see the elemental mapping of \(\text{MoS}_3\) on Ketjenblack at S:Mo 5:1 in ethylene glycol when sodium hydroxide has been added before the reaction. The incredibly homogenous and uniform dispersion of the particles of all the elements for both the catalyst at pH = 3-4 and the one at pH = 4-5 is definitely a consequence of the reaction occurred with a completely dissolved Mo-precursor.
As far as the electrochemical experiments are concerned, we can see an improvement in essentially all the relevant parameters. In the majority of the cases, the capacitance and the potential at -10 mA/cm² are increased (Fig. 3.96 and Tab. 3.43). In particular, the 2.65 pH catalyst reached -10 mA/cm² with only -159 mV, 7 mV better than the original one, while the 2.9 pH catalyst at 200°C showed a capacitance of 51.4 mF/cm², about the double of the original catalyst capacitance; it’s remarkable to say that the second catalyst also showed a huge area inside the curve of Cyclic Voltammetry, confirming that the high capacitance was responsible of movements of a high number of charges. We believe that in this catalyst synthesized at 200°C the effect of the reduction of particles size has been neutralized. Indeed, by increasing the temperature of the reaction we promoted the aggregation of particles over the nucleation and the reason of a worse activity in this catalyst may be due to particles bigger than the other catalysts made with NaOH. The charge-transfer resistances are around or below 30 Ω while the Tafel slopes remained constantly around 40 mV/dec without any anomalies (Fig. 3.97 and 3.99), as in the previous best cases.

To the best of our knowledge, there are no studies in literature but one showing similar or close related topics so to have comparisons. Back in 1985, Beckstead et al. conducted a study on the formation of MoS₃ via an acidification reaction of sodium tungstate solutions containing sodium carbonate²⁵. They explains how the yield to molybdenum sulfide strongly depends on the initial and final pH of the solution (Fig. 3.105). It is surprising that with different Mo-precursors we could get similar results: in order to increase the yield to MoS₃

the final pH should be around 3. However, the pH affects the reaction so much that a more accurate value is necessary, which is 2.65 according to our results.

Fig. 3.105 Effect of final pH on molybdenum precipitation by the rapid acidification technique\textsuperscript{25}.

Nevertheless, in our case this is true only if we add the sodium hydroxide, otherwise the pH value has no effect on the yield, as long as it is below 2, so to provide sufficient protons to the reactions. Indeed, with our usual procedure the final pH value was always around 0.5 and we were able to get a clear and transparent filtrate solution.

While Beckstead \textit{et al.} were detecting few ppm of residual Mo-precursor in the filtrate solution even at relatively big change in the pH, we had several mg of residual (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{4} in the filtrate. A good marker that visually told us the amount of Mo-precursor lost was the color of the solution. At pH higher (even 0.1 more) than 2.65 the unreacted Mo-precursor changed the color of the solution to shining orange, while at lower pH there probably are some side (or backward) reactions which generates molybdenum complexes. They still decrease the yield to MoS\textsubscript{3} and give a greenish more opaque filtrate solution (Fig. 3.100).
Indeed every time the filtrate wasn’t colorless and transparent the activity toward the HER decreased, probably due to a lower amount of MoS$_3$.

In conclusion, we were able to decrease the size of the particles and to improve the activity of molybdenum sulfide toward the HER thanks to the addition of 120 mg of sodium hydroxide. However, we found out that the only way to have an increased activity is to modify the amount of acid added, so to have a final pH of 2.65. We can firmly say that MoS$_3$ synthesized on Ketjenblack carbon with an initial S:Mo of 5:1 in ethylene glycol, with the addition of NaOH and acid in a proportional quantity to have a final pH of 2.65 can be considered the best catalyst for the Hydrogen Evolution Reaction in this study and one of the best at the present state of the art, hence opening the way to other improvements and future work.
3.5 REFERENCES


Chapter 4: Conclusions

We developed and tested a procedure for the synthesis of MoS$_3$ nanoparticles on a mesoporous carbon support and for the doping of the catalyst with particular transition metal ions (cobalt and iron), so to increase the surface area while maintaining high conductivity. The experiments were carried out by following a specific pathway, which is changing one variable at time and keeping all the other ones fixed. Ammonium tetrathiomolybdate ((NH$_4$)$_2$MoS$_4$) was decomposed to obtain MoS$_3$ nanoparticles via acidification reaction in liquid solution through sulfuric acid in different concentration and at 100°C and at 165°C, at which also the thermal decomposition of the Mo-precursor starts (section 3.1.2). Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O) was added to increase the S:Mo ratio and so the yield to MoS$_3$. The nanoparticles were synthesized on various carbon supports: Graphene Nanoplatelets (GNP), Ketjenblack EJ-300 and Vulcan XC 72R mesoporous carbon. Different solvents were studied (mostly water, ethylene glycol and dimethylformamide) to obtain different size nanoparticles in order to increase the surface area and hence the activity. We tried to incorporate cobalt and iron during the synthesis process through the addition of their respective acetates to the reaction flask. The catalysts have been characterized first by electrochemical analysis (LSV, CV and EIS), where 0.5 M H$_2$SO$_4$ was the electrolyte and then by physical analysis (SEM, XPS, ICP, CHNS analysis, S/TEM, elemental mapping). The ink, a solution of catalyst powder, ethanol and Nafion solution was loaded on the electrode with the drop-casting technique. During the electrochemical tests MoS$_3$ was reduced to MoS$_2$. 
We started the experiments by investigating the effects of the carbon support (GNP, Ketjenblack and Vulcan) and the initial atomic S:Mo ratio, by changing the ratio of the amount of S-precursor and Mo-precursor. Together with the S:Mo ratio and the carbon, we also investigated the role of the solvent.

Without a strict definition, the activity of these electrocatalysts is a combination of different parameters, which assume different importance depending on the main reason of the study. A good electrocatalyst for the HER should have high current density at low overpotential (for which we always reported the potential at -10 mA/cm²), low charge-transfer resistance ($R_{ct}$, an indicator of the difficulty of the process, we usually got the best activity at $R_{ct} < 30 \, \Omega$), low Tafel slope (when it was ~ 40 or lower, meaning mostly a Volmer–Heyrovsky mechanism, the reaction did not change mechanism during the tests), high-exchange current and high capacitance (mostly in case of electronic coupling with a conductive support).

4.1 EFFECT OF S:MO RATIO

By changing the initial S:Mo ratio we have been able to increase the yield to the product. However, this change was a balance between the increase in the activity due to the higher amount of MoS$_3$ and the decrease due to the presence of more unbonded elemental sulfur, which is a poison for the catalyst. Elemental sulfur was mostly present in catalysts synthesized on GNP or with a S:Mo ratio higher than 5:1, which is the reason of their poorer activity (section 3.1.9, XPS data). When the S:Mo ratio was above 5, the extra sulfur atoms were not integrated in the catalyst structure. Thus, the mechanism of reaction slightly changed (Tafel slope increased) and the catalyst’s activity decreased after few stability tests (section 3.1). The catalyst’s weight was a good indicator of the presence of unbonded
elemental S or of the loss of unreacted Mo-precursor. The practical effect of having more sulfur than we need was an increase in the initial current density, followed by a rapid decrease with a higher slope (in the LSV plots) than the catalysts at lower S:Mo ratio. Another effect was the increased stability (catalysts showed identical activity after several CV stability tests) of the catalysts made on Ketjenblack and Vulcan in water (sections 3.1.4 and 3.1.6, LSV). A high amount of S-precursor decreased the repulsion forces between carbon and water and modified the local charge density distribution in the MoS$_3$ nanoparticles, eventually allowing the electrochemical reaction to occur more with slower Volmer steps. This happens whenever the Tafel slope is above 40 mV/dec.

The amount of extra sulfur in the catalyst before the electrochemical tests was different from the one after the tests. The electrochemical analysis in an aqueous sulfuric acid solution was usually able to wash away part of the elemental sulfur, which blocked some active sites. The real S:Mo ratio was usually between 3 and 4.5, which in most cases meant the presence of elemental sulfur (section 3.1.9, XPS, ICP and CHNS).

The decision of changing solvent for the synthesis procedure came from the problem of dissolving the Mo-precursor and dispersing the Ketjenblack and the Vulcan. Indeed, in every experiments with water and ethylene glycol the solutions with the Mo-precursor was actually a suspension of visible particles, while in the solutions with Ketjenblack or Vulcan in water, after the mixing, we could always visually see large agglomerated particles floating in the solvent even after many hours of sonication.

Ethylene glycol always showed a significant improvement in the activity of the catalysts with all the three carbon tested (sections 3.1.3, 3.1.5 and 3.1.6). One reason was the good
dispersion of the carbons in it: the solution became homogeneous and black, and there were not visible particles.

4.2 EFFECT OF CARBON SUPPORT

The SEM and TEM tests confirmed that the dispersion on the electrode of catalysts on Ketjenblack and Vulcan is better and the elements inside the catalyst are more uniformly distributed than on GNP. Also, with Ketjenblack the surface and bulk composition are more similar while with Vulcan the catalyst particles are more spread on the surface (sections 3.1.9 and 3.1.10). Moreover, not only the elemental sulfur was completely absent on the surface of catalysts made on Ketjenblack and Vulcan, but 70% of the sulfur atoms in the lattice were bridging/apical, meaning that there were more active sites than in catalysts on GNP (section 3.1.9, XPS). The absence of elemental sulfur and molybdenum oxide, confirmed by results from XPS and ICP, validated the hypothesis of high purity for catalysts made on Ketjenblack and Vulcan. The conclusion is that the various-sized porosity of Ketjenblack and Vulcan is more suitable to deposit MoS$_3$ nanoparticles than GNP.

To make a comparison we need to assess catalysts at the same loading. However, when looking at a possible scale up of the process, we needed to know how much catalyst could be loaded on the electrode to increase even more the activity. The loading experiments (section 3.1.8) answered questions about the integrity and functionality of the catalyst film on the electrode. The drop-casting technique was repeated multiple times, which may give rise to a layered structure. The composition and support of the catalyst affected the dispersion of nanoparticles on the electrode. All the layers of MoS$_3$ were active until the thickness of the film reached a plateau value, which we suppose is when not all the active area of the catalyst
is in contact with the electrolyte. The higher amount of carbon (ICP and CHNS) is mostly responsible of the increased capacitance, but the activity improved thanks to the higher amount of MoS₃. GNP supported catalysts are easily detached from the electrode at higher loadings probably because the layers were weakly bonded. Vulcan supported catalysts showed better results but not as good as the Ketjenblack supported ones. Hence, Ketjenblack is a more suitable carbon support for our purpose. With the highest loading we reached with MoS₃/Ketjenblack 5:1 in ethylene glycol (1 mg/cm²), we have been able to maximize its activity and to know when the thickness of the film starts to block part of the active sites. At 250 μg/cm² the thickness of the film is 10-12 μm (sections 3.1.9 and 3.1.10).

4.3 EFFECT OF DOPANTS

As we discussed, the incorporation of cobalt and iron in the vacancies of MoS₃ lattice is not only possible, but also favorable because of the lower energy of doped MoS₃ with respect to the original one. The dopant atoms may increase the performance of the catalyst by increasing the rate of the Volmer or the Heyrovsky step. However, in this study we were not able to correctly dope our catalysts, mostly because of the synthesis technique. None of the doped catalysts showed an equal or better activity than the original undoped ones, but one: 2%Fe at 7:1 ratio, which had a lower amount of MoS₃ than the undoped catalyst and a real ratio of 6:1, but yet higher activity (section 3.2.3). In most cases the ICP data showed that the real weight percentage of cobalt was 0.1%, while iron was absent (sections 3.2.2 and 3.2.4): the dopants were apparently washed away during the filtration step without going into the molybdenum sulfide structure. The wide range of different results indicates that, even though the dopants have always been washed away, just their presence
during the synthesis reaction changed significantly the activity of the catalysts. The dopants were not directly responsible of the activity change. More likely, they changed indirectly the number of active sites, by modifying the morphology of the MoS₃ nanoparticles. Indeed, TEM results (sections 3.2.2 and 3.2.4) showed that the nanoparticles were bigger than in the undoped catalyst and the distribution of Mo, S and C atoms in the catalyst was worse. When the amount of dopant was enough to be seen with TEM, it was in the form of high-concentrated agglomerates.

The molybdenum content for doped catalysts was 3-6 % lower on average than the undoped ones and the S:Mo ratio is increased. Moreover, during the synthesis reaction cobalt sulfate was formed, which contributed to the lower activity (section 3.2.2, XPS).

We conclude that the reason of the worse performances for the doped catalysts relies on the amount of MoS₃ they had, which is lower than the undoped ones, and on the absence of a consistent amount of dopant in the catalyst structure.

The loss and poor dispersion of cobalt and iron were probably due to undissolved Mo-precursor and low temperature of the process (~ 165°C). The dissolution of reactants can be an issue both for the chemical reaction to MoS₃ and for the deposition of the dopants on the catalyst: the bigger are the reactants particles, the worse is the final dopants dispersion. The temperature might be another issue because we intended to insert the dopants in the catalyst vacancies. By increasing the temperature, the number of the vacancies increases too, and so the probability that the dopants are deposited into them is raised.
We believe that the transition metal ions can still improve the activity of the molybdenum sulfides, as long as they are synthesized with a procedure that allows cobalt and iron ions to go correctly inside the MoS$_3$ structure.

4.4 CHANGE IN THE CATALYST SYNTHESIS CONDITION: SOLVENT AND MO-PRECURSOR

The reason why we started thinking about the dissolution problem came from the idea that, since the nanoparticles of MoS$_3$ we synthesized were between 5 and 10 nm, we believed that smaller particles would increase the number of active sites and the activity. Amongst all the solvents tested, just the mixtures 125 ml H$_2$O + 175 ml DMF and 150 ml EG + 50 ml DMF were able to completely dissolve the Mo-precursor. With the other solvents the solution (which actually was a suspension) had a brownish opaque color, while with DMF mixtures the solution became shining orange.

We achieved our goal of decreasing the MoS$_3$ nanoparticles size in DMF to 1-2 nm. Also, the elemental mapping on MoS$_3$/Ketjenblack made in DMF gave us an idea of the great potential of this technique on the catalysts. A very good dispersion was visible, and all the nanoparticles were fairly spread on the carbon support (section 3.3.2, STEM).

As for the catalyst weight, when using the DMF we got lower yield to MoS$_3$ (10-30% less) than the experiments done in water and ethylene glycol. This may be due the H-bonds that DMF forms with the acid. Indeed, the similar final pH (~2.7, sections 3.3.1 and 3.3.3), despite the different amounts of acid, was evidence for the constant amount of free protons in solution, confirming the interactions between the DMF and the acid. However, since the electrochemical results were essentially identical to the best catalyst made in ethylene glycol
(the exchange current was always higher though), we increased the activity per catalyst weight.

With DMF, our intent was to reduce the particle size to 1-2 nm, but with NaOH we went even further. The product of the reaction between (NH₄)₂MoS₄ and NaOH (Na₂MoS₄) was still able to decompose into MoS₃ nanoparticles. Indeed, thanks to NaOH, MoS₃ has been synthesized as a uniform and indistinct thin film of nanoparticles smaller than 1 nm (section 3.4.2, STEM). The incredibly homogenous and uniform dispersion of the particles is definitely a consequence of the reaction occurred with a completely dissolved Mo-precursor (yield was 85-90%).

The final pH affected our reactions even if varied by 0.1 (section 3.4.1, LSV). The experiments showed that the activity is maximized when the pH value is close to 2.65. At higher pH we had unreacted Mo-precursor, at lower pH the yield to MoS₃ was decreased too, suggesting the occurrence of interactions between the acid and the products. This is true only in presence of NaOH, otherwise the pH value had no effect on the yield, as long as it was below 2, so to provide sufficient protons to the reactions. Indeed, with our normal procedure the final pH value was always around 0.5 without any losses of Mo-precursor (section 3.4.1).

At temperatures higher than 165°C, the aggregation of particles is promoted over the nucleation and the bigger particles are responsible of a worse activity (sections 3.4.2 and 3.4.3, STEM).

In conclusion, we can state that MoS₃ synthesized on Ketjenblack carbon with an initial atomic S:Mo of 5:1 in ethylene glycol, with the addition of NaOH and acid in a proportional quantity to have a final pH of 2.65 can be considered the best catalyst for the Hydrogen
Evolution Reaction in this study and one of the best at the present state of the art, hence opening the way to other improvements and future work (Tab. 4.1).

**Tab. 4.1 Summary data of relevant studies on the MoS$_2$ as a catalyst for the hydrogen evolution reaction.**

<table>
<thead>
<tr>
<th>Researchers</th>
<th>Compound studied</th>
<th>Potential at -7 mA/cm$^2$ (mV)</th>
<th>Potential at -10 mA/cm$^2$ (mV)</th>
<th>Potential at -23 mA/cm$^2$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luiso (this study)</td>
<td>MoS$_3$/Ketjenblack</td>
<td>-153</td>
<td>-159</td>
<td>-174</td>
</tr>
<tr>
<td>Chang <em>et al.</em>$^1$</td>
<td>MoS$_x$/graphene</td>
<td>-</td>
<td>-150</td>
<td>-</td>
</tr>
<tr>
<td>Li <em>et al.</em>$^2$</td>
<td>MoS$_2$/RGO</td>
<td>-</td>
<td>-165</td>
<td>-</td>
</tr>
<tr>
<td>Yan <em>et al.</em>$^3$</td>
<td>MoS$_3$/CNT</td>
<td>-</td>
<td>-200</td>
<td>-</td>
</tr>
<tr>
<td>Bian <em>et al.</em>$^4$</td>
<td>MoS$_3$/CNT</td>
<td>-155</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zheng <em>et al.</em>$^5$</td>
<td>MoS$_2$/RGO</td>
<td>-</td>
<td>-</td>
<td>-200</td>
</tr>
<tr>
<td>Liao <em>et al.</em>$^6$</td>
<td>MoS$_3$/graphene</td>
<td>-</td>
<td>-140</td>
<td>-</td>
</tr>
<tr>
<td>Merki <em>et al.</em>$^7$</td>
<td>Co-MoS$_3$</td>
<td>-</td>
<td>-184</td>
<td>-</td>
</tr>
<tr>
<td>Lin <em>et al.</em>$^8$</td>
<td>MoS$_3$/CNT</td>
<td>-</td>
<td>-200</td>
<td>-</td>
</tr>
</tbody>
</table>
4.5 REFERENCES


Chapter 5: Future work

Many hints on the possible future work have been pointed out throughout this study. First, the synthesis procedure may be further improved. During the experiments we noticed a change in the viscosity of the ink dependent on the sonication time. A study on this effect would be helpful for reducing the number of depositions on the electrode and eventually for the scale-up of the process.

The deposition technique is actually a step that could be improved. The drop casting technique has some defects, mostly in the real amount of ink deposited and on the dispersion on the electrode. The electrodeposition technique would probably be more suitable for having a homogenous and uniform film of catalyst on the electrode surface, even though this would require more efforts and changes in developing a totally new strategy for the deposition.

Speaking of changing procedure, while still keeping the general approach of the acidification technique, the solution with the Mo-precursor and the carbon could be poured in a bath with concentrated sulfuric acid and sodium sulfide. This would avoid the problem of an inhomogeneous pH in the flask after the addition of the acid and the issue of preventing H₂S from escaping while allowing a hole on the cap for pressure relief. Indeed, with a high concentration of sodium sulfide in the bath there wouldn’t be the problem of lack of sulfur atoms for the reaction to MoS₃.

The temperature of the reaction was an issue and we were able to test the catalyst just at 100°C, 165°C and 200°C. Investigating the thermal effect on the catalyst synthesis would bring more knowledge in terms of grain nucleation and aggregation control. Since the heat
could be used for the reduction of MoS$_3$ to MoS$_2$, a heat treatment on the catalyst powder before the electrochemical tests may be a good way to crystallize part of the catalyst before testing its activity: this may improve its performance. The temperature was an important factor also for the experiments with NaOH and DMF. The latter, in particular, is a great source of possible future work. With DMF and water, when 20 ml of acid were added, we were able to synthesize a catalyst with the same activity but less MoS$_3$ inside. By investigating the role of the solvent and the DMF interaction with the acids (Sulfuric and hydrochloric in particular) and other solvents, one may obtain an increased activity. This would need to be done with a strict and constant control of the pH before, during and after the reaction. Compounds other than DMF might dissolve the Mo-precursor and result more suitable, mostly if they have a wider range of temperatures to investigate (i.e. boiling temperature > 200°C).

One of the most important study which may come after this would be the doping of the catalyst after the reaction between the Mo-precursor and NaOH has occurred. As we stated before, the dissolution of the reactants can be an issue both for the chemical reaction to MoS$_3$ and for the deposition of the dopants on the catalyst. Generally speaking, it would be necessary a study on how to increase the vacancies in the molybdenum sulfides lattice and how to decrease their Gibbs free energy in order to have the dopants deposited into them.

The last section of chapter 3 showed how powerful the synthesis of MoS$_3$ is after the addition of sodium hydroxide as a new reactant. However, the outcome of adding 120 mg of NaOH was a solution with a pH ~ 11 and we never tried other amounts. There may be new
interesting results if the starting pH is lower, meaning adding less NaOH and consequently less acid, so to always obtain a pH of 2.65.

Finally, since there have been many studies on the catalytic activity toward the HER of other transition metal sulfides, it would be interesting to apply to them the knowledge gained from this study. In particular, with MoS$_3$ the activity increased when the size of the nanoparticles were less than 1 nm thanks to the NaOH: creating a film of very small nanoparticles may be a way to improve the activity of other compounds too. Also, we believe that the interactions with other transition metals (e.g. doping) may enhance the performances of the transition metal sulfides toward the HER (even doping them with molybdenum).
Appendix A – CHN/S Analysis

Principle of operation – The Perkin-Elmer PE 2400 CHN elemental analyzer:

Robert F. Culmo, Senior Staff Scientist

The PE 2400 Elemental Analyzer is a modern elemental analyzer for the rapid determination of the carbon, hydrogen and nitrogen content in organic and other types of materials. The CHN and CHNS modes are based on the classical Pregal and Dumas methods, where samples are combusted in a pure oxygen environment, with the resultant combustion gases measured in an automated fashion. In addition to carbon, hydrogen and nitrogen determinations, an accessory kit is available which allows the measurement of oxygen content of organic materials.

CHN and CHNS

A schematic diagram of the PerkinElmer 2400 Series II CHNS/O Elemental Analyzer is shown in Fig. 6.1.

The 2400 Series II system is comprised of four major zones:

- Combustion Zone
- Gas Control Zone
- Separation Zone
- Detection Zone
Operating gases include oxygen, for combustion of sample materials, and a carrier gas, either helium or argon. The use of argon as an optional carrier gas is unique to this design and assures cost-effective use of the PE 2400 CHN in those areas of the world where helium is difficult to obtain due to price or availability.

In the **Combustion Zone**, samples encapsulated in tin or aluminum vials are inserted automatically from the integral 60-position autosampler or manually using a single-sample auto injector.

In the presence of excess oxygen and combustion reagents, samples are combusted completely and reduced to the elemental gases CO$_2$, H$_2$O, N$_2$ and SO$_2$. Users have the flexibility of optimizing static and dynamic combustion conditions to meet the specific sampling need of their laboratory. The combustion products are then passed to the **Gas Control Zone** of the 2400 Series II. Gases are captured in the mixing chamber of the Gas Control Zone. Here, gases are rapidly mixed and precisely maintained at controlled
conditions of pressure, temperature and volume. By controlling the product gases from combustion/pyrolysis to the same exact conditions (pressure, volume and temperature) for every run, outside influences (barometric pressure changes, altitude) are eliminated. The combustion process is separated from the column and detector which gives the flexibility of varying combustion conditions in the same series of runs without influencing separation and detection and the gases are mechanically homogenized therefore providing precision and accuracy. After homogenization of product gases, the mixing chamber is depressurized through a column in the **Separation Zone** of the instrument. The separation approach used is a technique known as Frontal Chromatography. As the gases elute, illustrated in Fig. 6.2, they are measured by a thermal conductivity detector in the **Detection Zone** of the analyzer. Since measurements in this design are made as stepwise changes from the carrier gas baseline, the variations associated with the quantification of peak signals in other CHNS/O analyzers is eliminated.

![The PerkinElmer 2400 CHN Elemental Analyzer](image)

*Fig. 6.2 Chromatogram PE 2400.*
All of the steps described above are accomplished in under 5 minutes of analytical time after the sample is first introduced into the system.

The basic procedure was modified for MoS$_3$ samples on carbon support. The combustion temperature was increased to 985 degrees C and extra Oxygen (5 seconds) was added during the "Oxyfill" stage of combustion. (Normally the instrument is set for combustion of 925 degrees and "Oxyfill" of 3 seconds). The weight of the sample is usually determined by the material. Usually, high carbon samples are weighed out 4mg but for ours roughly 2 mg were weighed out.

*User benefits:*

There are many unique user benefits of the PE 2400 CHN Elemental Analyzer. The major ones include:

- Versatile combustion design that certifies complete combustion of most sample materials. Even if numerous different classes of samples are routinely analyzed, you can count on complete sample combustion.
- Broad linear range of operation allows the calibration of the PE 4200 with a single standard material. Time-consuming multiple standard calibration is not required.
- Diagnostic routines monitor electronic and pneumatic components and alert the operator in the rare event that a problem is encountered. The result is peace of mind that the analyzer is operating properly.
- Capability of handling a wide variety of sample types, including solids, liquids, volatile and viscous samples.
• Microprocessor control of all system functions assures reproducibility from run to run, day to day and month to month.

• Rapid analysis time of under 5 minutes improves laboratory productivity.

• 60-position autosampler allows automated unattended operation, even at night and on weekends.

• A unique “WAKEUP” routine allows the automatic equilibration and standardization of the PE 3400 CHN at any operator-selected date and time. This feature allows the system to be ready when you are, such as when you arrive in the morning.

• Single keyboard entry of parameters and operating conditions simplifies operation and makes learning how to use the system easy.
Appendix B – ICP

Method digestion:

Samples were quantitatively weighed to the nearest 0.0001 g into 7 ml Teflon screw cap CEM Microwave digestion vessels. Next, 3.5 ml of freshly prepared aqua regia (3:1 conc HCl: conc. HNO3) was added to each vessel. The loosely capped samples predigested overnight in a hood. After the pre-digestion phase, the samples were capped, loaded into the CEM X1500 plus vessels, secured and microwaved (CEM,Mars 5, Matthews, NC) at the following parameters:

- 100% at 600 W for 7 min, then 330 W for 30 min which maintains 70 psig.

After cooling the samples were uncapped and quantitatively transferred to 50 ml Corning tubes by filtering through a Whatman 41 paper filter. The filter and residue was washed with 5% Optima HCl. The digestates were brought to volume (20 ml) with DI water in the 50 ml tube.

Instrumentation:

Samples were analyzed using inductively-coupled plasma optical emission spectroscopy (ICP-OES), which was performed on a Perkin Elmer 8000 DV ICP-OES utilizing a cross-flow nebulizer with the following parameters: plasma 12.0 L Ar(g)/min; auxiliary 0.2 L Ar(g)/min; nebulizer 0.55 L Ar(g)/min; power 1500 W; peristaltic pump rate 1.40 ml/min. Elemental concentrations were determined by measuring one or more emission lines (nm) to check for interferences: Mo 202.031, 204.597; S 181.975, 180.669. Samples were diluted
x10, so that concentrations would fall within the prepared multi-point calibration curves. Multi-point calibration curves were made from certified standards. Calibration curves were verified by preparing a calibration check solution from a different stock standard. Laboratory check standards were analyzed every 12 samples, with instrument re-calibration if check standards were not within \( \pm 10\% \) of the initial concentration. Instrument reproducibility \((n=10)\) determined using 1 mg/L elemental solutions resulted in \( <\pm 2\% \) error.