



Universiteit
Leiden
The Netherlands

The electrode-electrolyte interface in CO₂ reduction and H₂ evolution: a multiscale approach

Cecilio de Oliveira Monteiro, M

Citation

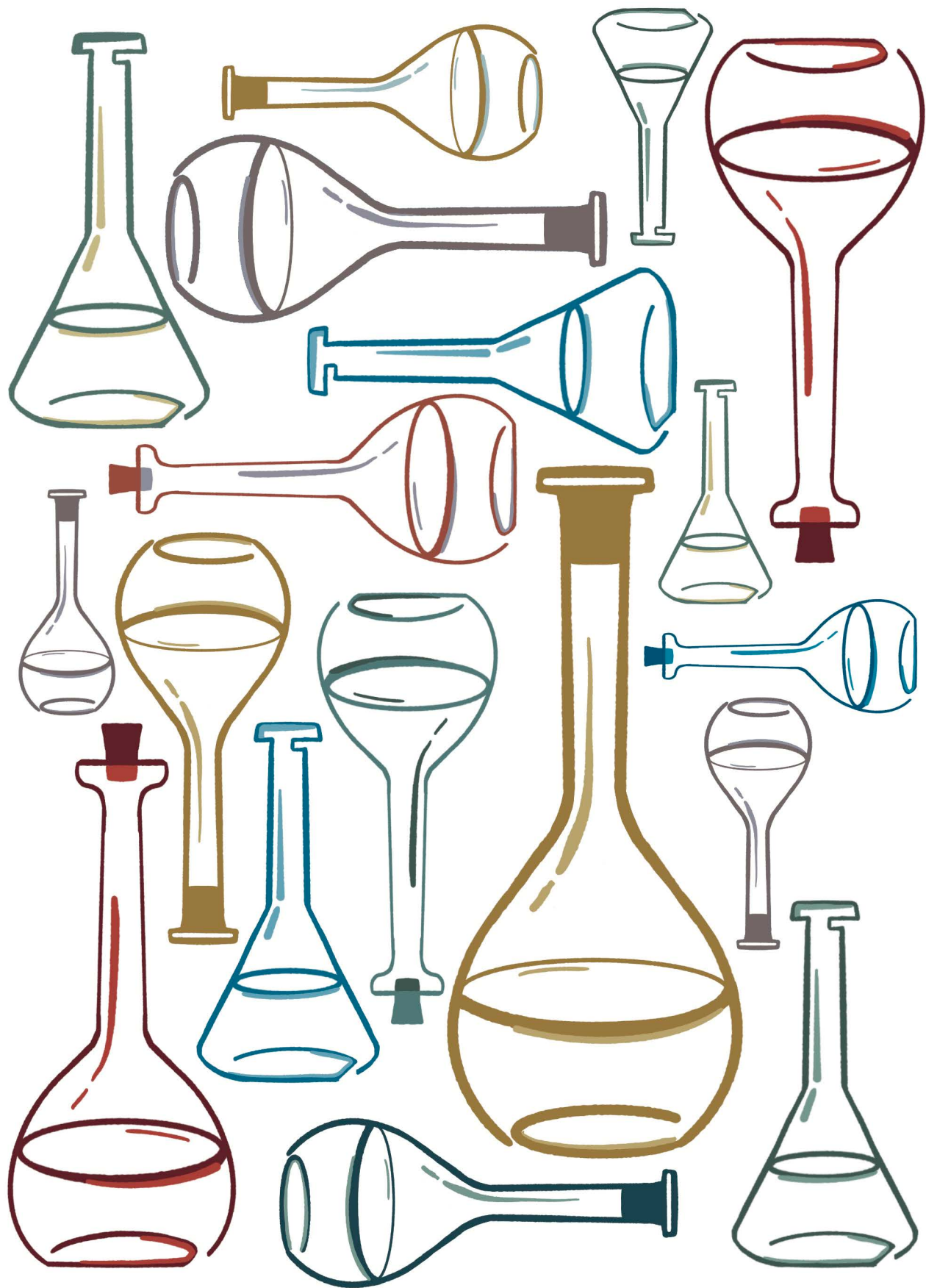
Cecilio de Oliveira Monteiro, M. (2022, February 15). *The electrode-electrolyte interface in CO₂ reduction and H₂ evolution: a multiscale approach*. Retrieved from <https://hdl.handle.net/1887/3274033>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/3274033>

Note: To cite this publication please use the final published version (if applicable).



List of publications



Chapter 2

Measuring local pH in electrochemistry

Monteiro, M. C. O., Koper, M. T. M. *Curr. Opin. Electrochem.* 25, 100649. (2021)

Chapter 3

Mediator-free SECM for probing the diffusion layer pH with functionalized gold ultramicroelectrodes.

Monteiro, M. C. O., Jacobse, L., Touzalin, T., Koper, M. T. M. *Anal. Chem.* 92 (2), 2237–2243. (2020)

Chapter 4

Time-resolved local pH measurements during CO₂ reduction using Scanning Electrochemical Microscopy: buffering and tip effects.

Monteiro, M. C. O., Mirabal, A., Jacobse, L., Doblhoff-Dier, K., Barton, S. C., Koper, M. T. M. *JACS Au*, 1 (11), 1915–1924. (2021)

Chapter 5

Understanding the voltammetry of bulk CO electrooxidation in neutral media through combined SECM measurements.

Monteiro, M. C. O., Jacobse, L., Koper, M. T. M. *J. Phys. Chem. Lett.* 11 (22), 9708–9713. (2020)

Chapter 6

Interfacial pH measurements using a Rotating Ring-Disc electrode with a voltammetric pH sensor.

Monteiro, M. C. O., Liu, X., Hagedoorn, B., Snablié, D., Koper, M. T. M. *ChemElectroChem* 8, DOI: 10.1002/celec.202101223 (2021)

Chapter 7

Alumina contamination through polishing and its effect on hydrogen evolution on gold electrodes.

Monteiro, M. C. O., Koper, M. T. M. *Electrochim. Acta* 325, 134915. (2019)

Chapter 8

Absence of CO₂ electroreduction on copper, gold and silver electrodes without cations in solution.

Monteiro, M. C. O., Datilla, F., Hagedoorn, B., García-Muelas, R., López, N., Koper, M. T. M. *Nat. Catal.* 4 (8), 654–662 (2021)

- Cations play an essential role in CO₂ reduction. Chen, L. D. *Nat. Catal.*, News and Views 4 (8), 641–642 (2021)
- Insight into the effect of metal cations in the electrolyte on performance for electrocatalytic CO₂ reduction reaction. Li, J. J., Zhang, Z. C., & Hu, W. P. *EEM*, Highlight, DOI: 10.1002/eem2.12294 (2021)
- Leiden chemists improve electrochemical production of sustainable chemical building blocks. Moezelaar, R. *Leiden University News*, 16th August (2021)
- Metal cations drive carbon dioxide's chemical reduction. Lopatka, A. *Physics Today online*, 27th August, DOI: 10.1063/PT.6.1.20210827a (2021)
- Metal cations drive carbon dioxide's chemical reduction. Lopatka, A. *Physics Today* 74, 10, 20, DOI: 10.1063/PT.3.4852 (2021)

Chapter 9

The role of cation acidity on the competition between CO₂ reduction and hydrogen evolution on gold electrodes

Monteiro, M. C. O., Datilla, F., López, N., Koper, M. T. M. *J. Am. Chem. Soc.*, DOI: 10.1021/jacs.1c10171 (2022)

Chapter 10

Understanding cation trends for hydrogen evolution on platinum and gold electrodes in alkaline media.

Monteiro, M. C. O., Goyal, A., Moerland, P., Koper, M. T. M. *ACS Catalysis*, 11, 14328–14335 (2021)

Chapter 11

Efficiency and selectivity of CO₂ reduction to CO on gold gas diffusion electrodes in acidic media.

Monteiro, M. C. O., Philips, M. F., Schouten, K. J. P., Koper, M. T. M. *Nat. Commun.* 12 (1), 4943 (2021)

- pH dependence of CO₂ reduction to CO. *Dioxide Materials News*, November (2021)

Chapter 12

Probing the local activity of CO₂ reduction on gold gas diffusion electrodes: effect of the catalyst loading and CO₂ pressure.

Monteiro, M. C. O., Dieckhöfer, S., Bobrowski, T., Quast, T., Pavesi, D., Koper, M. T. M.; Schuhmann, W. *Chem. Sci.* 12, 15682–15690 (2021)

Other publications

Electrolyte buffering species as oxygen donor shuttles in CO electrooxidation.

Marcandalli, G., Monteiro, M. C. O., Koper, M. T. M. *Phys. Chem. Chem. Phys.*, DOI: 10.1039/D1CP05030C (2022)

In situ observation of the Cs⁺-Au(100) interactions at acidic and alkaline pH using Surface X-Ray Diffraction.

Monteiro, M. C. O., Jacobse, L., Vonk, V., Deng, X., Koper, M. T. M., Stierle, A., in preparation

Electrolyte Effects on CO₂ Electrochemical Reduction to CO.

Marcandalli, G., Monteiro, M. C. O., Goyal, A., Koper, M. T. M. *Acc. Chem. Res.*, in preparation

Best Practices for Experimentation, Analysis, and Benchmarking of Electrochemical Water Splitting

Shih, A., Ojha, K., Monteiro, M. C. O., Park, S., Vos, R., Marques da Silva, A., Pavesi, D., Philips, M., McCrum, I., Dattila, F., Mom, R., López, N., Koper, M. T. M. *Nat. Rev. Methods Primers*, in preparation

From waste to valuable resource: lignin as a sustainable anti-corrosion coating.

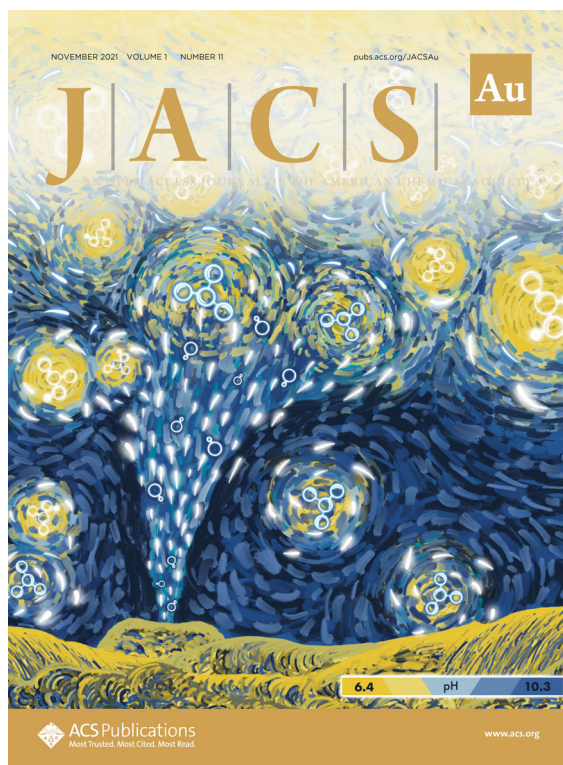
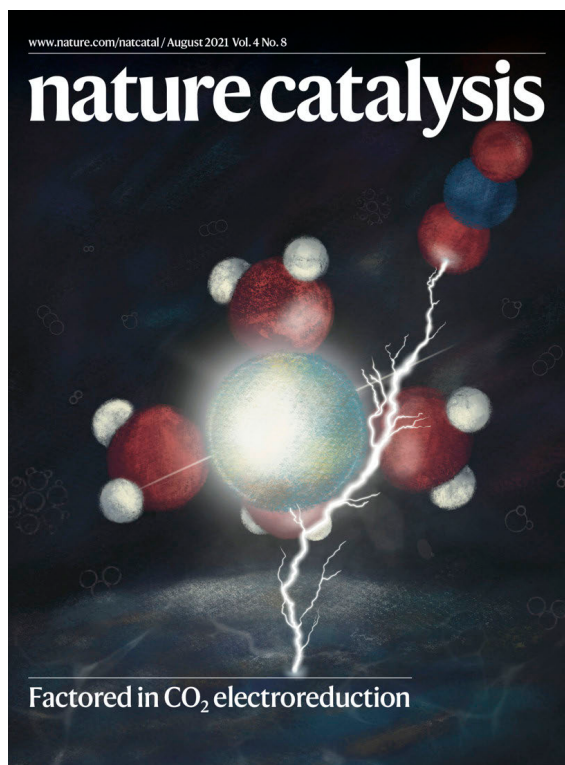
Dastpak, A., Yliniemi, K., Monteiro, M. C. O., Höhn, S., Virtanen, S., Lundström, M., Wilson, B. *Coatings* 8 (12), 454 (2018)

Metal–phosphate bilayers for anatase surface modification.

Monteiro, M. C. O., Cha, G., Schmuki, P., Killian, M. S. *ACS Appl. Mater. Interfaces* 10 (7), 6661–6672 (2018)

Tuning anatase surface reactivity toward carboxylic acid anchor groups.

Monteiro, M. C. O., Schmuki, P., Killian, M. S. *Langmuir* 33 (49), 13913–13922 (2017)



Curriculum vitae

Mariana Cecílio de Oliveira Monteiro was born on the 21st of February 1991 in Belo Horizonte, Minas Gerais, Brazil. During high school (2006-2009) she developed a strong interest for chemistry, while having many extracurricular activities as a Classical Ballet and Jazz dancer and teacher. In 2009 Mariana decided to further explore her interest in chemistry and started her bachelor studies in Chemical Engineering at the Federal University of São Joao Del-Rei, in Ouro Branco, Brazil. In parallel to her studies, she still worked as a teacher at a local dance school. During her bachelors, Mariana had her first contact with the scientific research world thanks to Prof. Dr. Jorge D. A. Bellido, with whom she worked for 2 years with as an undergraduate research assistant investigating heterogeneous catalysts for the ethanol steam reforming.

In 2012 Mariana was awarded a full scholarship from the Brazilian National Council for Scientific and Technological Development (CNPQ) under the “Science Without Borders” program, which gave her the unique opportunity to study in The Netherlands. Mariana did part of her bachelor studies in the University of Groningen and during her stay, worked as an undergraduate research assistant in the group of Prof. Dr. Francesco Picchioni, investigating the synthesis of polyketones. This led to her master thesis research, which was carried out in the same group, entitled “Polymeric amines by chemical modifications of alternating aliphatic polyketones for arsenic removal of wastewater”. To expand her experiences beyond academic research, Mariana also worked for 6 months as an R&D intern in the paper department of the Dutch starch industry Avebe, optimizing paper surface sizing solutions.

Mariana continued her education in 2015, following the Elite Master’s Programme in Advanced Materials and Processes at the Friedrich-Alexander University Erlangen-Nürnberg (FAU), Germany, with specialization in Nanomaterials and Advanced Processes. Beyond the master curriculum, Mariana followed several soft-skill courses, was a member of the Elite Network of Bavaria, and class representative in the program board. In the interest of pursuing a career in research, during her masters Mariana worked as a graduate research assistant in various groups. At the Institute of Chemical Reaction Engineering, Mariana worked in the group of Prof. Dr. Peter Wasserscheid on projects regarding the decomposition of formic acid and catalyst synthesis via electrophoretic deposition. At the Institute of Biomaterials, Mariana worked in the group of Prof. Dr. Aldo Boccacini on the synthesis of Bioglass® and Bioglass®-chitosan coatings. At the Institute of Surface Science and Corrosion, Mariana worked for 1.5 years on projects for Siemens regarding the corrosion behavior of pipeline materials. Mariana developed her master thesis at the same institute, under the supervision of Prof. Dr. Manuela S. Killian in the group of Prof. Dr. Patrick Schmuki. She graduated *cum laude* with a master thesis entitled “Boosting anatase surface reactivity towards carboxylic acid anchor groups”, which also resulted in her first two scientific publications. Besides the publications, in 2017 Mariana was awarded the FAU Deutschlandstipendium prize, and in 2018 Mariana’s master thesis was awarded the Luise Prell Prize.

Mariana moved back to the Netherlands in 2017 to pursue a PhD in electrocatalysis under the guidance of Prof. Marc Koper, at Leiden University. The project was part of the Marie Curie ITN ELCOREL and involved seven partner institutions, creating a very dynamic and exciting research atmosphere. Mariana's initial task was to unveil electrolyte effects on the electrochemical CO₂ reduction reaction. However, Mariana dedicated the first years of her PhD to building a dedicated Scanning Electrochemical Microscope (SECM) from scratch, together with miniaturized (pH, H₂, CO) sensors. This and many other techniques were used during her PhD to answer questions related to CO₂ and H₂ electrocatalysis and the interaction between the electrolyte and metal electrodes. Mariana also had the chance to transfer the fundamental insights obtained in Leiden into a larger-scale CO₂ electrolysis system, while being a visiting researcher at the company Avantium, in Amsterdam, under the supervision of Dr. Klaas Jan Schouten and Matthew Philips. Mariana continued bridging fundamental and applied research also in a collaboration with the group of Prof. Dr. Wolfgang Schuhmann at the University of Bochum, Germany. During a month stay, she used shear-force-based SECM to probe the local activity of technologically relevant gas diffusion electrodes. During her PhD, Mariana also established collaborations with theoreticians from the group of Prof. Dr. Núria López from the Institute of Chemical Research of Catalunya (Spain), and Prof. Dr. Scott Calabrese Barton from the Michigan State University (USA). Finally, Mariana also performed Surface X-Ray Diffraction measurements at the German Electron Synchrotron DESY as part of a (still ongoing) collaboration with the group of Prof. Dr. Andreas Stierle, to investigate cation-surface interactions at the molecular/atomic level.

During her PhD, Mariana supervised 3 master and 4 bachelor students, and taught instrumental analysis in the "Organic Chemistry" practical course. She was a member of the Holland Research School of Molecular Chemistry (HRSMC) PhD platform. Mariana gave invited oral presentations at the FunCOS seminar (Erlangen, Germany), Bernoulli Symposium (Groningen, The Netherlands), Vlaamse Instelling voor Technologisch Onderzoek (VITO, Mol, Belgium) and at the University of Copenhagen (Copenhagen, Denmark). Mariana also presented her research work in various (inter)national conferences. She was awarded poster prizes at the SurfCat Summer School (2018, Denmark), and at the 71th and 72th meetings of the ISE - International Society of Electrochemistry (2020, Belgrade and 2021, Jeju). Mariana gave contributed talks in the 72nd ISE (2021, Jeju), nanoGE Conference (2021, online), Electrochemical Society Fall meeting (2021, Chicago/online), HRSMC Symposium (2022, Amsterdam) and at the Netherlands' Catalysis and Chemistry Conference (NCCC) in 2020, where she was also appointed a lecture award. Mariana's work has been highlighted in the cover of Vol. 4 Issue 8 of *Nature Catalysis*, Vol. 1 Issue 11 of *JACS Au* and the *Journal of The American Chemical Society* (in press) through the beautiful artwork from Katrina Goretskaya; and *ChemElectroChem* 1/2022 with a cover picture developed by her.

Starting from April 2022, Mariana will continue her scientific career as a postdoc fellow in the Interface Science Department of the Fritz-Haber-Institute of the Max-Planck-Society in Berlin with Prof. Dr. Beatriz Roldán Cuenya and Dr. Sebastian Oener. Mariana will keep bridging fundamental and applied electrochemistry using SECM and Scanning Ion Conductance Microscopy (SICM) to study bipolar membranes and gas diffusion electrodes.

Acknowledgments

First, I want to thank Prof. Marc Koper for providing me with the opportunity to join the Catalysis and Surface Chemistry (CASC) group four years ago. Marc, thank you for giving me the freedom to develop my own ideas and for the subtle yet impactful advises you gave me throughout the way. Beyond all the scientific knowledge, you thought me a lot about scientific conduct, which I will always carry with me in my career. Thank you for encouraging me to pursue my curiosities and develop new projects, but also for saying “enough is enough” in the right moments. I also want to express my gratitude to my former mentors, Prof. Jorge Alguier Bellido and Prof. Manuela Killian, who contributed to my PhD, years ago, by helping to shape who I am as a researcher.

Secondly, after these four years, I am certain that one cannot do science alone. This thesis only came to be due to the valuable contributions of several people along the way. I want to express my gratitude to all former and current members of CASC with whom I had the chance to work with. You created a healthy and stimulating work environment, thank you for all the valuable inputs on my research. I also want to thank José Dijkzeul for the care and Wen Tian Fu for the funny conversations while sharing the X-Ray/SECM lab. Some colleagues became good friends and made these four years go by in a light and fun way. My dear paranymph Thomas, thank you for introducing me to the 4-NTP molecule, for helping me with the SECM struggles, for celebrating with me every step of the way, and for the scientific and non-scientific conversations over a glass of bubbles. Sabine, thank you for being such a good friend, and for all the support. Elena, Richard, Stefan, Giulia and Akansha, thank you for your friendship, the discussions, the relaxing and happy moments. To my Master students: Max, Bellenod and Demi; I hope I contributed to your scientific formation at least as much as you contributed to this thesis.

Besides CASC, I was lucky to be part of the Marie Curie ITN ELCoREL, which provided me with an exciting research and learning environment and also brought me good friends. I want to thank all ELCoREL members, especially Federico and Rebecca, for the nice moments we shared during (and outside) project meetings. Also, my gratitude to the friends Vlad and Katrina, for all the efforts to make my thesis artwork. Katrina, I have no words to describe how talented you are.

Furthermore, the large body of work of my thesis was, in part, only possible due to the successful collaborations I established along the way. I want to thank Prof. Scott Calabrese Barton and Alex Mirabal for taking up the challenge of simulating my local pH experiments, which led to the contributions to Chapter 4. Also, I thank my co-promotor Prof. Núria López and Federico Dattila, for educating me in the world of theoretical electrocatalysis, and for the contributions to Chapters 8 and 9. I also thank Dr. Klaas Jan Schouten for giving me the opportunity to be at Avantium, and Matthew Philips for the guidance in the lab work, which resulted in Chapter 11. I want to also thank Prof. Wolfgang Schuhmann for warmly welcoming me in his group in Bochum during weird pandemic times, and Stefan Dieckhöfer for the intense but exciting three weeks we shared by the SECM, which

resulted in Chapter 12. Finally, I want to thank Prof. Andreas Stierle for the nice collaboration we developed for performing synchrotron-based X-Ray Diffraction measurements, which I am sure will still lead to many interesting results as we continue.

My last words of gratitude go to those who not always fully understood my work but were always enthusiasts and supporters. I have an amazing family, thank you for being inspiring, for all your support and cheering. Tia Bú (*in memoriam*), you left us when I was halfway this journey, but your love and support I carry with me forever. A special thanks to Tia Rosa and to Tati, for the care and advises; and to Manu and Mumu, for bringing joy to my life. To my childhood friends, in special Isis, Ana, Paula, Livia, Bárbara, Ligia; to my friends from República Só Benzeno; Bel, Loreny, to the friends from Groningen, and everyone else that somehow is in my life, thank you for, from close or far away, being with me at every step. A special thanks to Mari and Gui for being my rock in The Netherlands, and always being there for me.

My dear Leon, all my love and gratitude for how you helped shaping my PhD, for your care, for letting me be me, but also for driving me to be a better person. Thanks for inspiring and challenging me, and for all the “never boring days”. We started this journey as colleagues who were also good friends, and we now continue as partners in life and in science. I could not have wished for more. Many thanks also to your family, for being there for me, their love and care.

Finally, and most important, I would like to thank my parents, Marcelo and Elvira, for their unconditional support and for always being so close to me, no matter how physically far we actually have been from each other for the past years. We came a long way, that none of us thought was possible... this is “our” thesis. You keep reminding me that even the small victories should not be taken for granted and are my biggest examples. I love you, your kindness, and your funny advises. Thank you and let’s see what next adventures wait for us.

Agradecimentos

Em primeiro lugar, quero agradecer o Prof. Marc Koper pela oportunidade de ingressar no grupo de Catálise e Química de Superfície (CASC), em Leiden. Marc, obrigado por me dar liberdade para desenvolver minhas próprias ideias e por seus conselhos sutis, mas impactantes, ao longo do caminho. Além de todo conhecimento científico, você me ensinou muito sobre conduta científica, ensinamentos que levarei para minha carreira. Obrigado por me encorajar na exploração de minhas curiosidades e desenvolvimento de novos projetos, e por ter dito “basta” nos momentos certos. Minha gratidão também aos meus ex-mentores, Prof. Jorge Alguair Bellido e Prof. Manuela Killian, que contribuíram para o meu doutorado, quando há anos atrás, incentivaram a minha formação como pesquisadora.

Após esses quatro anos, estou certa de que a ciência é um trabalho de equipe. Esta tese só é possível devido às pessoas que me rodeavam nesta caminhada. Quero expressar minha gratidão a todos os membros do CASC, antigos e atuais, com quem tive a oportunidade de trabalhar. Vocês criaram um ambiente de trabalho saudável e estimulante. Obrigado por todas as contribuições valiosas para minha pesquisa. Quero agradecer também a José Dijkzeul pelo cuidado e a Wen Tian Fu pelas conversas engraçadas no laboratório que compartilhávamos. Algumas pessoas, além de colegas tornaram-se bons amigos e fizeram esses quatro anos leves e divertidos. Meu querido paraninfo Thomas, obrigado por me apresentar à molécula 4-NTP, por me ajudar com os problemas do SECM, por comemorar comigo cada passo do caminho e pelas conversas científicas e não científicas durante uma taça de espumante. Sabine, obrigada por ser uma amiga extraordinária e pelo suporte. Elena, Richard, Stefan, Giulia e Akansha, obrigado pela amizade, pelas discussões, e pelos momentos relaxantes. Aos meus alunos de mestrado: Max, Bellenod e Demi; espero ter contribuído para a sua formação científica tanto quanto vocês contribuíram para esta tese.

Além do CASC, tive a sorte de fazer parte do projeto Marie Curie ELCoREL, que me proporcionou um ambiente estimulante de pesquisa e aprendizado e me trouxe bons amigos. Gostaria de agradecer a todos os membros do ELCoREL, em especial Federico e Rebecca pelos bons momentos que compartilhamos durante (e fora) das reuniões do projeto. Minha gratidão aos amigos Vlad e Katrina, por todos os esforços para a arte da minha tese. Katrina, não tenho palavras para descrever a dimensão do seu talento.

O grande volume de trabalho da minha tese, em parte, só foi possível, devido às colaborações bem-sucedidas que foram estabelecidas ao longo do caminho. Quero agradecer o Prof. Scott Calabrese Barton e Alex Mirabal por aceitarem o desafio de simular meus experimentos de pH local, o que resultou em contribuições para o Capítulo 4. Agradeço também a minha co-promotora, Prof. Núria López e a Federico Dattila, por me educar no mundo da eletrocatalise teórica e pelas contribuições aos Capítulos 8 e 9. Agradeço ao Dr. Klaas Jan Schouten pela oportunidade de estagiar na Avantium, e a Matthew Philips pela orientação no laboratório, o que resultou no Capítulo 11. Quero também agradecer o Prof.

Wolfgang Schuhmann, por me receber em seu grupo, em Bochum, durante tempos estranhos de pandemia, e ao Stefan Dieckhöfer pelas intensas, mas divertidas três semanas que compartilhamos ao lado do SECM, resultando no Capítulo 12. Finalmente, devo agradecer ao Prof. Andreas Stierle pela colaboração que desenvolvemos para realizar medições de Difração de Raios-X no síncrotron, as quais espero que ainda nos levem a muitos resultados interessantes, a medida que continuarmos.

Minhas últimas palavras de agradecimento vão para aqueles que nem sempre compreenderam totalmente o meu trabalho, mas sempre foram entusiastas e me apoiaram. Tenho uma família e amigos incríveis, obrigada por serem inspiradores, e pela torcida. Tia Bú (*in memoriam*), você nos deixou quando eu estava na metade dessa jornada, mas seu amor e apoio levo comigo para sempre. Um agradecimento especial à Tia Rosa e à Tati, pelo carinho e conselhos; e a Manu e o Mumu, por trazerem alegria à minha vida. Minhas amigas de infância, em especial Isis, Ana, Paula, Livia, Bárbara, Ligia; às amigas da República Só Benzeno; Bel, Loreny; amigas e amigos de Groningen, e todos aqueles que de algum forma se fazem presentes na minha vida; obrigado por, de perto ou de longe, estarem comigo a cada passo dessa caminhada. Um agradecimento especial a Mari e ao Gui, por serem meu porto seguro na Holanda, e por estarmos sempre juntos.

Meu querido Leon, todo meu amor e gratidão por tudo; pela sua ajuda no desenvolvimento do meu doutorado, pelo seu cuidado, por me deixar ser eu, mas também por me levar a ser uma pessoa melhor. Obrigado por me inspirar e desafiar, e por todos os “dias nada entediante”. Começamos esta jornada como colegas e também bons amigos, e agora seguimos como parceiros na vida e na ciência. Eu não poderia ter desejado mais. Muito obrigado à sua família, por estar ao meu lado, pelo amor e carinho.

Por fim, e mais importante, quero agradecer meus pais, Marcelo e Elvira, pelo apoio incondicional e por sempre estarem tão próximos de mim, por mais distantes que estivemos fisicamente nos últimos anos. Percorremos um longo caminho, que nenhum de nós pensava ser possível... essa é a “nossa” tese. Vocês me lembram constantemente que as pequenas vitórias devem ser celebradas, e são meus maiores exemplos. Amo vocês, sua bondade e seus conselhos engraçados. Obrigado, e vamos ver quais próximas aventuras nos esperam.