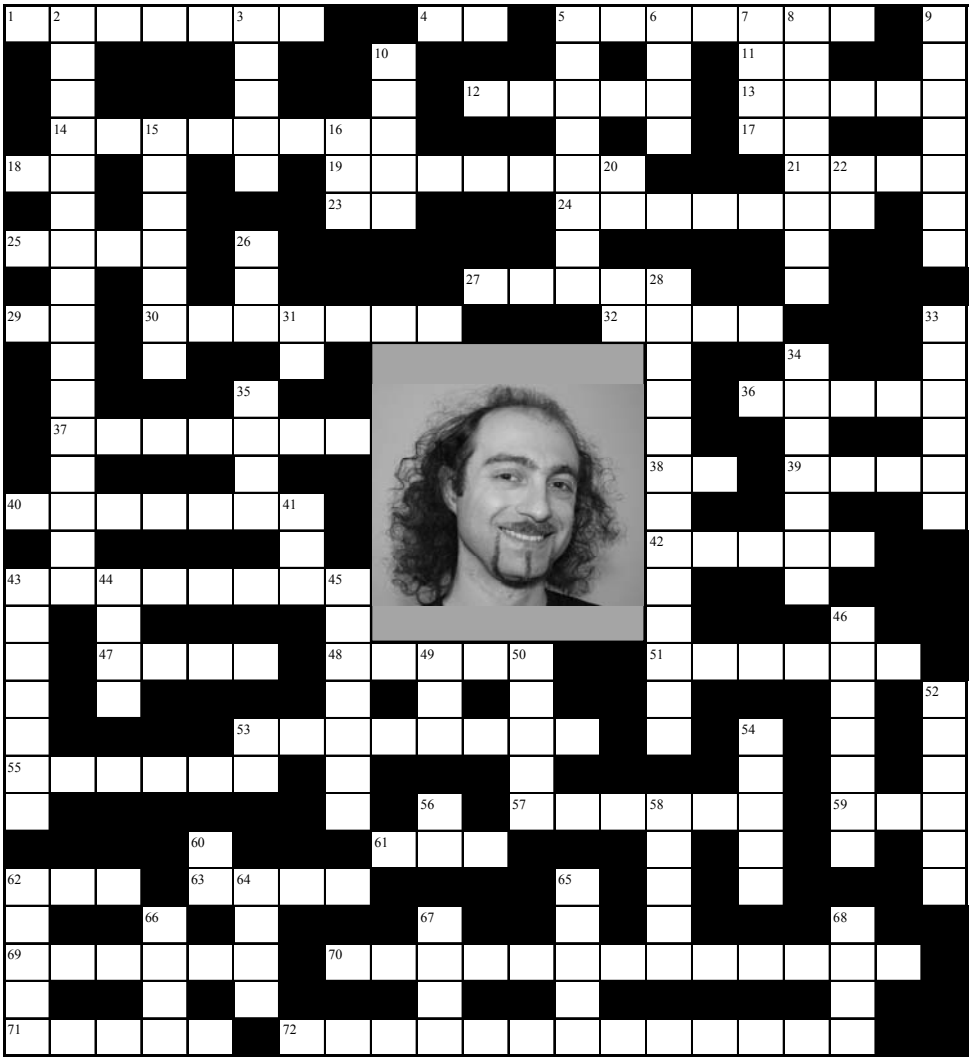
Electrocatalysis of the nitrite reduction : a mechanistic study

Duca, M.

List of publications

- Duca, M.; van der Klugt, B.; Koper, M.T.M., *Electrocatalytic reduction of nitrite on transition and coinage metals*, accepted for publication in *Electrochimica Acta*
- Duca, M.; Figueiredo,M.C. ; Climent, V.; Rodriguez, P.; Feliu, J.M.; Koper, M.T.M., *Selective catalytic reduction at quasi-perfect Pt(100) domains: a universal low-temperature pathway from nitrite to N_2, J. Am. Chem. Soc.* **2011**,*133*, 10928-10939.
- Yang, J.; Duca, M.; Schouten, K.J.P.; Koper, M.T.M., *Formation of volatile products during nitrate reduction on a Sn-modified Pt electrode in acid solution*, *J.Electroanal.Chem.*, **2011**, *662*, 87-92
- Duca, M.; Cucarella, M. O.; Rodriguez, P.; Koper, M. T. M., *Direct reduction of nitrite to N_2 on a Pt (100) electrode in alkaline media, J. Am. Chem. Soc.* **2010**, *132*, 18042-18044.
- Duca, M.; van der Klugt, B.; Hasnat, M. A.; Machida, M.; Koper, M. T. M., *Electrocatalytic reduction of nitrite on a polycrystalline rhodium electrode, J. Catal.* **2010**, *275*, 61-69.
- Duca, M.; Kavvadia, V.; Rodriguez, P.; Lai, S. C. S.; Hoogenboom, T.; Koper, M. T. M., *New insights into the mechanism of nitrite reduction on a platinum electrode, J. Electroanal. Chem.* **2010**, *649*, 59-68.
- Duca, M.; Khamseh, S.; Lai, S. C. S.; Koper, M. T. M. *The influence of solution-phase HNO_2 decomposition on the electrocatalytic nitrite reduction at a hemin-pyrolytic graphite electrode*, *Langmuir* **2010**, *26*, 12418-12424.
- Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. M., *Nitrogen Cycle Electrocatalysis, Chem. Rev.* **2009**, *109*, 2209-2244.



Discover the missing words to complete my Crossword Vitae! "v" means vertical, "h" horizontal.

Matteo …(44-v) was born in… (1-h) in 1983. He first attended the Technical School for Chemistry "G. …. (13-h)" (1997-2002) to play with reactions and test tubes instead of spending his ….(39-h) years translating ….. (25-h) of texts from ancient Greek and ….. (50-v) at the Lyceum, (although now he kind of regrets having too little familiarity with these languages). The interest in all things chemical motivated his move to ……(33-v) to attend the Course in Chemistry at the "Università degli Studi" (2002-2007). He obtained his

B.Sc. degree …….. (14-h) with a thesis in …….. (2-v) focused on the reduction of organic …… (43-v) in non-aqueous solvents, under the supervision of Prof. P. ……. (15-v) (2005). He then left Italy for a six-month …… (9-v) project (2006) that let him discover …… (52-v) University (and the Netherlands) for the first time; his project, dealing with a ….. (30-h), was performed under the supervision of Dr. A. …. (63-h) and Dr. A. Korobko. After this first encounter with …….. (72-h), Matteo joined Prof. Sergio …….(8-v)'s group, where he studied the optimization of ….. (43-h) evolution on …… (57-h) cathodes with electroless ….. (37-h) deposition. Finally, Matteo was awarded his M.Sc. *cum laude* in December 2007. Later on, he chose to continue working with electrodes, ….. (48-h) slopes and potentiostats; so, Matteo successfully applied for a PhD position at Prof. M. …. (58-v)'s group at Leiden University, starting in February 2008. His research dealt with the electrochemistry of the …….. (28-v), and in particular with one anion: …….. (45-v). Transition ……. (3-v) electrodes were investigated for electrochemical NO_2^- reduction, which can generate several products : ….. (61-h), N_2, ….. (19-h), hydroxylamine, but one should …. (65-v) the selectivity to obtain harmless …. (56-v). …….. (5-v) (100) electrodes can achieve this goal, and such results were published in a ……. (68-v) communication. Other platinum …….. (70-h) electrodes (i.e. …… (40-h) surfaces) were also used as …….. (36-h) surfaces to gain further insight … (67-v) the peculiarities of the (100) surface: Matteo collaborated with an …. (55-h) in the field, Prof. J. ……. (54-v) at ……(53-h) (Spain), within the European training network …. (62-v). Nitrite reduction was also studied on several other electrodes, such as… (27-h)-modified GC electrodes and Pt…. (69-h) nanoparticles. This thesis, whose … (71-h) is "Electrocatalysis of the nitrite reduction: a mechanistic study" summarizes the most important results obtained so far. CVs that are only written in past tense are boring, so what lies ahead? Matteo hopes that a …(12-h) will let him pursue a …(34-v) project somewhere in the world, to continue his career in Electrochemistry.

Other definitions to help you

4-h: A product of HNO_2 decomposition; *5-h*: Bergamo's archetypal staple; *6-v*: Not early; *7-v*: 10^{-9}; *10-v*: Online mass spectrometry; *11-h*: Argon; *13-h*: 1963 Nobel laureate in Chemistry, who died in Bergamo in 1979; *16-v*: Amster… is an important Dutch city; *17-h*: Osmium; *18-h*: Platinum; *21-h*: A chemical element is an…; *22-v*: Tantalum; *23-h*: Mass spectrometry; *24-h*: Venue of the 2011 ISE meeting.; *26-v*: Sn; *29-h*: Rhodium; *31-v*: Opposite of "off"; *32-h*: Japan's archetypal staple; *35-v*: Venue of the 2010 ISE meeting.; *38-h*: Glassy Carbon; *41-v*: Department Of Energy; *42-h*: "Japan" in Japanese; *46-v*: Venue of the 2008 ISE meeting.; *47-h*: Lake … is the deepest in Northern Italy.; *49-v*: Frequency Response Analyzer; *51-h*: A PhD student's best liquid friend; *53-v*: @; *59-h*: Light-emitting diode; *60-v*: United Kingdom; *62-h*: A long time; *64-v*: Rotating Ring Disk Electrode; *66-v*: One needs to … glassware with an acid mixture to clean it.

Acknowledgments

"I'm going back to the start", sings Chris Martin, lead vocalist of the Coldplay in their song *The Scientist*, and I'd better follow suit to get started. But when does "the start" date back to? I'd say the late summer of 2007, when the insane idea of getting a PhD leaked into my mind. So, I should definitely thank Prof. (Patrizia) Mussini for introducing me to Electrochemistry and supporting my application at Marc's group. It goes without saying that I wouldn't have come here if Prof. (Sergio) Trasatti hadn't guided me throughout my Master thesis in 2007, encouraging me to give it go for a PhD at Marc Koper's. He was a true mentor, and the notes of his Electrochemistry course safely lie hidden and locked in one of the drawers of my desk, only to be consulted as an invaluable reference whenever I need it.

February 2008 is truly another brand new start. My first humble abode in Leiden was a small *zolderkamer* beneath the roof in a very *burgerlijk* neighborhood and I should really thank José if I didn't end up sleeping under a bridge! I couldn't have found this accommodation without her, and her invaluable assistance has supported me plenty of times all the way from my interview in September 2007 to today. Thijs, your help in creating all sorts of things and devices has been fantastic and this thesis bears witness to your skills. *Hartstikke bedankt!*

I like to say that the research group is like the painter's workshop of the Renaissance. Accordingly, remembering colleagues and friends should ideally be like scrutinizing every single brushstroke of a painting to recognize everyone's contribution. But that's way too much, and so I'll resort to some personalized anecdotes. Stanley, I'm still wondering how you managed to share your room with me for an entire week. I've enjoyed your colleagueship and I've always liked our coffee-corner contests about our views on life. Janneke, it was you that finally convinced me that I should accept Stanley's gift when he turned a cabinet of the office into my private changing room. At least, I can be proud of having "trousers in my closet" rather than "skeletons in the closet". François, you supported me "from behind" when I started, and you made the office very sporty, and not only when we talked about rugby, football or cycling! On top of that, you coined the unforgettable "Matteo's dance". Stefan, there would be so many things to remember, from the hospital in Seville to my wedding in Como, but let me just say you made life a better place. There's something yours on my finger too! Dima, you should get honorary Italian citizenship for your love of *torrone*; your sofa was my "home far from home" in Leiden and I could have a great time with friends thanks to your hospitality: you'll always be a welcome guest wherever I am. Andrey, you've made this thesis easier because you resuscitated my laptop, and, on top of that, I enjoyed welcoming you in front of the elevator to chat about this and

that. Gonzalo, it would be too easy to say thanks for organizing all those delicious barbecues…so I'll thank you for your warm friendship, your (many) practical tips in the lab, and for showing me how to look at life from a different perspective. Para, the same for you, it would be too obvious to thank you for your supervision and for sharing electrochemical knowledge, and so I'll write that I've found a great friend who has stimulated my curiosity for all things Hispano-Latinoamerican. Who's next? So many people! Christine, life is not a piece of cake, but a slice of chocolate cake always sweetens life (particularly on a rainy Monday); Angela, you've energized the social life of the group and I really regret missing the upcoming events. Klaas-Jan, I simply admire you and I'll miss your "balancing" effect that you have on my intrinsic entropic behavior; Steven, you learn Italian, I learn Dutch, we'll meet halfway sooner or later, and I'll always be happy to let you in on secrets of Italian cooking. As promised, I'd especially like to acknowledge your contribution to the *Nederlandse Samenvatting* of the thesis. Youngkook, I'm happy you enjoyed yourself in Milano and I hope I will myself guide you to discover the beauty of my country one day or another. Dennis, I still regret missing the chance of being your paranymph but I had so much fun when I handed out our presents for you. Alex, the word "Japan" will always remind me of our culinary discoveries (you were far braver than me), the sultry hot days in Niigata, and my endless quest for a yukata for Cecilia. Needless to say, thanks for your scientific help too. Federico, let's gossip about the Danes again! Oscar, I wish you all the best for your research, and don't get angry if they open your suitcase at Schiphol again! Arban, drop me a line to talk about the last news in Italian football! Anyone else? Vasiliki, God save Greece! I must say you contributed to my first successful experiments and your lively smile brightened up my first hard days as a PhD. Björn, I had great fun working with you, and I enjoyed being a member of your graduation committee too! Mar, you let me experience that unforgettable eureka moment when we sniffed N2 with the OLEMS! Javi, I was fascinated by your weird nanoparticle suspensions. Rubén, I am in love with the Villajoyosa's chocolate and our visit to Altea at night was simply fantastic.

Marc deserves a separate mention, also because he's way too tall to fit in the previous, already crammed paragraph! While my supervisors at Milano launched me on my journey towards electrochemistry, it's Marc who corrected my trajectory in the course of the first, critical years of my career. For a PhD student, a minimal error can be fatal, like for a rocket on its way to the Moon; Marc has supervised me brilliantly throughout these four years, helping me to keep improving and avoiding my going astray, which is one of the main "professional illnesses" of a PhD student. If I can call me an electrochemist, I owe this name to what Marc has done, and if my flight ever successfully lands onto an academic position, I will especially remember Marc's guidance and supervision when I finally hoist my flag on my professor's desk! Thank you ever so much, Marc.

I won't forget family and friends! I'll start from the Netherlands, where I met Fabiola and Luca: I'll miss talking ill of the Dutch with you! When one acknowledges one's parents, it's always tempting to rely on big words, commonplace sentences and mellow feelings. Yet, I never want to lose my tongue-in-cheek attitude, and avoid sentimentalism. Let's try then! Electrochemistry sounds like a funny portmanteau word that keeps reminding me of where I started from, where I tried to go and where I've finally end up. A couple of generations on both sides of my family tree have dealt with electricity, and I guess that has been a latent driving force which came into action when, life's pinball sent me on my way towards the electrical side of Chemistry. So, I'd better take the opportunity to thank my father, for his unwavering support and the interest in science that he shared with me from so early in my life! I thank my mother for her patient, endless attempts to try and understand his son's path in life: you don't need to understand me Mum, just enjoy and take things easy! It's time to mention my little sister, too: Maria Grazia, thanks for…being my sister!

Bergamo, the Promised Land flowing with *polenta e osei* (polenta with roasted wild birds), is a step-mother that has left an unfading mark on me. Plenty of good friends live in the shadow of the Orobian Alps: Oscar, my best man at my wedding, Silvia, Monica and Maria Vittoria (MaVi), who is the bravest of all of us after surviving a PhD in Italy!

It takes three hours to get from my village to Como by train (an 80-km journey across Lombardy). But it's worthwhile…and Cecilia, don't think that I'm just talking about you! I mean, the romantic lakefront, the mountains crowning the city on three sides, the "Tempio Voltiano", a museum dedicated to Alessandro Volta (1745-1827, born himself in Como), one of the fathers of Electrochemistry, and last but not least the proximity to Switzerland, which makes it easy to bring money abroad if one needs to do so (or simply cross the border to find cheaper gasoline). I want to thank my parents in law for their trust in me and patient interpretation of my improper "Gallic" pronunciation of the Italian language. Climbing the branches of your family tree, what about that young shoot I have intertwined my own twigs with? I have truly lived only since my blurred, weary sight bathed in the crystal waters which mingle and mirror the lapis lazuli skies and the purest turquoise brine around the basalt pupil where your secret lies condensed. That liquid fire melted the wax which kept my life sealed and still. In the beginning it was a book, or "*Galeotto fu il libro e chi lo scrisse:/quel giorno più non vi leggemmo avante*", as Dante writes when he describes Paolo and Francesca: I would not mind ending up in Hell for the rest of times if you were still by my side down there. Whenever our eyes meet I cannot help recalling to my mind what another famous lover once said, "What light through yonder windows breaks?" Cecilia, words cannot but trace their limits to talk of love, which is "such stuff / as dreams are made on", and to such realm you have carried me away with you.

Notes

Cover idea: Matteo Duca & Cecilia Bernardini

Cover design: Cecilia Bernardini & Matteo Duca

Front cover: *The nitrogen whirpool cycle*.

Back cover: *Ammonium and nitrate engaging in a fertile but explosive relationship*.

ISBN/EAN: 978-90-6464-535-8

Printed in Ede by GVO | Ponsen & Looijen, February 2012.