Final report on the project "Studying electrochemical processes having a key role in energy conversion and storage", PD124079

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The aim of the project was to study two important electrode reactions — namely, the electrochemical reduction of carbon dioxide (CO_2) and electrochemical hydrogen evolution. Both these reactions have a high relevance to both applied and fundamental science. Within this project, we successfully applied — for the first time — a combination of *operando* Raman and X-ray photoelectron spectroscopies in order to study the stability of metal oxide based catalysts of CO_2 reduction, and have also devised new experimental approaches to study the limiting role of transport exerted on the rate of this important process. With regard to the hydrogen evolution reaction (HER), we developed a kinetic model that is able to describe the peculiar two-step polarization curves of HER, measurable in mildly acidic solutions. This model — in a rather unprecedented way — considers hydrogen evolution as a combination of two processes: the reduction of H^+ ions and that of H_2O molecules, and takes the autoprotolysis reaction into account. The new model can well be fitted to polarization curves measured on rotating disk electrodes, and performs remarkably well when used to describe hydrogen evolution as a side reaction of base metal (Ni or Co) electroplating. Both of the above research topics were investigated in cooperation with the Interfacial Electrochemistry Group of Dr. Peter Broekmann at the University of Berne, continuing an already well-established international collaboration. As a result of work conducted in the 3 project years, altogether 9 papers were published in peer-reviewed scientific journals.

Studies on CO_2 electroreduction

Motivation

To preserve the environment from the consequences of global warming and other effects linked to anthropogenic CO_2 emissions is one of the greatest challenges facing our society today. Technologies that can potentially lead to a decrease of atmospheric CO_2 concentrations thus became extremely important, and many of these technologies are based on electrochemical reduction. The vision of chemically transforming CO_2 into organic molecules on a large scale offers a very attractive way to decrease atmospheric CO_2 concentrations. The products of CO_2 reduction —light-weight molecules such as carbon monoxide, formic acid or methanol— could either be used as chemical feed-stock and turned into other value-added products, or be used as fuels themselves. Either way, the electrochemical reduction of an inert molecule such as CO_2 has a very considerable practical and fundamental appeal.

The number of scientific papers describing new catalyst materials for CO_2 electroreduction is ceaselessly rising, yet it seems that issues related to the stability of catalysts — as well as other aspects of the electrode process, such as the limiting role of reactant transport — often skip researchers’ attention. When stability does come into question, the majority of scientific workers tend to rely on *ex-situ* spectroscopic characterization (performed before and after electrolysis) in order to explain activity or selectivity variations based on structural changes. As opposed to this approach, we suggested the use of *operando* spectroscopies [1] for monitoring the structural and chemical changes that catalysts undergo in the course of the catalysed process. In order to gain a better insight into the effects of transport phenomena and their limiting role in determining the rate of CO_2 reduction, we carried out investigations in both organic (ionic liquid) media [2] and aqueous environments [3].

Probing the chemical state of tin oxide NP catalysts during CO_2 electroreduction. A complementary operando approach

In [1] we combined two *operando* methods, Raman spectroscopy and X-ray absorption spectroscopy (XAS), in order to probe reduced graphene-oxide supported tin(IV) oxide nanoparticles (SnO_2NPs@rGO) as they are being used to catalyse CO_2 electroreduction. To achieve high reaction rates it was necessary to apply sufficiently cathodic electrode potentials. Under such conditions, however, not only CO_2 was reduced electrochemically, but also the catalyst particles were transformed from the initial Sn(IV) state to Sn(II) or, in an extreme case, to metallic Sn. While Sn(II) species still favoured CO_2 electroreduction, yielding formate as a primary product, on metallic Sn CO_2 reduction was disfavoured with respect to the competing hydrogen evolution reaction. We showed that operando XAS, a robust technique yielding information averaged over a large surface area and a relatively large thickness of the catalyst layer, is a very expedient method able to detect the reduction of SnO_2NPs@rGO to metallic Sn. XAS can thus be used to establish an optimum potential for the electroreduction in practical electrolysing cells. It takes, however, a complementary method offered by *operando* Raman spectroscopy, having greater sensitivity at the catalyst/electrolyte solution interface, to probe reduction intermediates such as the Sn(II) state, which remain undetectable for *ex situ* spectroscopies. As it was shown in [1], Raman spectroscopy may also find further use when investigating the recovery of catalyst particles following exposure to extreme reducing conditions.

Transport matters: Boosting CO_2 electroreduction in mixtures of the ionic liquid $[BMIm][BF_4]$ and water by enhanced diffusion

In [2] we studied CO_2 electroreduction in room-temperature ionic liquids (RTILs) that were previously identified as promising new electrolytes for efficient carbon dioxide reduction. We found that due to their high viscosity, the mass transport of CO_2 in RTILs is typically slow, at least one order of magnitude slower than in aqueous systems. One possibility to improve mass transport in RTILs was to decrease their viscosity by dilution with water. We added defined amounts of water to the hydrophilic RTIL 1-butyl-3methylimidazolium tetrafluoroborate ($[BMIm][BF_4]$). Electrochemical measurements on quiescent and hydrodynamic systems both indicated an enhanced CO_2 electroreduction. We have successfully established that this enhancement has its origin in thermodynamic/kinetic effects (the addition of water increases the availability of H^+, which is a reaction partner of CO_2 electroreduction) and in an increased rate of transport due to lower viscosity. Electrochemically determined diffusion coefficients for CO_2 in

$[BMIm][BF_4]$/water systems showed a clear correlation with values determined by NMR spectroscopy.

Toward CO_2 electroreduction under controlled mass flow conditions. A combined inverted RDE and gas chromatography approach

In order to gain more insight into the limiting role of transport on the electroreduction of CO_2, a new measurement system was built featuring a hermetically closed cell, an inverted rotating disk electrode (iRDE) and a gas chromatograph, the latter used as means for product detection [3]. The use of rotating disk electrodes (RDEs) is probably the most convenient way of studying simple electrode reactions under well-defined transport conditions. Standard RDEs become, however, less expedient when the studied electrode process is a complex one, leading to the formation of various reaction products. In these cases, the accurate detection and quantification of the formed products are desirable. If the formed products are gaseous, then the usual way of quantifying them is the use of online gas chromatography (GC), a method that is not compatible with open RDE cells. In order to overcome these difficulties, we presented a sophisticated inverted RDE (iRDE) cell design. This new design [3] combines various advantages: it is amenable to the same mathematical treatment as standard (downward-facing) RDEs; it can be operated airtight and coupled to online GC; and due to its upward-facing design, the electrode surface is less prone to blockage by any formed gas bubbles. The iRDE&GC design was tested using simple model reactions and was demonstratively used for studying the electrochemical reduction of CO_2, accompanied by parasitic hydrogen evolution, on a silver electrode.

Studies on the electrochemical hydrogen evolution reaction (HER), primarily as a side reaction of base metal electrodeposition

Motivation

In our studies [4–6] we were primarily interested in understanding the mechanism of hydrogen evolution from the point of view of base metal electroplating: an industrial process where HER always occurs as a parasitic reaction. It is known that hydrogen evolution can take place in mildly acidic reaction media by two processes: by the reduction of H^+ ions and that of water molecules. Both reactions lead to an increased *p*H in the vicinity of the cathode surface and may cause the formation of insoluble metal hydroxides. Metal hydroxide particles, when incorporated to the deposited metal layer can cause severe changes in the layer's physical properties and may lead to a higher electrical resistivity. Understanding HER (by the use of electrochemical measuring techniques and by computer-aided modelling) thus has a key role in optimizing metal plating processes.

Modelling the two-step polarization curves of hydrogen evolution, measured on RDEs in dilute acid solutions

Polarization curves of the hydrogen evolution reaction (HER), recorded on rotating disk electrodes (RDEs) in mildly acidic solutions, usually show a "two step" behaviour. That is, two exponentially rising segments (the first commonly assigned to H^+, the second to water reduction) are separated by a limiting current plateau.

In [4] we devised an analytical model for the full polarization curve by assuming that HER proceeds according to a quasi-reversible two-electron reaction, $H^+ + H_2O + 2e^- \rightleftharpoons H_2 + OH^-$, obeying the Erdey-Grúz–Volmer–Butler equation. Our model was able to reproduce the two step behaviour of polarization curves and could also be used for the fitting of measured currents over a broad range of *p*H, rotation rate, and electrode potential, on both Au and Pt electrodes.

We showed that the length of the limiting current plateaus measured on RDEs for HER is inversely related to the electrocatalytic activity of the electrode and that at a given rotation rate a linear relationship exists between the plateau length and the bulk solution *p*H. By analyzing this relationship, we could estimate kinetic parameters, even in cases where the transport performance of the RDE would otherwise not be sufficient to measure well-defined kinetic currents at low overpotentials [4].

The Faradaic efficiency of base metal electrodeposition from mildly acidic baths to rotating disk electrodes

Based on the theoretical description of HER, outlined in [4], we developed a mathematical model [5] that was successfully used to describe the dependence of the Faradaic efficiency of base metal deposition on many factors like the applied current density, the composition (primarily, the metal ion concentration and the *p*H) of the depositing bath, and the rate of convection.

Analysing how the Faradaic efficiency (*FE*) depends on the current density *j* under well-defined transport conditions (e.g., by the use of rotating disk electrodes) became an integral part of industrial approaches to the screening of bath compositions applied for base metal electroplating. Yet *FE*(*j*) curves were not very well understood so far, and most studies contented themselves with their mere qualitative analysis, reaching no conclusions as to the mechanisms of the underlying reactions. We believe to have successfully filled this gap by creating a simple model for *FE*(*j*) curves based on first principles. The model described in [5] can very well be fitted to experimental data obtained for the electrodeposition of nickel and of cobalt, and it yields a consistent set of kinetic and transport parameters over a broad range of *p*H, rotation rates and current densities. The model described in [5] thus paves the way towards a knowledge-driven benchmarking strategy of base metal electroplating baths.

In order to complement the theoretical work described above, further experimental investigations have also been made in order to study the effect of plating bath additives on the Faradaic efficiency of base metal depositions. For this purpose, the iRDE&GC approach (described in the previous section) was used to identify "missing terms" in the Faradaic efficiency of base metal depositions [6].

Miscellaneous results

In a few more publications several further results were described. These do not belong to the core of the project; they, however, are based on the methodologies related or developed during the project. These publications include a work on the electrochemical dissolution of titanium [7]; another on the fundamentals of finite element simulations in electrochemistry [8]; and another on a new data analysis strategy for the evaluation of cyclic voltammograms [9].

List of Publications

During the three project years, I published the following 9 papers in peer-reviewed, scientific journals, where project PD124079 was mentioned in the Acknowledgement section:

1. A. Dutta, A. Kuzume, V. Kaliginedi, M. Rahaman, I. Sinev, M. Ahmadi, B. Roldán Cuenya, S. Vesztergom, P. Broekmann, *Nano Energy* **2018**, *53*, 828–840.
2. A. Rudnev, Y.-Ch. Fu, I. Gjuroski, F. Stricker, J. Furrer, N. Kovács, S. Vesztergom, P. Broekmann, *ChemPhysChem* **2017**, *18*, 3153–3162.
3. P. Moreno-García, N. Kovács, V. Grozovski, M. de J. Gálvez-Vázquez, S. Vesztergom, P. Broekmann, *Anal. Chem.* **2020**, *92*, 4301–4308.
4. M. de J. Gálvez-Vázquez, V. Grozovski, N. Kovács, P. Broekmann, S. Vesztergom, *J. Phys. Chem. C* **2020**, *124*, 3988–4000.
5. N. Kovács, V. Grozovski, P. Moreno-García, P. Broekmann, S. Vesztergom, *J. Electrochem. Soc.* **2020**, *167*, 102510.
6. P. Moreno-García, V. Grozovski, M. de J. Gálvez-Vázquez, N. Mysuru, K. Kiran, N. Kovács, Y. Hou, S. Vesztergom, P. Broekmann, *J. Electrochem. Soc.* **2020**, *167*, 042503.
7. N. Kovács, L. Sziráki, S. Vesztergom, Gy. G. Láng, *J. Electrochem. Sci. Eng.* **2018**, *8*, 141–149.
8. S. Vesztergom, *J. Electrochem. Sci. Eng.* **2018**, *8*, 171–181.
9. T. Pajkossy, S. Vesztergom, *Electrochim. Acta* **2019**, *297*, 1121–1129.