Breaking scaling relations in electrocatalysis

Justus Masa¹ · Wolfgang Schuhmann²

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If we had to decide today about a career perspective, we would probably decide for electrochemistry. Electrochemistry is of utmost importance to contribute to technological solutions for solving challenging societal problems including but not limited to corrosion and corrosion protection, sensors, biosensors, biomedical devices, battery technology, electrocatalysis, photoelectrocatalysis, electrosynthesis, fuel cells, electrolyzers, etc. Electrochemistry is of vital importance for developing countries from bringing light into cottages, prevention of tree cutting for firewood and mobile phone communication to powering water pumps or cleaning contaminated water, etc. And evidently with economic growth, the energy consumption per person is increasing as a basis for improving the standard of living. Hence, to overcome poverty and provide education, to synthesise fertilisers and provide energy for heating and transportation, human kind has to cope with a tremendous increase in energy consumption which logically cannot be satisfied by increased burning of fossil fuels considering the associated impact on the climate.

Electrochemical energy storage and conversion technologies, including batteries, electrolyzers and fuel cells, are providing the only hope for broad-based energy storage applications [1, 2], including conversion of N₂, H₂O and CO₂ into chemical energy carriers, fertilisers and industrial chemicals [3]. However, in order to achieve sufficient product formation rates, both electrolyzers and fuel cells have to be operated at far higher voltage than thermodynamically suggested. Moreover, if multiple reaction products are possible as, e.g. in the case of the CO₂ reduction reaction, selectivity to increase the yield of the preferred products is a great challenge. In addition, industrial processes require an outstanding

catalyst stability. Hence, the three main challenges for industrial application of electrocatalytic N₂, H₂O and CO₂ conversion into valuable energy carriers and chemical feedstock are insufficient activity, poor product selectivity and unsatisfactory stability.

At electrocatalytically active sites at the interface between an (catalyst-modified) electrode and the electrolyte, complex chemical phenomena take place, including adsorption and desorption processes, electrostatic interactions and electron and charge transfer reactions. The reactions at this interface are sensitive on a complex interplay of parameters such as the geometric and electronic structure at the surface, electrolyte properties (including concentration, ionic strength and pH) and the applied potential which contribute to the strength of the electric field. Moreover, for a catalyst to be active, the adsorption energy of the substrate to one or several active sites has to be known, and even more challenging, for a coupled multielectron/multiproton transfer reaction, the adsorption properties of all intermediates have to be known. Despite most focus in electrocatalysis being dedicated to finding the most active catalyst, it is extremely challenging to derive the intrinsic catalytic activity of a given catalyst from the multi-parameter system of an ensemble of catalyst particles embedded in a catalyst layer on top of an electrode surface due to the complex and dynamic nature of the electrochemical interface. Hence, to successfully fight against climate change, the discovery of complex catalysts for complex multielectron/multiproton transfer reactions and an in-depth understanding on how to substantially lower the required overpotential is necessary. This is only possible using new tools of experiment-guided large data strategies and combinatorial materials discovery in connection with increased precision of *in silico* models of the electrochemical interface between the solid electrode material and the electrolyte, including a realistic description of the electrochemical double layer and its dynamic changes, and ion movement upon electron transfer across the interface.

Due to the scaling relations, a minimum overpotential is inevitable for multistep reactions [4], in which multiple intermediates have to be stabilised during the reaction and at least two of them bind to the catalyst surface similarly. If the adsorption energy of one active site is optimised for one of such intermediates, it simultaneously weakens stabilisation of the other intermediate.

✉ Wolfgang Schuhmann
wolfgang.schuhmann@rub.de

Justus Masa
justus.masa@cec.mpg.de

¹ Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, D-45470 Mülheim an der Ruhr, Germany

² Analytical Chemistry-Center for Electrochemical Sciences (CES); Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstr. 150, D-44780 Bochum, Germany

Ultimately, novel and by far more complex electrocatalysts are required to break the scaling relations and by this to optimise all involved reaction steps simultaneously [5, 6]. Circumventing the scaling relation with an ideal catalyst would increase the current by more than six orders of magnitude, e.g. in the case of the oxygen reduction reaction. The next step in electrocatalysis requires a paradigm shift and exploration of completely different catalyst design strategies towards more exotic and multifunctional active sites [7]. Entering the material combination space of more complex alloys with multiple principal elements providing bi-/multifunctional active sites, which allow a variety of interactions with the different intermediates, could be one promising approach with already few reported attempts. As a promising example, we want to highlight the application of so-called high-entropy alloys (HEA) or complex solid solutions (CSS) for electrocatalysis [8, 9]. A single solid solution phase across the whole NP may contribute to circumvent the scaling relation challenge with interactions tailored by a rational choice of elemental configuration and composition. HEA are alloys formed by the combination of at least five metals exhibiting an atomic scale proximity of various atoms with a continuous distribution of adsorption energies as suggested from DFT calculations [8], and a fast-growing number of reports demonstrate the applicability of HEA as highly active catalysts for the oxygen reduction reaction [10, 11], the oxygen evolution reaction [12, 13], the hydrogen evolution reaction [14] and the reduction of CO and CO₂ [15, 16]. Such multi-active site catalysts seem to fulfil the early vision by Bockris and Minevski who already proposed in 1992 to develop designer surfaces comprising of multi-element patches which are optimised to catalyse specific steps in a complex reaction mechanism involving many intermediates [17].

Hence, to follow the task by the editor to answer the question about our view on the most important “future tasks of electrochemical research”, we suggest the design of new multinary catalysts using tools of data-driven high-throughput material discovery to ultimately discover catalysts for the most important reactions to cope with the growing population, the energy demand to sustain the increasing standard of living without CO₂ release and the related negative impact on the climate. However, the catalyst with the highest intrinsic activity which is converting its substrate close to the thermodynamic prediction by breaking the scaling relation needs to be simultaneously highly selective and most importantly very stable to be successfully applied in technological processes.

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