Meeting Abstract **Open Access**

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The modeling gap: What we are missing between molecular dynamics of electrode reactions and simulation of battery packs*

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At the very beginning (and still thereafter) electrodes (not exactly the proper designation following W. Nernst) for electrolytic and galvanic processes (think of chlor-alkaline, aluminum production, copper refining) were flat and smooth ones, only some coarse surface structuring supporting gas bubble transport was applied sometimes. On the contrary electrodes in electrochemical conversion and storage devices were non-flat (with the notable exception of lithium, zinc and copper in primary batteries). Even today this contrast persists, only recently packed bed electrodes, *i.e.* porous bodies, have been suggested for some electroorganic processes [1]. The reasons are well-known: Many of the electrode reactions in the latter devices proceed at fairly low rates causing possibly large charge transfer overpotentials. And because overpotentials (in this case more precisely charge transfer or activation overpotentials) are related by the Butler-Volmer equation to the charge transfer current density increasing the operating surface area is the most obvious way to smaller overpotentials. These porous electrodes provide further benefits beyond the large surface area: They enable the establishment of stable three-phase boundaries in gas-diffusion electrodes.

A proper distinction between these basically two classes of electrodes has never been clearly established. At first glance the flat ones can be called 2D, the non flat 3D. A rough electrode with a low roughness factor (the ratio of the true area vs. the apparent or geometric surface area; numerous methods to determine electrochemically active surface areas are known [2]) may still appear flat and may thus be assigned to the first class - but where is the boundary in terms of roughness factors separating these electrodes from 3D ones? Porous electrodes for high-power batteries and supercaps may be rather thin, thus the concept of a porous body as found in an alkaline battery anode or zinc carbon battery cathode is hardly suitable. This confusion may be of minor importance, but its effects are still felt today. In a report by Chabi *et al.* [3] an ideal 3D-electrode having short electronic and ionic pathways is characterized in an otherwise somewhat confusing or confused report, the term 3D architecture has been employed before frequently [4–10]. Apparently some general aspects of structural optimization seem to emerge. In case of carbon materials for supercapacitor electrodes this has been reviewed recently with a clear statement that focus on the BET-surface is simply inadequate [11].

The situation is much less satisfying and promising when looking into the theoretical aspects of structure design (whether rational or not or simply empirical). Modeling is well-established on the atomic and molecular level both with respect to structure and dynamics, and the same picture emerges at the cell and battery pack level. In between – at the electrode level – a different picture emerges. Also at this level modeling in terms of the precise description of the structure of a porous electrode on the mesoscopic level and in terms of a description of the dynamic behavior, *i.e.* the electrode kinetics (current, potential, concentration gradients), derived from the parameters describing the electrode (both the data from the structural model and the operating parameters) has made some progress for lithium ion battery electrodes based in particular on the emerging tomographic techniques as recently reviewed [12, 13]. Based on microscopic images *i.e.* the Bruggemann exponent describing the tortuosity of a porous electrode can be estimated [14–17]. Predictions of cell swelling and stress development could be made [18], modeling of microstructural inhomogeneities was done [19], even a galvanostatic discharge of an actual $LiCoO_2$ battery electrode indicating local inhomogeneities could be performed based on a 3D-image obtained by nan-

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* Notes from a workshop on „Synergy of Material Design and Modeling“

otomography [20, 21]. Unfortunately these efforts are apparently limited to this particular class of storage systems.

Carefully prepared and well organized an "Indo-German Workshop on Electrochemical Storage Systems: Synergy of Material Design and Modeling" addressing this "modeling gap" was held at the Indian Institute of Technology Kharagpur from February 17th to 20th, 2016. This editorial briefly collects some of the salient topics and relates them to the field covered in this journal putting them into perspective from the editor's point of view. A more extended version prepared by the organizers is on its way.

U. Krewer nicely illustrated in her overview using typical battery and fuel cell electrode reactions how far at the atomic/molecular level modeling of reaction mechanisms and kinetics has progressed. This level of understanding, description and finally prediction has been enabled by progress made in molecular modeling, but it is certainly based on extensive earlier work focused on reaction thermodynamics, in particular of adsorptive interactions between electrode surfaces and reactive species (see *e.g.* Volcano plots as applied to heats of adsorption of fuel cell reactants on numerous metal surfaces [22–29]) and of energetics of reaction intermediates (think of heats of formation of radical intermediates in electroorganic reactions, oxidation electrode potentials and related rates of transformation and reaction product properties [30–33]).

T. Turek went a step further on the dimensional scale when reporting on recent progress in modeling and material development for oxygen reducing electrodes in the chlor-alkaline electrolysis [34, 35]]. Although these electrodes are basically porous gas-fed electrodes similar to those used in phosphoric acid fuel cells methodology and results hardly fit to electrodes in supercapacitors and alkali ion batteries. The rather empirical approach in the latter fields was illustrated in several reports, among them by G. Garnweitner on nanostructured metal oxides and by M. M. Shaijumon on graphene-based hybrid materials for energy storage. Most talks highlighted particular morphologies, spectacular synthetic procedures or specific materials properties. A more general view at structure-properties-performance relationships going beyond reports of the obvious and speculations was mostly absent.

Beyond the scope of the workshop – which was focused on materials (not systems) and modeling – the well advanced modeling at the cell and battery (pack) level was not covered, many examples have been already published [36–38].

A specific feature of this workshop – something presumably possible only at such small meeting – were working groups addressing the workshop subjects from various angles. Criticism of some current trends (synthesis-driven research, incomplete materials characterization and reporting, missing standards for performance determination and reporting, disregard for scale-up possibilities) developed into a few recommendations: Prepare model structures/materials enabling measurements of transport properties (frequently overlooked or mentioned only in passing on an empirical-speculative level) finally resulting in models of a working porous electrode.

Certainly a challenge, but a worthy one.

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