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Development of multi-scale structure homogenization approaches based on modeled particle deposition for the simulation of electrochemical energy conversion and storage devices

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ABSTRACT

In this work multi-scale homogenization approaches for porous electrodes are developed and compared. The results are used for the simulation of mass transport, and charge transfer processes at different active material loadings in various power sources, such as batteries, fuel cells and supercapacitors.

A general pore-scale model is developed by mimicking the layer fabrication process. Electrode structures are virtually generated taking into account the interaction between the deposited particles during layer formation and surface relaxation. The effective transport and kinetic coefficients of the layers are calculated by different homogenization approaches and used in macro homogeneous models to predict macroscopic behaviour of fuel cells, supercapacitors and Li-ion batteries. The model predictions are compared with experimental kinetic and transport coefficients of fuel cells and supercapacitors and a good agreement was found.

The results imply that porosity, tortuosity and specific surface area may follow a power law scaling with increasing deposited mass as a consequence of agglomeration during layer deposition. Consequently, effective transport and kinetic coefficients depend on the active material loading of the electrode.

1. Introduction

The electrode micro, meso and macro structure all have a significant influence on the performance of electrochemical systems [1]. For this reason, their optimization is of utmost importance for producing highly efficient fuel cells, batteries (especially Li-ion) and supercapacitors [2–4]. It is very difficult to simulate all the physico-chemical phenomena with micro structural details at electrode scale. Therefore different homogenization approaches have been developed to couple microstructure and macroscopic behaviour. In the following, we present a brief overview of the characterization of disordered media and of homogenization approaches to calculate effective transport and kinetic coefficients. Experimental and theoretical results are collected, which suggest that homogenization may depend on the length scales considered. Therefore the main focus of this paper is to understand scaling effects and propose an improved multi-scale modelling approach. We start with the virtual generation of active layers, following the introduction of scaling analysis and universality classes. Then, the electrochemical performance of an active layer at different length scales by varying active material loading (thickness) is simulated. Finally the developed multi-scale homogenization approaches are used for the optimization of active material loading of Li-ion batteries. The work also points out some limits of the homogenization of microstructures.

1.1. Characterization of disordered media at multiple length scales

Active electrode layers are prepared by many different techniques such as painting, spraying, sputtering [5–8], and atomic layer deposition [9]. The result of the deposition is a disordered media, which porous structure affects the characteristics of dynamic processes such as effective transport coefficient [10] and apparent reaction rate [11]. In few cases transport in a disordered media can be exactly predicted theoretically. These cases are very specific (i.e. Sierpinski-gaskat, Cayle tree) [12], but demonstrate, how transport processes are dependent on the length and time scales. Simulation techniques, such as Monte-Carlo or Lattice-Boltzman, can be solved at pore scale, but because of the random nature of the geometry, general conclusions require several hundreds of executions [13,14]. Therefore they are very time consuming and can hardly be used for optimization [15].

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Homogenization approaches average the details of the microstructure. Depending on the extent of homogenization they substantially reduce the number of parameters required to describe the porous structure. It results in information loss, but may allow the optimization at macro scale much faster than for a fully detailed simulation. The most commonly applied homogenization is macroscopic homogenization, in which geometrical dimensions, active material loading, specific surface area, porosity and tortuosity are used to characterize the active layer. They all can be measured at macro scale. Void volume fraction is usually calculated by applying the following formula [3,16–19]:

$$\varepsilon_V = 1 - \frac{W_{AL}}{\sum_i \frac{m_i}{\rho_i}} \tag{1}$$

where W_{AL} (m) is the thickness of the active layer, m_i ($\mathrm{kg\,m^{-2}}$) is the mass per unit geometrical area of the i^{th} material, (i.e. active material, filler etc.) and ρ_i ($\mathrm{kg\,m^{-3}}$) is the bulk density of the i^{th} material. The specific surface area of the active layer can be calculated by taking into account the particle's diameter dispersion [3,16,20]:

$$a_{AL} = 3(1-\varepsilon_V)\sum_k \frac{\varepsilon_k}{r_k} \tag{2}$$

where ε_k is the volume fraction of the k^{th} particle with r_k radius. Alternatively it can be calculated as follows [3,7]

$$a_{AL} = \frac{SSA \cdot m_{AL}}{W_{AL}} \tag{3}$$

where SSA is the surface area per unit mass ($\mathrm{m^2\,kg^{-1}}$) measured by e.g. Nitrogen adsorption porosimetry.

Tortousity is usually estimated by the Bruggeman expression [21]:

$$\tau = \varepsilon^{-1/2} \tag{4}$$

where ε is the volume fraction of the phase (can be void or material matrix phase).

Different types of tortousity relationships have been described and collected by Shen et al. [22] for different systems. For electrodes with idealized spherical particles of radii within a standard deviation Vijayaraghavam et al. [23] found that tortousity and consequently the prediction of macroscopic (homogenized) diffusion coefficient follows Eq. (4), therefore in the following chapters Eq. (4) is used.

These four homogenized parameters completely describe the porous structure in macro homogeneous models. On these bases the macroscopic (at electrode level) performance of fuel cells, batteries and supercapacitors can be simulated/predicted. Eqs. (1)–(4) are independent of length scale, because thickness and loading are linearly dependent. Therefore they do not depend on material loading and models can be scaled up linearly, i.e. increasing the thickness of the active layer leaving the other parameters unchanged.

The widespread use of microstructural characterization techniques, such as X-Ray-CT [24] and FIB-SEM [25] showed that tortousity, specific surface area and porosity depend not only on particle size, but also on shape, connection network [26] and orientation of particles [27,28]. Furthermore they do not necessarily follow the previously assumed material laws, such as the Bruggeman assumption for tortuosity. To reduce the complexity of the calculation a representative part of the electrode's microstructure, termed representative elementary volume (REV), is generated by simulation (e.g. Monte-Carlo simulation [29,30]) or regenerated from experimental data. The average transport and kinetic parameters are subsequently calculated for this reduced volume, and the results are transferred into a macro homogeneous model by periodically repeating the results of REV scale simulation. Consequently, despite the more accurate and realistic calculation of transport properties at micro scale, they are independent of length scales, similarly to the case of the macroscopic homogenization methods (Eqs. (1)–(4)). However, the assumption that REV scale results can be periodically repeated is not trivial. Therefore the effect of REV size on the homogenized parameters is also thoroughly studied in this work.

Previously Gasteiger et al. [31] found that mass activity of fuel cells is independent of the Pt loading, which is equivalent to the assumption that the effective kinetic coefficient is independent of length scales. Consequently, REV can be periodically repeated. However in our previous works [7,32], it was found that the effective transport and kinetic parameters of a fuel cell electrode depend on the Pt loading (i.e. thickness). As Pt loading was decreased by an order of magnitude (from 0.4 to 0.05 $\mathrm{mg\,cm^{-2}}$), the specific activity ($\mathrm{A\,cm^{-2}}$ of Pt electrochemically active area) of fuel cells increased by a factor of two. Gogotsi's results show a very similar non-linear relationship between volumetric capacitance of supercapacitors and the deposited layer thickness [33,34]. Wagner et al. [35] found that MEAs' performance is likely to suffer large losses at high power (high current) at Pt loadings below 0.2 mg $\mathrm{cm^{-2}}$, contrary to the expectation that thinner layers have lower transport resistance. Weber [19] concluded that the increased diffusion resistance is a local effect, but the effective transport and kinetic coefficients were kept constant during the simulation of Pt loading reduction. Our theoretical calculation showed [14], that although thickness is linearly dependent on loading, specific surface area significantly decreases until saturation is reached at a certain loading. It was supposed, that this non-linear scaling behaviour may account for the observed unwanted performance losses, but the transport processes were not simulated in detail. In this work we develop further and extend the model to elaborate transport processes at multiple length scales. A combination of scaling theory and the classical macro homogeneous approach (hybrid model) is proposed. This model is only the first step to develop a theory which is able to capture scaling effects occurring in a porous electrode.

For Li-ion batteries, Dillon et al. [1] suggested that the normalization of the current density by the rated capacity (C-rate) is not always adequate to compare the gravimetric and the volumetric energy and power densities of the same chemistry, but with different micro structures. A better normalization is likely to require the assumption of non-linear scaling effects.

In general, as a system is driven further away from equilibrium, structure of the electrode layer become more complicated and may result in fractal objects (but not exclusively) [12]. For fractals, the measurable properties such as porosity, shortest path etc. are dependent on the scale [12]. For isotropic fractal objects (fractals) the mass (M_F) and the overall system size (L_F) scales by the following function [12]

$$M_F = \Lambda m \left({}^{L_F}/_{r} \right)^{d_f} \tag{5}$$

where Λ is the lacunarity, m is the mass of the particle, r is the size of the particle and d_f is the scaling factor, called fractal dimension. This implies that porosity (or density) depends on the overall size of a fractal object as follows [12]

$$\varepsilon \sim {L_F}^{d_f - D} \sim {M_F}^{(d_f - D)/D} \tag{6}$$

where D is the dimension of the embedded space (i.e. 3 for 3D objects). In this case d_f is usually non-integer and smaller than the embedded dimension. If shapes grow under close-to-equilibrium conditions the resulting object is Euclidean. In this case d_f is equal