Tortuosity and Transport in Systems for Electrochemical Energy Storage and Conversion

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The efficiency of systems for electrochemical energy storage and conversion is based on their advantageous surface chemistry, i.e., the crystalline structure of the materials and the chemical bonding. In addition to the intrinsic properties of the constituent components, the 3D morphology of electrocatalysts has to be tailored, as it is closely related to the exposed facets and active sites. The design of electrocatalytic systems with an optimized hierarchical morphology and surface structures with high activity, resulting in highly performant and durable systems, is a task that is expected to play an increasing role in the future [1].

The total surface area of an electrocatalytic active material and the fluid-dynamic processes depend on the morphology of the formed nanostructures. Parameters such as porosity and tortuosity strongly influence the transport properties of the material. Multiphase and porous materials can be effectively modelled taking into account their hierarchical structure. Detailed 3D information about the morphology of porous materials and quantitative parameters that describe the transport properties (permeability, tortuosity) can be derived from tomography studies. Depending on the typical size of the studied objects, electron tomography (ET) in the TEM or X-ray computed tomography (XCT), both nano-XCT and micro-XCT, are suitable techniques to provide the morphology of the (sub-)structures of the hierarchical materials.

High-resolution allows to distinguish existing sub-structures. Each sub-structure can be modelled as a continuum, without explicitely separating it into the pore space and the solid skeleton. Thus, macroscopic concentrations, fluxes and other properties describing fluid-dynamic processes are given for each point $\boldsymbol{x}$ in the space occupied by material. However, these quantities are defined as the averages over a representative elementary volume. For example, the macroscopic concentration $c_i(\boldsymbol{x},t)$ is the microscopic concentration $c_i^{mic}(\boldsymbol{\xi},t)$ averaged over a specific volume. Using the homogenization method [2], it can be shown that the mass balance equation for nonhomogeneous materials must be transformed to a form taking into account the material porosity and a so-called effective diffusion coefficient $D_i^{eff} = \phi D_i / \tau^2$ which is a molecular diffusion coefficent modified by two empirical parameters that characterize a porous material: porosity ϕ and tortuosity τ [3]. Similarly, the homogenization method can be effectively used for energy, charge and momentum balance equations, enabling the description of kinetic processes in real electrochemical systems considering their 3D morphology.

Specially designed *operando* studies in laboratory XCT tools provide information about the material's morphology and kinetic processes in electrochemical systems. We will demonstrate materials ageing and system degradation during charging/discharging cycles of batteries [4].

References

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