The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Li-Ion Transport in Nanotubes and Ordered Mesoporous Oxides

Michael Wark
Institut für Chemie, Technische Chemie I, Universität Oldenburg, Carl-von-Ossietzky Str. 9-11, 26129 Oldenburg, Germany
E-Mail: michael.wark@uni-oldenburg.de

Ordered nanostructures are very attractive for realizing efficient new architectures for battery materials. Already in 2004 Long *et al.* proposed three-dimensional nanostructures with intergrown anode, cathode, and electrolyte [1].

TiO_2 was the first oxide being studied for battery application with defined and ordered 1D, 2D or 3D architectures. We could demonstrate that highly ordered mesoporous 3D-networks of well-crystalline anatase lead to very fast electron/ion transport and large amounts of charges storable in such thin films [2]. The employment of templating polymers ensuring high crystallinity in the applied soft-templating route is an important prerequisite (Fig. 1). Since the polymer stability is that limiting and applicable polymers are very expensive, the nanocasting approach employing porous oxides (mostly SiO_2) or carbons as hard templates rendered high attraction as more practical alternative. Ordered mesoporous oxide films and powders like TiO_2, SnO_2, Co_3O_4 or even $CuCo_2O_4$ [3] have been 3D-nanostructured by nanocasting. Intercalation of Li^+ ions and their dynamics in the pores have been intensively studied by the groups of Bruce [4] and Wilkening [5]. The talk will discuss their findings and will compare them to results on 1D nanotube structures.

TiO_2 nanotubes, for example, have the advantage that they can be much easier prepared in high quantity from a simple hydrothermal route [6]. Involved titanates are interesting for Li ion intercalation by themselves; most promising for battery applications, however, are the quite high amounts of TiO_2-B being formed [7].

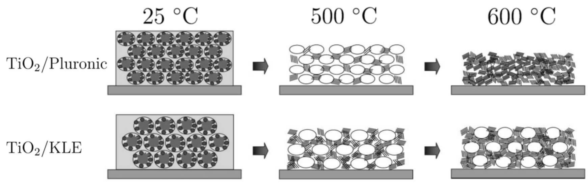

Figure 1: Simplified model for the crystallization of mesoporous KLE- and Pluronic P123-templated TiO_2 films. The more temperature stable KLE-block-copolymer ensures high crystallinity under preservation of the pore ordering and thus the high active inner surface area [2].

[1] Three-Dimensional Battery Architectures, J. W. Long, B. Dunn, D. R. Rolison, H. S. White, Chem. Rev. 104 (2004) 4463.
[2] Highly Organized Mesoporous TiO_2 Films with Controlled Crystallinity: A Li-Insertion Study, D. Fattakhova-Rohlfing, M. Wark, T. Brezesinski, B. Smarsly, J. Rathouský, Adv. Funct. Mater. 17 (2007) 123.
[3] Synthesis of Ordered Mesoporous $CuCo_2O_4$ with Different Textures as Anode Material for Lithium Ion Battery, S. Sun, Z. Wen, J. Jin, Y. Cui, Y. Lu, Microporous Mesoporous. Mater. 169 (2013) 242.
[4] Lithium Intercalation into Mesoporous Anatase with an Ordered 3D Pore Structure, Y. Ren, L. J. Hardwick, P. G. Bruce, Angew. Chem. Int. Ed. 49 (2010) 2570.
[5] Li Ion Dynamics in TiO_2 Anode Materials with an Ordered Hierarchical Pore Structure – Insights from ex situ NMR, P. Bottke, Y. Ren, I. Hanzu, P. G. Bruce, M. Wilkening, Phys. Chem. Chem. Phys. 16 (2014) 1894.
[6] Theoretical and Experimental Study of Anatase Nanotube Formation via Sodium Titanate Intermediates, M.-Chr. Runkel, O. Wittich, A. Feldhoff, M. Wark, T. Bredow, J. Phys. Chem. C 119 (2015) 5048.
[7] Elektrochemische Charakterisierung von lithiierten Titandioxid-Nanoröhren, O. Wittich, PhD thesis, Leibniz Universität Hannover, 2015.