EFFECT OF SURFACE ROUGHNESS ON LITHIUM DIFFUSION IN DISORDERED NANOPOROUS MATERIALS

K.Malek, M.-O. Coppens

Department of Chemical Technology, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

The physics of diffusion phenomena in disordered media has attracted a lot of attention, due to its close connections with major technological applications like heterogeneous catalysis [1] and electrochemistry [2]. Disordered nanoporous materials, e.g. amorphous transition metal oxides, with a vast pore network and a rough internal pore surface stay in the center of interest of electrocatalysis, batteries and fuel cells. Many of these processes are diffusion controlled, so that a correct assessment of their efficiency depends on more accurate determinations of the diffusion on the topological and morphological textural parameters. For instance, the performance of a porous electrode in high-energy density batteries depends on its ability to intercalate lithium reversibly into the host lattice. Lithium diffusion in the oxide is a key factor that determines the rate at which a battery can be charged and discharged.

Although systematic theoretical study of lithium diffusion in layered crystalline transition metal oxides, e.g. Li_xCoO_2, has been done extensively, the effect of the morphology, i.e. roughness of the oxide matrix in the lithium diffusion remains unknown. This effect could be more significant in disordered amorphous transition metal oxides. We have used Monte-Carlo simulation as well as analytical calculation to investigate the effect of pore surface roughness on lithium diffusion in disordered nanoporous electrodes. The effect is studied for three-dimensional pores, Fig.1, with fractal surface roughness within a realistic finite range, because it has been demonstrated [3] that many disordered porous electrodes prepared by common sol-gel synthesis have a fractally rough internal surface down to molecular scales. The jump diffusion coefficient D_J in the fractal pore, can be expressed as:

$$D_J = \left(\frac{1}{4N_{Li}}\right)\lim_{t\to\infty}\frac{1}{t}\left\langle\left\{\sum_{i=1}^{N}\left[\vec{r}_i(t)-\vec{r}_i(0)\right]\right\}^2\right\rangle \qquad (1)$$

in which, N_{Li} corresponds to the number of diffusing lithium ions and $\vec{r}_i(t)$ is the displacement of the i*th* lithium ion after time t.

Figure 2 illustrates calculated values for the jump (self-) diffusion coefficient as a function of Li ratio, x (1-x is concentration of vacancies), for a smooth and rough pore. The Monte-Carlo simulations predict that above x=0.6, the Li self-diffusivity drops by several orders of magnitude. On the other hand, there is clearly a large influence of roughness on self- diffusion of lithium ions: the self-diffusivity decreases as the fractal scaling range widens, i.e., with increasing roughness. Although the details of the diffusion mechanism are clearly different in a crystalline-layered material compare to an amorphous metal-oxide electrode, similar conclusions are likely to hold for, e.g. crystalline Li_xCoO_2. In the latter case, the trapping in the tetrahedral sites is qualitatively comparable to the geometrical trapping by surface indentations, i.e. roughness, in amorphous media.

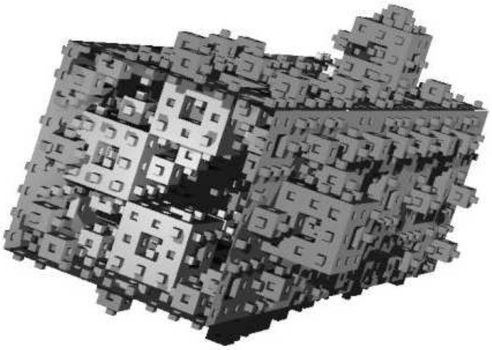

Fig.1. Part of a typical 3D rough pore with square cross section.

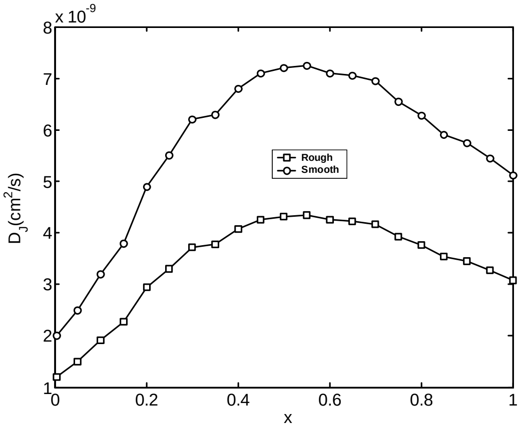

Fig.2. Calculated values for the jump (self-) diffusivity D_J as a function of Li concentration ratio, x, for a smooth (circle) and rough (square) pore.

References

[1] G.F. Froment and K.B. Bischoff, *Chemical Reactor Analysis and Design* (wiely, New York, 1991). 2^{nd} ed.

[2] D. O'Hare, in *Inorganic Materials*, edited by D.W. Bruce and D.O'Hare (John Wiley&Sons, Ltd., Chichester, UK, New York, 1996), pp. 171-254.

[3] K. Malek and M.-O. Coppens, Phys. Rev. Lett. 87, 125505 (2001).