Supporting information

ALD Al_2O_3 coated TiO_2 nanotube layers as anodes for lithium ion batteries

Hanna Sopha[†], *Girish D. Salian*[‡], *Raul Zazpe*[†], *Jan Prikryl*[†], *Ludek Hromadko*[†], *Thierry Djenizian*[§,*], *Jan M. Macak*[†,*]

[†]Center of Materials and Nanotechnologies, Faculty of Chemical Technology, University of Pardubice, Nam. Cs. Legii 565, 53002 Pardubice, Czech Republic

[‡]Aix Marseille Université, CNRS, Electrochemistry of Materials Research Group, MADIREL UMR 7246, F-13397, Marseille Cedex 20, France

[§]Ecole Nationale Superieure des Mines de Saint-Etienne, Flexible Electronics Department, Center Microelectronics Provence, 13541, Gardanne, France

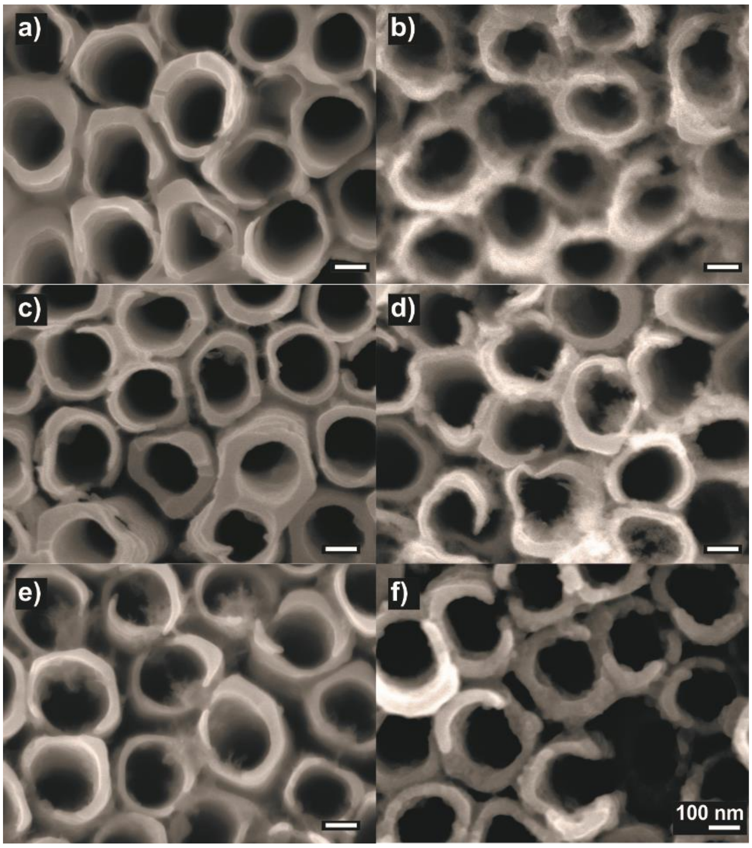

Figure S1. Post-cycling (100 charge/discharge cycles) SEM images of a) uncoated TiO_2 nanotube layer, b) 0.2 nm (2 ALD cycles), c) 1 nm (9 ALD cycles), d) 2 nm (18 ALD cycles), e) 5 nm (46 ALD cycles), and f) 10 nm (92 ALD cycles) Al_2O_3 coated TiO_2 nanotube layers.

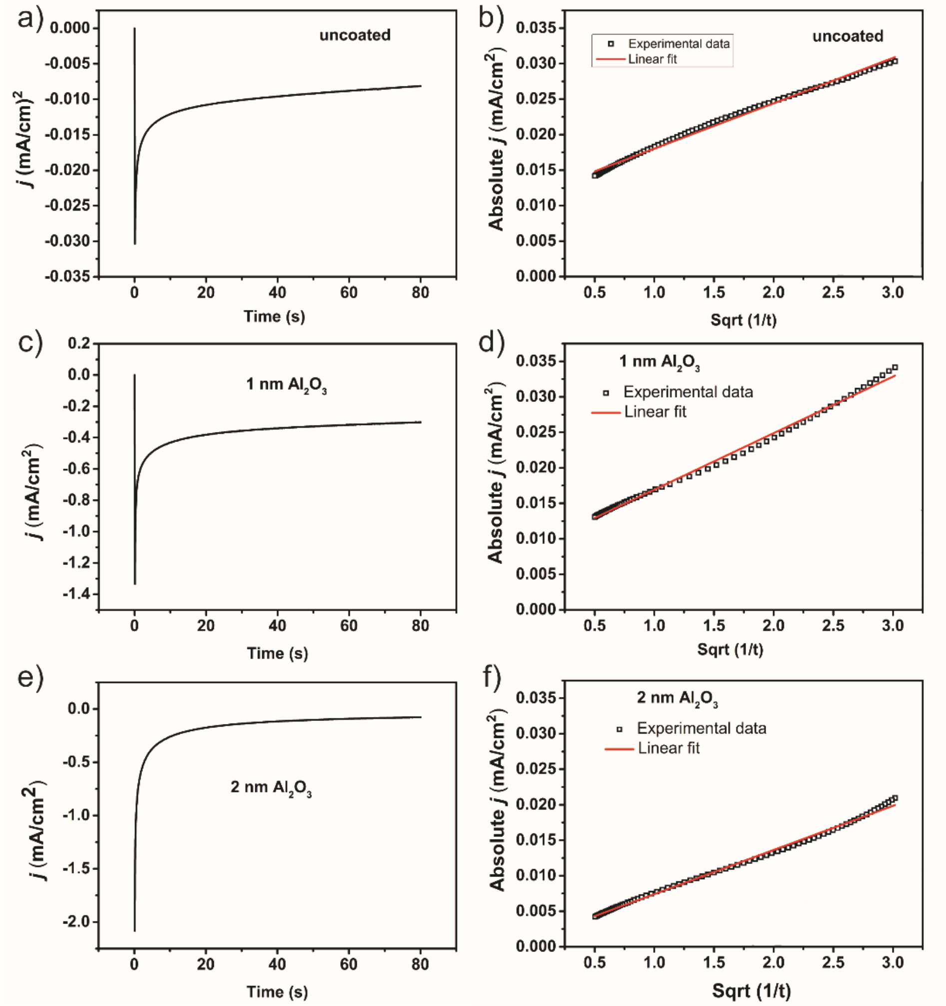

Figure S2. Chronoamperometric plots of the a) uncoated, c) 1 nm Al_2O_3 coated, and e) 2 nm Al_2O_3 coated TiO_2 nanotube layers, and the linear fits of the Cottrell plots for the b) uncoated, d) 1 nm Al_2O_3 coated, and f) 2 nm Al_2O_3 coated TiO_2 nanotube layers.

The reversible insertion reaction of Li^+ in anatase TiO_2 is given by eqn (1).

$$TiO_2 + xLi^+ + xe^- \leftrightarrow Li_xTiO_2 \quad \text{for } 0 \le x \le 0.5 \qquad (1)$$

The chronoamperometric plot was obtained by applying a constant potential of 1.7 V vs. Li/Li^+, which is the potential of the insertion of Li^+ into the lattice (Figure S2, a, c, e). The current observed for the electrochemical reaction at the mass transport limited condition is described by the Cottrell equation: [2]

$$j = nFCD^{1/2}\,\pi^{-1/2}\,t^{-1/2}$$

where n is the number of moles of Li^+ involved in the redox reaction of Ti^{3+}/Ti^{4+} which is equal to 0.5 according to Equation (1), F is the Faraday constant, C is the maximum concentration of Li^+ (or Ti^{3+}) in the lattice (0.024 $mol.cm^{-3}$ at x = 0.5)[1, 2], D is the Diffusion coefficient of Li^+ and t is the time (s).

The Cottrell equation is valid only in the diffusion control region. The diffusion coefficient can be estimated by plotting the absolute current density (j) vs. $t^{-1/2}$. Ideally, the plot is a straight line when the kinetic is controlled by mass transport. The value of the slope which is equal to $nFCD^{1/2}\pi^{-1/2}$ can be determined by the linear fit of the Cottrell plots (Figure S2, b, d, f).

References

1) Lindstrom, H.; Sodergren, S.; Solbrand, A.; Rensmo, H.; Hjelm, J.; Hagfeldt, A.; Lindquist, S. E. Li^+ Ion Insertion in TiO_2 (Anatase). 1. Chronamperometry on CVD Films and Nanoporous Films *J. Phys. Chem. B* 1997, 101, 7710−7716.
2) Kavan, L.; Rathouský, J.; Grätzel, M.; Shklover, V.; Zuka, A. Surfactant-Templated TiO_2 (Anatase): Characteristic Features of Lithium Insertion Electrochemistry in Organized Nanostructures. *J. Phys. Chem. B* 2000, 104, 12012–12020.