Fully reversible heterogeneous Li-storage in RuO_2 electrodes

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We present here the results of our investigation on the performance of RuO_2 as active electrode material for rechargeable lithium batteries. RuO_2 shows a high Li-storage capacity of 1120 mAh/g upon uptake of 5.6 Li, with 98% Columbic efficiency at the first discharge/charge cycle[1].

Based on XRD, Raman spectroscopy and HRTEM measurements performed at various stages of discharge/charge processes, it is observed that full Li-uptake transforms polycrystalline RuO_2 into nanocrystalline composite of Ru and Li_2O with a grain size of 2-5 nm covered by a 5-10 nm surface solid/electrolyter interphase (SEI) layer. In the fully Li-extraction state, nanocrystalline RuO_2 formed again and the SEI layer disappeared completely.

The overall reaction can be written as:

$$RuO_2 + 4\ Li^+ + 4\ e^- \leftrightarrows Ru/Li_2O$$

This is analogous to the decomposition reaction observed in other transition metal oxides[2] and fluorides[3]. When the cycling is limited between 1.2–0.05 V, a reversible capacity of 150 mAh/g with a good cyclablity is observed. We believe that this reversible Li-storage is caused by a heterogeneous interfacial storage process[4].

Among the materials studied so far, it is worth mentioning that only RuO_2, allowed complete extraction of Li^+ (nearly 100 % Coulombic efficiency) in the first cycle, while in other materials only 75 % or less Li^+ can be extracted. We discuss in detail the cause for the complete extraction of Li^+ in case of RuO_2 in comparison with few other materials such as TiF_3 and CoO in terms of the microstructure of M/LiX (X = O, F) nanocomposite and mass (e^-, Li^+ and O^{2-}/F^-) transport.

References

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