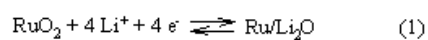


High capacity and Columbic efficiency of RuO₂ as electrode material for rechargeable battery

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Recent studies have shown that transition metal oxides (M = Co, Ni, Cu, Fe) can be used as a high-capacity anode material for rechargeable lithium batteries¹. RuO₂ is a well-known material for proton-based electrochemical supercapacitor, however, less attempts have been made for its optimal use in lithium batteries. We present here our detailed investigation on the performance of RuO₂ as active electrode material for rechargeable lithium batteries over a wide voltage window 4.3–0.05 V.

RuO₂ shows a high Li-storage capacity of 1120 mAh/g upon insertion of nearly 5.5 Li, with nearly 100% Columbic efficiency even at the first discharge/charge cycle (Fig.1). The overall reaction can be written as:



The above mechanism is confirmed by XRD and Raman spectroscopy measurements done at various stages of discharge/charge processes. The voltage profile exhibits three characteristic regions during the first discharge: two plateau regions followed by a sloped region. The first plateau region occurs at 2.1 V due to the formation of Li_{0.86}RuO₂, followed by the second plateau at 0.9 V, which is related to the formation of a Li_{1.3}RuO₂ phase. Upon insertion of 4 Li, the above phases undergo complete decomposition, forming a Ru/Li₂O nanocomposite, with a capacity of about 800 mAh/g. Beyond this, the sloped region with a capacity of about 300 mAh/g is observed. HRTEM and electron diffraction indicate further that upon insertion of 4 Li, Li₂O is dispersed uniformly with Ru on a nanoscale (2-5 nm), associated with the formation of a thin surface layer (1-3 nm) of solid/electrolyte interface (SEI). A fully lithiated RuO₂ has a similar nanocomposite microstructure, but covered by a thick layer (5–10 nm) of SEI (Fig. 2). During charging up to 1.2 V, Ru/Li₂O still retains its nanostructure. Upon complete charging (extraction of Li), a nanocrystalline RuO₂ phase restore, while the SEI surface layer becomes negligible (Fig. 2). This seems to be one of the main reasons for obtaining almost 100% Columbic efficiency in RuO₂ unlike other transition metal oxides, having roughly 75% efficiency due to the retention of some amorphous Li₂O phase in their fully charged states². Electrochemical impedance spectroscopy (EIS) study suggests further that the electrode impedance drops significantly upon insertion of Li. This is especially kinetically favorable for the complete extraction of Li.

It has been confirmed by HRTEM that the SEI formed during discharge in the sloped region, starts decomposing mainly beyond the sloped region (1.2V) during charge. It is also noticed that the Li-storage capacities in the sloped regions during discharge and charge processes are 300 and 150 mAh/g respectively (Fig 1). It means that the Li-storage during discharge cannot be only contributed to the SEI formation. Moreover, when the cycling voltage is limited between 1.2–0.05 V, we observe a reversible capacity of 150 mAh/g with a very good cyclability (Fig. 1). In addition, EIS measurement has shown a systematic increase and decrease of diffusion impedance during insertion and extraction of Li around the slope regions respectively. However, beyond the sloped region (1.2 V), impedance increases during charging. In view of these observations, we propose that the excess reversible capacity of 150 mAh/g might be due

to the interfacial charge of extra Li deposited within the Ru/Li₂O matrix. Such a phenomenon is found to be consistent with the results obtained on M/LiF systems³.

It is also interesting to note that when the cycling is limited within 4.3–0.8 V, nearly 100% Columbic efficiency still can be achieved with a capacity of about 800 mAh/g (see Fig.1). The capacity obtained in this voltage range is much larger than for other known metal oxide systems, such as CoO, CuO, MnO₂ and V₂O₅. Furthermore, when the discharge/charge is limited to the range of 2.5–0.05 V, cyclic performance was found to be remarkably good.

The above studies suggest that a reversible Li-storage in RuO₂ via phase formation and decomposition of Li₂O can be achieved with a very high capacity of 1120 mAh/g associated with almost 100% Columbic efficiency. We believe, this should be due to the high transport rates in RuO₂ and the size effects, such as reduced transport pathways and advantageous interfacial chemistry⁴.

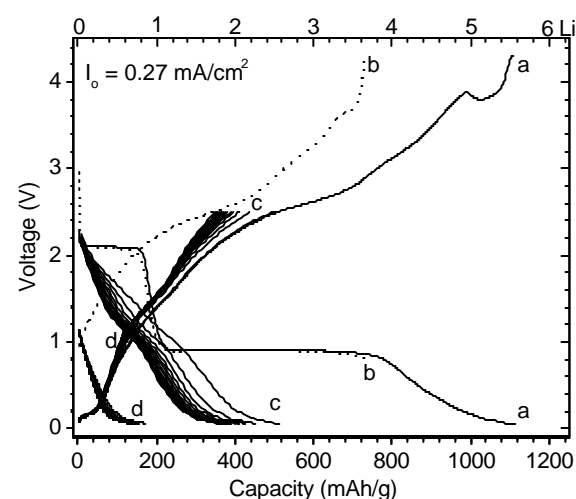


Fig.1 Voltage profiles of a Li/RuO₂ cell cycled between various range : (a) 4.3-0.05 V, (b) 4.3-0.8 V, (c) 2.5-0.05 V and (d) 1.2-0.05 V

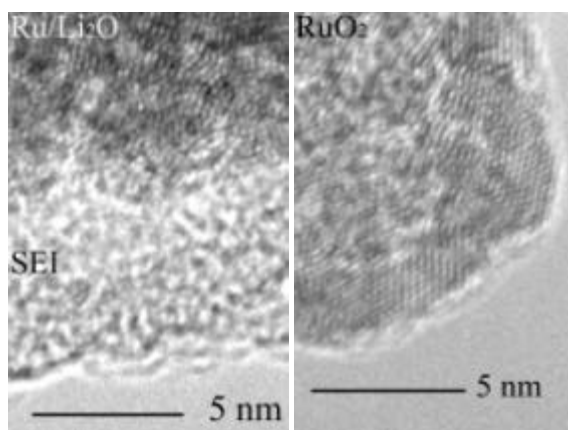


Fig. 2 HRTEM images of fully discharged (left) and charged (right) RuO₂

References

1. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, *Nature*, 2000, 407, 496
2. A. Debart, L. Dupont, P. Poizot, J-B. Leriche, J.M. Tarascon, *J. Electrochem. Soc.* 2001, 148 A1266
3. H. Li, G. Richter, J. Maier, submitted to *Advanced Materials*
4. J. Maier, *Solid State Ionics*, 2002, 148, 367