

## Insertion of lithium into RuO<sub>2</sub>–TiO<sub>2</sub> electrodes

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### Abstract

The insertion of lithium into the solid system RuO<sub>2</sub>–TiO<sub>2</sub> was investigated. Both the potential and the rate of insertion decrease with the increase of titanium concentration, due to lowering the density of electronic states.

### Introduction

Murphy [1] and Dalard [2] described the electrochemical insertion of lithium into RuO<sub>2</sub> at 2.1 V (versus Li) and with estimated diffusion coefficient of lithium  $D_{\text{Li}} = 0.9 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$  at 25 °C. The insertion is accompanied by a small volume change up to the composition Li<sub>0.5</sub>RuO<sub>2</sub> and by the transformation from tetragonal to rhombohedral symmetry with 11% volume change [3].

On the contrary, the insertion of Li in isostructural TiO<sub>2</sub> (rutile) is fairly slower and occurs at more negative potential [3]. This difference does not originate from mere geometric factors, but indicates a strong influence on the nature of metal in rutile-like oxides MeO<sub>2</sub> on Li insertion. We have attempted to illustrate this phenomenon.

Therefore, we have studied the insertion of Li into electrodes, manufactured from solid system RuO<sub>2</sub>–TiO<sub>2</sub> as a model system of two species with almost identical lattice parameters, but rather different chemical nature.

### Experimental

A mixture of Ru(OH)Cl<sub>3</sub> and H<sub>2</sub>TiO<sub>5</sub> aqueous solutions was evaporated either in a crucible, or on a titanium foil as a substrate, and converted to MO<sub>2</sub> by temperatures of 500 to 600 °C. Polytetrafluoroethylene (PTFE)-bonded electrodes were fabricated by pressing in a conventional way on a platinum screen from the powders, to which 36% PTFE was added. For all experiments, 1 M LiClO<sub>4</sub> in dry propylene carbonate (PC) was used. All potential values refer to a Li electrode in the same solution.

### Results

#### *PTFE-bonded electrodes*

Capacity was estimated from the cathodic plateau on a chronopotentiometric curve on PTFE-bonded electrodes (0.04–0.08 g, apparent diameter 1 cm, 0.3 mA).

The charge of the cathodic wave is plotted in Fig. 1. It is higher than  $400 \text{ A s g}^{-1}$  (i.e.,  $110 \text{ A h kg}^{-1}$ ) when the ratio Ru:Ti is higher than 70:30, and it passes through a maximum close to  $1000 \text{ A s g}^{-1}$  ( $250 \text{ A h kg}^{-1}$ ) at Ru:Ti=80:20. The highest charge corresponds to 1.1 atoms of Li in 1 formula of oxide. At Ru content lower than a ratio 50:50, the charge is fairly lower.

The maximum capacity of  $1000 \text{ A s g}^{-1}$  of mixture (containing 36% of PTFE) corresponds to 2.07 atoms of Li per 1 formula of host oxide.

### Voltammetry

Thin-layer electrodes on Ti foil were studied by cyclic voltammetry at scan rates in the range  $0.001\text{--}0.02 \text{ V s}^{-1}$ . Two examples of such curves are shown in Fig. 2. Their quantitative description is given in Table 1. Maximum peak current was found for 90%  $\text{RuO}_2$  and the drop of peak current with increasing concentration of Ti is faster than in Fig. 1.

The diffusion coefficient,  $D_{\text{Li}}$ , was estimated from the cathodic voltammetric peak under assumption of an average Li concentration  $\text{Li}_{0.5}\text{RuO}_2$  and the validity of Randles-Ševčík-Matsuda equation for the peak current of a voltammetric process [4]:

$$i_p = \text{const.} \cdot \sqrt{D\nu}$$

where  $\nu = dE/dt$  is the scan rate and the constant contains the surface area.

### A.c. impedances

The a.c. impedances were measured on the same thin-layer electrodes in two potential ranges, i.e., at the potential of Li insertion and at 0.5 V higher, when no insertion occurs. The behavior of the electrodes can be described by an equivalence circuit containing a series resistance  $R_s$ , a pseudo-capacity  $C_1$  (rather a constant-phase element with a phase angle 0.75 to 0.8 of  $\pi/2$ ), a reaction resistance  $R_1$  and a Warburg-like immitance  $W_1$ . The two latter are apparent at insertion potential only. The results are summarized in Table 1 and in Fig. 3.

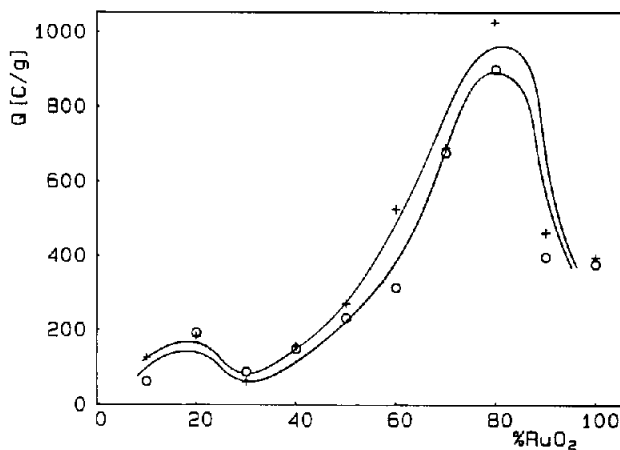


Fig. 1. The influence of the ruthenium concentration (in mol%) on cathodic charge of (+) first and (O) second discharge at constant current 0.3 mA; electrodes: 0.04 to 0.08 g in 1 M  $\text{LiClO}_4/\text{PC}$ .

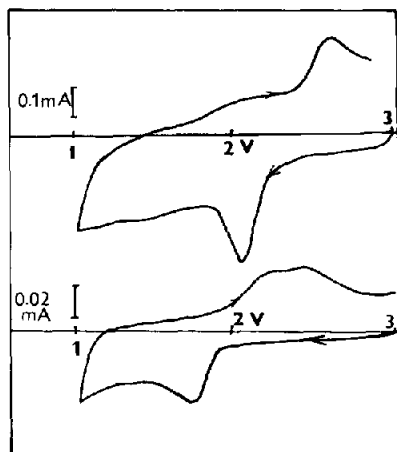


Fig. 2. Voltammograms of thin-layer electrodes, electrode area: 0.5 to 0.8 cm<sup>2</sup>, scan rate: 0.002 V s<sup>-1</sup>. Upper curve: 100% RuO<sub>2</sub>, lower curve: 60% RuO<sub>2</sub>+40% TiO<sub>2</sub>.

TABLE 1

The lithium insertion into RuO<sub>2</sub>-TiO<sub>2</sub> electrodes<sup>a</sup>

RuO <sub>2</sub> (%)	$E_p$	$I_p$	$D_{Li}$	$R_s$	$C_1$	$W_1$
100	2.4	0.7	2.2	55	710	220
90	2.0	0.73	2.6	62	420	870
80	1.8	0.32	0.50	25	1080	230
70	1.75	0.12	0.073	10	1290	64
60	1.65	0.086	0.036	39	842	21
50	1.45	0.024	0.0027	290	794	11

<sup>a</sup> $I_p$  (mA cm<sup>-2</sup>) is peak current at  $E_p$  (V, versus Li), estimated  $D$  (10<sup>13</sup> cm<sup>2</sup> s<sup>-1</sup>),  $R_s$  ( $\Omega$  cm<sup>2</sup>) is series resistance,  $C_1$  ( $\mu$ F cm<sup>-2</sup>) double-layer capacity, and  $W_1$  ( $\mu$ S cm<sup>-2</sup>) is diffusion admittance at  $\omega=1$ .

## Discussion

The inhibiting action of Ti on Li insertion into RuO<sub>2</sub>-TiO<sub>2</sub> oxides seems clear both from Fig. 1 and Table 1. The chronopotentiometry (Fig. 1) was performed on plastic-bonded powder electrodes using a longer time in comparison with other experiments with thin-layer electrodes. Therefore, the decrease of  $D_{Li}$  becomes apparent at higher concentration of Ti on powder electrodes than on thin-layer ones. Small difference between Table 1 and Fig. 1 should be explained either in this way or by a slightly different morphology of mixed oxides of both types. Further, the capacity of the thin-layer electrodes ( $C_1$  in Table 1) does not vary more than in the ratio 1:3. Therefore, the inhibition of Li insertion cannot be explained just by the change of surface area.

The decrease of diffusion coefficient and reversible potential of insertion should be explained similarly as it is in the case of transition metals dichalcogenides. RuO<sub>2</sub>

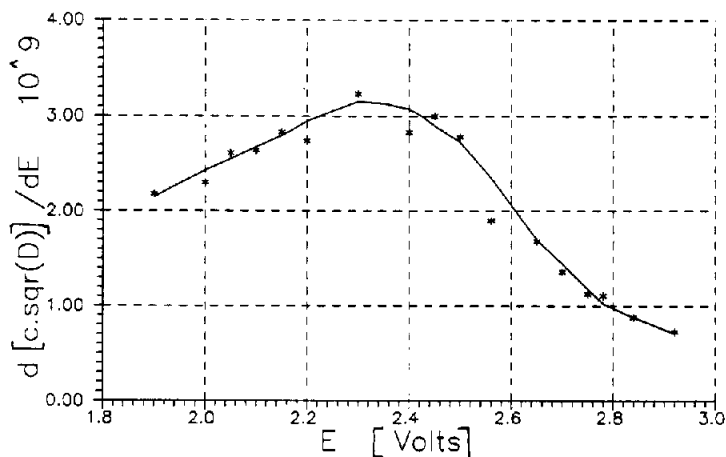


Fig. 3. The quantity  $\partial(C\sqrt{D})/\partial E$ , evaluated from diffusion component of the impedance of an electrode 100%  $\text{RuO}_2$ .

is a quasi-metallic oxide, which has a rather broad and half-empty conduction band, while  $\text{TiO}_2$  is a typical oxidic semiconductor with the band gap close to 3 eV. Therefore, the affinity of the oxide lattice towards Li atoms is much lower if the Fermi level approaches the bottom of conduction band and the density of electron state becomes much smaller than in pure  $\text{RuO}_2$  (compare with the increased resistivity at 50%  $\text{TiO}_2$ , indicated by the increased series resistance  $R_s$ ). This is in agreement with the difficult insertion of Li in rutile even in the form of single crystals [5].

Ruthenium-free electrodes are quite different. As-prepared electrodes are photoelectrochemically active, but their photoresponse in 1 M  $\text{LiClO}_4/\text{PC}$  electrolyte is fairly poor and unstable [6]. The electrochemical insertion of Li followed by anodic delithiation increases the concentration of electron donors by one order of magnitude, and the stability of photocurrent in time is much better.

On the basis of experiments described in this paper, the mutual influence of electronic properties and Li insertion in  $\text{RuO}_2\text{-TiO}_2$  electrodes seems to be verified.

## References

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