Short communication

Electrochemical insertion of magnesium in open-ended vanadium oxide nanotubes

Lifang Jiao [a], Huatang Yuan [a,*], Yuchang Si [b], Yijing Wang [a], Jiansheng Cao [a],
Xiuling Gao [a], Ming Zhao [a], Xingdi Zhou [a], Yongmei Wang [a]

[a] *Institute of New Energy Material Chemistry, Nankai University, Tianjin 300071, China*
[b] *Medical College of Chinese People's Armed Police Force, Tianjin 300162, China*

Abstract

Vanadium oxide nanotubes were obtained as the main product in a sol–gel reaction followed by hydrothermal treatment from V_2O_5 precursors and octadecylamine. The tubes consist of concentric shells of highly crystalline vanadium oxide separated by alternation organic amine layers. The vanadium oxide nanotubes are redox-active and can electrochemically insert magnesium reversibly. The electrochemical insertion magnesium properties of vanadium oxide nanotubes were studied by electrochemical impedance (EIS) and cyclic voltammogram.
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1. Introduction

Rechargeable magnesium battery may be a candidate of high energy density battery due to its natural abundance, a relatively low price of its raw materials [1], and an expected higher safety of batteries based on metallic magnesium compared to lithium. Moreover, it has relatively low equivalent weight and negative standard potential. Therefore, magnesium is an attractive anode material for large battery system.

Rechargeable magnesium batteries had not been paid much attention because of mainly two problems. First owing to the chemical activity of Mg, only solutions that neither donate nor accept protons are suitable as electrolytes; but most of these solutions allow the growth of passivating surface films, which inhibit any electrochemical reaction [2–4]. Second, the choice of cathode materials has been limited by the difficulty of intercalating Mg ion in many hosts [5]. Recently, however, Aurbach et al. [6–9] reported that the electrolyte solution using organohaloaluminate salt allowed Mg

to dissolve and deposit reversibly and it had drawn more attention to Mg battery systems combined with Mo_3S_4 as a cathode material [10]. These systems showed reversible charge/discharge behavior, yet their operation potential was relatively low, about 1.3–1.0 V. Various kinds of candidates for cathode materials were reviewed by Novák et al. [5]. polycrystal V_2O_5 and V_2O_5 aerogel were studied as cathode materials [10,11], but it is difficult for the divalent Mg ion to intercalate and diffuse in solid-state materials compared to the monovalent Li ion. We intend to prepare nanosructured materials to enhance the rate of Mg^{2+} diffusion.

The recently discovered vanadium oxide nanotubes (VO_x-NTs) [12–16] are of particular interest since vanadium oxides are widely applied in catalysis and in electrochemistry. Starting with vanadium pentoxide precursor and alkylamine, a sol–gel reaction combined with a subsequent hydrothermal treatment resulted in pure vanadium oxide nanotubes. This highly selective procedure is reproducible and leads to the tubes in an excellent yield. The organic template molecules are embedded between vanadium oxide layers inside the tube walls. The tube has a very advantageous shape for intercalation magnesium ion, for example, the considerable large

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distance between the layers, a wide inner and outer diameter, and the open tube ends.

2. Experimental

Vanadium pentoxide (10 mmol) and octadecylamine (10 mmol) were added to 5 ml ethanol, and the resulting mixture was stirred for about 2 h. Then, 15 ml of distilled water was added, and the stirring continued for 48 h and hydrolyzed vanadium oxide component was obtained. The hydrothermal reaction of this composite in an autoclave at 180 °C for 7 days. The resulting solid was filtered, washed repeatedly with ethanol and hexane and finally dried at 80 °C under vacuum to give a black crystalline product.

Electrolyte solution 0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF for rechargeable magnesium batteries was prepared according to the research by Aurbach [8]. The decomposition potential of the electrolyte is about 2.4 V (versus Mg reference).

Chemical analysis was performed by C, H, and N microelement analyses (elementar vario EL). The metal contents were determined by induced coupled plasma atomic emission spectroscopy (ICP-9000(N + M), USA Thermo Jarrell-Ash Corp.).

Electrochemical magnesium insertion from Mg(AlBu$_2$Cl$_2$)$_2$/THF solution was performed in battery. The sample electrode pellet was prepared by pressing the 50:37.5:12.5 (in wt.) mixture of VO$_x$-NTs, acetylene black and PTFE. Magnesium ribbon was used as the counter electrode. The electrochemical measurements were performed using a Solartron 1287 electrochemical interface and Solartron 1250 frequency response analyser. All procedures and cell construction were carried out under dried argon atmosphere in a glove box.

3. Results and disscussion

3.1. Characterization of the nanotube material

According to chemical analysis and ICP, the black vanadium oxide has the nominal composition of VO$_{2.37}$ [C$_{18}$H$_{40}$N]$_{0.26}$, indicating that a relatively large amount of organic template was built into the oxide structure during synthesis. There were many reports on the synthesis of vanadium oxide nanotubes which characterization of the material was described in detail [12–20]. Therefore, we laid emphasis on the electrochemical properties of the nanotubes. The results of characterization of the nanotubes are that the nanotubes are 1–3 μm long, 60–100 nm for their outer diameter, 15–40 nm for their inner diameter and have open ends.

3.2. Electrochemical measurements

The first two voltammetric cycles of the vanadium oxide nanotubes are shown in Fig. 1, performed at a sweep rate 0.1 mV s^{-1}. Each cycle curve shows a pair of redox peaks.

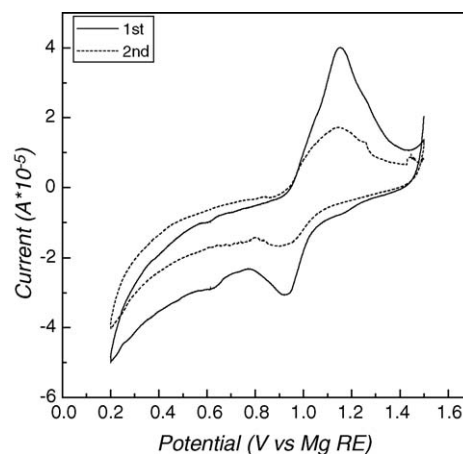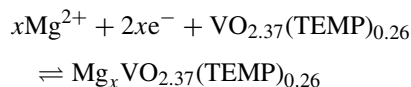Fig. 1. Cyclic voltammograms of the vanadium oxide nanotubes at 0.1 mv s^{-1} in 0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF.

The reduction peak at ca. 0.9 V versus Mg/Mg^{2+} corresponds to the electrochemical insertion of magnesium into the nanostructured material

$$x\mathrm{Mg}^{2+} + 2x\mathrm{e}^- + \mathrm{VO}_{2.37}(\mathrm{TEMP})_{0.26}$$
$$\rightleftharpoons \mathrm{Mg}_x\mathrm{VO}_{2.37}(\mathrm{TEMP})_{0.26}$$

The corresponding oxidation process begins at about 1.2 V versus Mg/Mg^{2+} which corresponds to the Mg deintercatlation from the nanotubes. The change in shape between the first cycle and the second cycle indicates a change of the material during cycling. The material has lost electroactivity to some extent. The most likely reason is the amorphization or other structure changes of the material upon cycling [21]. The first five cycles of performance of rechargeable Mg/VO$_x$-NTs batteries during cycling at constant current (5 mA g^{-1}) in 0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF are shown in Fig. 2. The shape of the charge–discharge curves from the third cycle changes a little with cycle number. From Figs. 1 and 2, it can be concluded that the electrochemistry properties of the material have been activated at the first two cycles and the electrochemistry properties and the layered structure of the material are kept after the third cycle. Though the specific capacity is lower than lithium ion battery, the material presents possible reversible. The nanotubes were also used for electrochemical insertion of lithium [16].
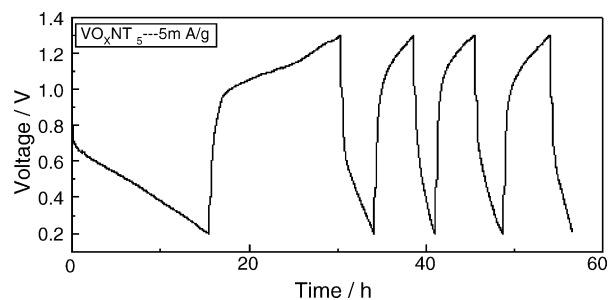

Fig. 2. Performance of rechargeable Mg-VO$_x$-NTs batteries during cycling at current density (5 mA g^{-1}) in 0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF.
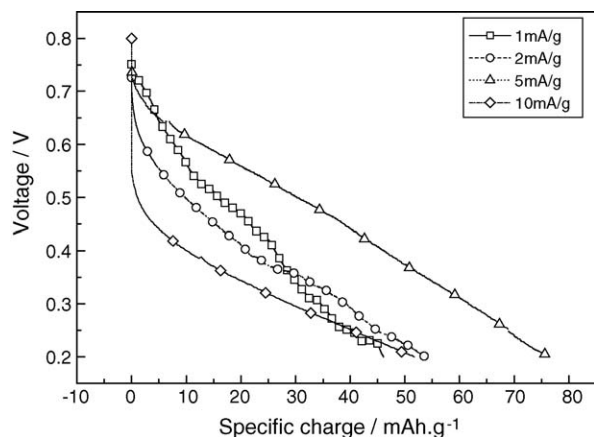
Fig. 3. The first discharge curves at different discharge currents to the cutoff voltage 0.2 V. The discharge capacity in any electrode was based on the amount of the active material not including the weight of the additives in the electrode.

The charge–discharge behavior of the rechargeable Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_{2.37}$ [C$_{18}$H$_{40}$N]$_{0.26}$ battery has been carried out. When the battery discharged (magnesium intercalation into cathode) at 5 mA g^{-1} to the cut off voltage 0.2 V, then the cathode was washed for several times by dry THF which in order to exclude the effect by the magnesium content of the electrolyte in glove box. Then the magnesium in the cathode was analyzed by ICP which in accordance with the result by electrochemical measurement. Therefore, side reactions in this battery system have not appeared and the capacity of the battery is produced by magnesium intercalation/de-intercalation.

Fig. 3 presents the first discharge curves at different discharge current densities. The curves without voltage plateau indicate the insertion reaction of magnesium into VO$_x$-NTs, and it also can be seen from the experiment results that the material presents a good electrochemical behaviors at 5 mA g^{-1} discharge current density. The material exhibits good cycle behaviors and relatively high specific capacity at the first cycle at higher current, which is due to the very advantageous shape for intercalation magnesium ion, for example, the considerable large distance between the layers, a wide inner and outer diameter, and the open tube ends.

Fig. 4 shows Nyquist plots obtained from Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_x$-NTs discharged at different depth, i.e. at different content of inserted magnesium. The battery discharged at 5 mA g^{-1} current density for 1 h, 11 h and 21 h. The battery was kept for about 12 h until the change of OCP voltage was less than 1 mV. The impedance spectra consist of two depressed arcs. The high frequency arc is probably due to the charge transfer reaction at the electrolyte/electrode interface and the medium frequency arc is probably due to the magnesium diffusion in solutions and adsorption on the surface of electrode. The intercept of the high frequency arc and *x*-axis is ascribed to the resistance of the electrolyte. Fig. 5 shows the equivalent circuit of the battery, and Table 1 gives some results from simulation of the
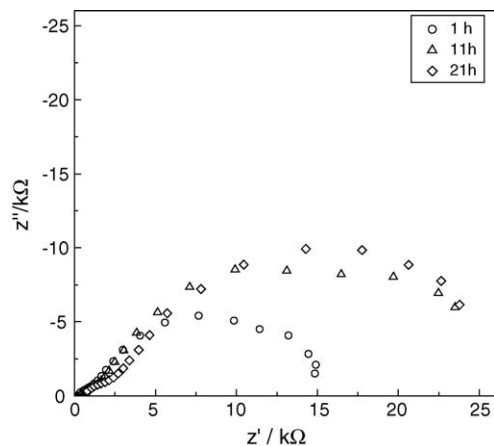

Fig. 4. Nyquist plots obtained from Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_x$-NTs discharged at different depth (current density: 5 mA g^{-1}).
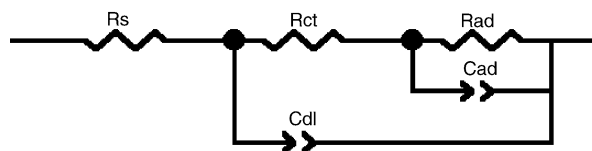

Fig. 5. An equivalent circuit of the Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_x$-NTs secondary battery.

Table 1
Some results from simulation of the equivalent circuit for Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_x$-NTs secondary battery

	Discharge time		
	1 h	11 h	21 h
Rs (Ω)	224.7	325.1	586.3
Rct (Ω)	1639	1677	3087
Rad (Ω)	14263	25459	26096
Cad (μF)	55.89	74.395	71.42
Cdl (μF)	26.37	18.219	24.75

equivalent circuit for Mg|0.25 M Mg(AlBu$_2$Cl$_2$)$_2$/THF|VO$_x$-NTs battery. It can be concluded that the electrode reaction is not under the control of the Mg^{2+} diffusion because (i) the diffusion path in the nanotubes is shorter; (ii) the heterogeneous kinetics are faster with higher surface-to-bulk ratios; and (iii) the tubes can provide electrolyte-filled channels for faster transport of the ions to the insertion sites.

4. Conclusions

Vanadium oxide nanotubes have the considerable large distance between the layers, a wide inner and outer diameter, and the open tube ends, which are favorable for the magnesium ion insertion. VO$_x$-NTs are a new kind of material with a unique nanostructured morphology, which can electrochemically insert/deinsert magnesium ions reversibly, but the cyclic charge–discharge curves demonstrate the decrease

of the discharge capacity during cycling. Thus, further investigations are needed before the properties of this new material will be fully understood and practical applications realized.

Acknowledgments

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