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Synthesis of nanocrystalline layered manganese oxides by the electrochemical reduction of AMnO_4 ($\text{A} = \text{K}, \text{Li}$)

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Abstract

Layered manganese oxides containing lithium and/or potassium have been synthesized by the electrochemical reduction of permanganate solutions. The synthesis provides products with manganese near an oxidation state of four. The products as shown by XRD have the rancieite-type structure and crystallite size on the order of 10 nm. In this paper, the synthesis and characterization will be presented along with the initial cycling of these materials as positive electrodes in Li-batteries. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electrochemical synthesis; Reduction of permanganate; Cathodes; Layered manganese oxides; Rancieite

1. Introduction

Manganese oxides are amongst the best positive electrode materials for lithium batteries due to their high insertion voltage, large specific capacity and good cyclability. Recent studies have shown that it is possible to prepare new layered compounds having interesting lithium insertion properties by the chemical reduction of permanganate solutions [1–19]. Included amongst them are materials having the rancieite-type structure [17–19], which have open structures that tend to have lower V_{redox} . The lower working potential found in these materials should preclude the potential necessary for the Jahn-Teller distortion which is more common in those having the spinel structure and higher voltages [20].

The Li-form of layered manganese oxides having the rancieite-type structure were prepared previously by our group [17,18] by a 3-step procedure that consisted of an acid catalyzed reduction of an aqueous solution of KMnO_4 , followed by full proton exchange for the K, and finally Li was exchanged for the protons. The trend in making Li-containing materials is often to make a K or Na-type layered manganese oxide and then ion exchange Li for the present ions in solution or by Li-insertion using the material as the cathode in a Li-battery [21]. Amongst the few direct preparations of Li-phyllomanganates is one reported by Pistoia

et al. [22] that consisted of the oxidation of a Mn(II) salt by H_2O_2 in a LiOH solution which resulted in Li-birnessite.

The aim of this work was to electrochemically reduce aqueous Mn(VII) solutions to form Li–manganese oxides directly, i.e. carry out the electrochemical reduction only in the presence of Li-ions rather than other cations such as K or Na. It was also of interest to compare these purely Li-phases to layered manganese oxides containing purely K as well as study the behavior of products that were made with a mixture of K and Li.

2. Experimental

2.1. Film growth

The electrochemical reaction was carried out by using a platinum working electrode (total surface area of 80 cm^2) mounted between two counter electrodes (Pt or vitreous carbon), and an Ag/AgCl reference electrode. Chronopotentiometry mode was used for film growth by reducing the permanganate. An EG&G 273 potentiostat was connected to the electrodes after they were placed in 500 ml of a 0.075 M $\text{AMnO}_4/0.15 \text{ M A}_2\text{SO}_4$ solution ($\text{A} = \text{Li}$ or K) and the synthesis was performed at 0.1 mA/cm^2 . The K-permanganate solutions were made directly with KMnO_4 , and the LiMnO_4 solutions were made by ion exchanging Li for K using ion exchange resin. In order to maintain a relatively constant concentration throughout the reaction, the reactants were used in excess so that less than 30% of the available

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manganese was consumed. For films grown at temperatures greater than room temperature the reaction vessel was placed in a sand bath and controlled by a thermocouple. After the film growth period is completed, the electrode is first rinsed with water to remove any residual products that may have settled on the electrode and then the film is dried in a 100°C oven. The drying process causes the film to crack into minute particles which allows it to be removed easily from the Pt. The small film particles were then washed thoroughly with water and dried before further analysis.

2.2. Preparation of swagelok Li-cells

Composite electrodes were prepared by first mixing the active material (85% by mass) with carbon black (Super P from Chemetals) (10%) and an organic binder (PVDF) (5%), and then this mixture was adhered to a 1 cm² Al disk using cyclopentanone as a solvent for the polymer. The batteries were made using two-electrode cells and 2 EC/DMC/1 M LiPF₆ electrolyte. A Mac-Pile galvanostat/potentiostat was used for all of the electrochemical experiments.

2.3. Analysis

X-ray diffraction was carried out on finely ground powder samples using a Siemens D5000 powder diffractometer. EDS elemental analysis was done on a Joel system as a first pass to verify that no K was present in the Li-samples as well as the samples being absent of impurities. Elemental analysis was done using ICP spectroscopy for Li, Mn and K (emission for Mn and K, and absorption for Li). To verify the absence of K, flame emission spectroscopy was also used. Thermogravimetric studies were carried out using a Perkin-Elmer Model TGS-2 TGA. The oxidation state of manganese in the products was determined by titration analysis using the Vetter and Jaeger method [23].

3. Results and discussion

3.1. Film growth

Before growing the film on the electrode, a study was done of the electrolyte to be sure there would be no side reactions in the range of the permanganate reduction phenomenon. The A₂SO₄ solution without permanganate showed a non-reactive window in our range of interest. Cyclic voltametry was done of the permanganate solution to get an approximate value of the reduction potential of the permanganate solution. A scan done at 50 mV/s showed the reduction peak for the permanganate at -0.19 V. The chronopotentiometry-electrodeposition reaction, which was run at 0.1 mA/cm² for up to 80 h, began at -0.14 V and, as the film was forming, reached a maximum magnitude at -0.17 V, and did not shift to lower voltage. This, we felt, was important as a means of forming products having manganese at a high oxidation state.

3.2. Compositional analyzes

The results of X-ray diffraction show that the materials prepared by the electrochemical method are of the layered rancieite-type structure. There are only three broad, but distinguishable peaks for the room temperature synthesis, whereas the reactions done at higher temperatures, 80 and 90°C, show in addition the (0 0 2) peak at 3.70 Å. The powder X-ray diffraction scans of two of these compounds, one synthesized at room temperature and the other at 90°C, can be seen in Fig. 1. The peaks found in the patterns are assigned from those given for rancieite [17], whose peaks in the reference are as follows: $d = 7.49 \text{ \AA}$ (0 0 1); 3.74 \AA (0 0 2); 2.463 \AA (1 0 0); 1.425 \AA (1 1 0).

For this phase of the work, it was of interest to study the materials as synthesized rather than annealed compounds. Therefore, thermal analyzes were done in order to determine what temperature needed to be used to remove the loosely bound water prior to running cells. Fig. 2 shows the thermal weight loss for the K_yMnO_z species (a) overlaid with the Li_xMnO_z product (b). Consequently, the drying of the cathodes was carried out by heating the materials to 140°C under vacuum. These conditions cause the potassium sample to undergo a weight loss of 12% without causing an irreversible structure change, whereas the Li-compound experienced a 23% weight loss causing it to reach the first plateau seen in the TGA figure. As for compounds made at varying temperatures, the shapes of the curves were dependent only on the elemental content of the compounds and were independent of the synthesis temperature. The species containing a mixture of K and Li, that was synthesized, had similarly shaped curves to that of pure K. A study is ongoing to investigate what phases can be obtained at higher temperatures including a possible intermediate phase at the plateau above 200°C for the lithium compound.

Elemental spectroscopy analyzes were done on the samples for the determination of Mn, K, and Li and the results are shown in Table 1. The water content is from the TGA to 200°C and the oxygen content is reported as determined by oxidation state titration.

3.3. Performance in Li-cells

Cells were run using these materials as the positive electrode versus Li-metal in the potentiodynamic mode using a scan rate of 20 mV/h. The first three cycles of K_yMnO_z and Li_xMnO_z, both of which were synthesized at 90°C, are shown in Fig. 3. The Li-material demonstrated a slight loss in capacity over these first cycles, whereas the K sample was inconsistent in developing a trend. These capacities are slightly lower than those found by Leroux et al. [18] for rancieite-type structured manganese oxides at a cycling rate of C/80. For the Li_xLi_yMnO_z prepared by a three-step procedure, they found $x_{\text{max}} = 0.42$ (x is the electrochemically intercalated amount of Li and y is that found upon synthesis), however, the values of capacity in

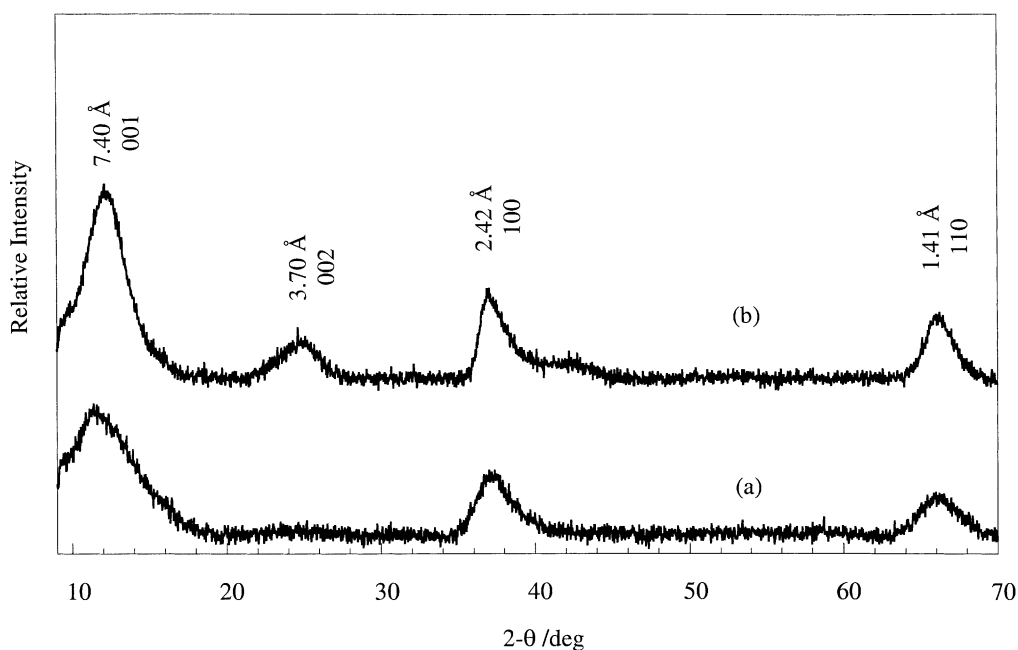


Fig. 1. Powder X-ray diffraction of the electrochemically synthesized materials: (a) is the Li_xMnO_2 product synthesized at room temperature; and (b) is the Li_xMnO_2 material synthesized at 90°C .

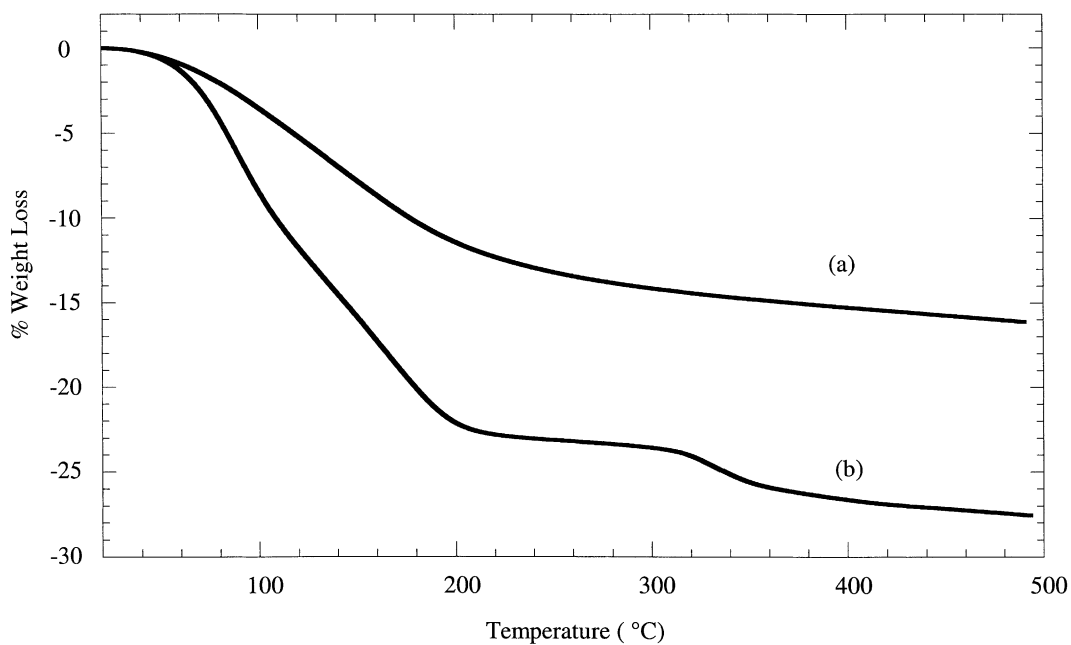


Fig. 2. Thermogravimetric analysis plots for the: (a) K_yMnO_2 ; and (b) Li_xMnO_2 compounds. Both samples were run in air at $5^\circ\text{C}/\text{min}$.

Table 1
Elemental determination of synthesized compounds

Sample preparation	Moles (A/Mn) from ICP-AAS		Water (%)	Oxygen from titration	Formula
	Potassium	Lithium			
Li_xMnO_2 at 22°C	0.00	0.45	13	2.22	$\text{Li}_{0.45}\text{MnO}_{2.22}\cdot 0.81\text{H}_2\text{O}$
Li_xMnO_2 at 90°C	0.00	0.50	23	2.25	$\text{Li}_{0.50}\text{MnO}_{2.25}\cdot 1.6\text{H}_2\text{O}$
K_yMnO_2 at 22°C	0.38	0.00	13	2.19	$\text{K}_{0.38}\text{MnO}_{2.19}\cdot 0.86\text{H}_2\text{O}$
K_yMnO_2 at 90°C	0.32	0.00	12	2.16	$\text{K}_{0.32}\text{MnO}_{2.16}\cdot 0.81\text{H}_2\text{O}$
$\text{Li}_x\text{K}_y\text{MnO}_2$ at 22°C	0.17	0.29	15	2.23	$\text{Li}_{0.29}\text{K}_{0.17}\text{MnO}_{2.23}\cdot 1.0\text{H}_2\text{O}$
$\text{Li}_x\text{K}_y\text{MnO}_2$ at 80°C	0.19	0.31	16	2.25	$\text{Li}_{0.31}\text{K}_{0.19}\text{MnO}_{2.25}\cdot 1.0\text{H}_2\text{O}$

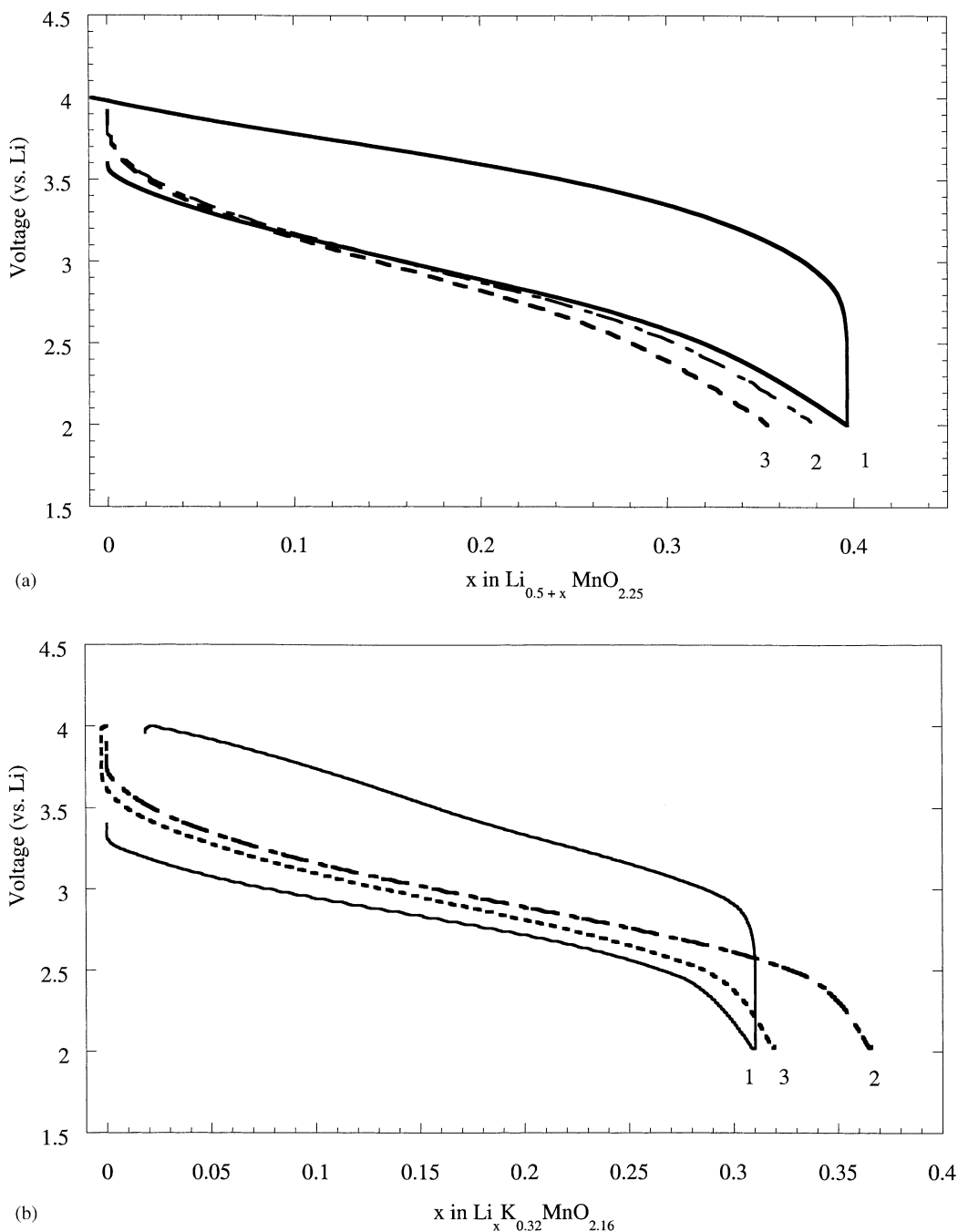


Fig. 3. Potentiodynamic cycling done at 20 mV/h on: (a) the material made with only Li at 90°C; and (b) the material made only in the presence of K at 90°C. The scans are labeled as (1) first cycle; (2) second discharge; (3) third discharge.

these electrochemically prepared materials are higher than what they found for $\text{Li}_x\text{H}_y\text{MnO}_z$ prepared in a single step, with a value of $x_{\text{max}} = 0.1$.

4. Conclusions

The electrochemical reduction of permanganates provides a simple method of obtaining layered manganese oxides with varying interlayer cations. The method also provided a

way to make Li_xMnO_z in a one step reduction process which could be of interest in industrial processing in order to decrease the loss of product or increase of impurities in subsequent ion exchange steps that are typically used in going from AMnO_z to the pure Li-form. The reason why the capacity is lower than that previously found for rancieite-type Li_yMnO_z materials, is being investigated. Since the capacity lies between that of the pure Li-form and the H-form, it is being investigated as to the possibilities of the presence of protons in the structure causing the lower

values. Also further studies are being pursued on annealed materials as well as long term cycling in order to see if there might be a trend towards increasing capacity upon cycling due to increasing order in these low ordered materials.

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