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Electrochemical performance of cathodes based on LiMn_2O_4 spinel obtained by combustion synthesis

E.I. Santiago, S.T. Amancio-Filho, P.R. Bueno, L.O.S. Bulhões*

Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Departamento de Química, Universidade Federal de São Carlos, C.P. 676, 13565-905 São Carlos SP, Brazil

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Abstract

Composite cathodes have been fabricated based on LiMn_2O_4 spinel powders, which were synthesized by combustion process and characterized by X-ray diffraction as a pure phase. The electrochemical response of the electrode was analyzed by cyclic voltammetry, chronopotentiometric curves and electrochemical impedance spectroscopy (EIS). Cyclic voltammograms showed two reversible processes, which is the typical response of LiMn_2O_4 . The charge–discharge curves showed two plateaux with the charge density of 107 mAh g^{-1} . From the EIS data the Li^+ diffusion coefficient was determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray diffraction; Charge–discharge curves; PVDF

1. Introduction

The lithium insertion solid state materials are promising as cathodes for rechargeable lithium batteries, due to their higher energy density, higher voltage and longer shelf-life, compared with other competitive systems. This class of materials is also important as anodes in rocking chair batteries [1]. Layered oxides, such as LiCoO_2 and LiNiO_2 , when used as cathodes show high specific energy. However, the complex and expensive synthesis processes of these layered oxides render the LiMn_2O_4 spinel a promising material for positive electrodes. Several synthetic routes have been described in the literature in order to improve the electrochemical performance of $\text{Li}_x\text{Mn}_2\text{O}_4$ cathodes. Synthesis methodology is an important tool to determine the structural properties of the materials and consequently it affects the kinetics of the electrochemical insertion/deinsertion processes, leading to materials with specific electrochemical performances and minimum production costs. Combustion synthesis is an alternative powder preparation process, by which several compounds can be prepared at low costs comparing with other chemical synthesis processes [2,3].

The aim of the present work is to investigate the electrochemical response of LiMn_2O_4 spinel oxide powders,

correlating the synthesis methodology with the structural and electrochemical properties.

2. Experimental

The preparation of LiMn_2O_4 powders by combustion method was carried out mixing manganese nitrate tetrahydrate with urea (manganese nitrate/urea ratio of 1:1.75 mol%) in a glassy silica crucible. The mixture was heated up to 300°C occurring the ignition with the oxide formation. The resulting oxide was heated at 800°C during 4 h and was characterized by X-ray diffraction as pure LiMn_2O_4 phase. The working electrodes were prepared by mixing poly(vinylidene fluoride) (PVDF), carbon black and LiMn_2O_4 powders in the ratio of 5:10:85% w/w, respectively. The composite powder was dissolved in dimethylformamide, sonicated during 12 h in order to reach the appropriated viscosity, painted on the platinum plates (1 cm^2) and dried under vacuum at 120°C for 24 h. Electrochemical measurements were performed in a dry box using lithium metallic plates as counter and reference electrodes. The electrolyte was 1.0 M anhydrous LiClO_4 solubilized in a 1:1% v/v ethylene carbonate and dimethyl carbonate mixture. Cyclic voltammograms were performed at 0.1 mV s^{-1} and the charge–discharge curves were obtained at C/30 rate ($70 \mu\text{A}$). Electrochemical impedance data were obtained at +4.05 and +4.2 V with a superimposed ac potential of 5 mV rms with the frequency changing between 100 kHz up and 1 mHz.

* Corresponding author. Tel.: +55-16-260-8214; fax: +55-16-260-8214.
E-mail address: dlob@power.ufscar.br (L.O.S. Bulhões).

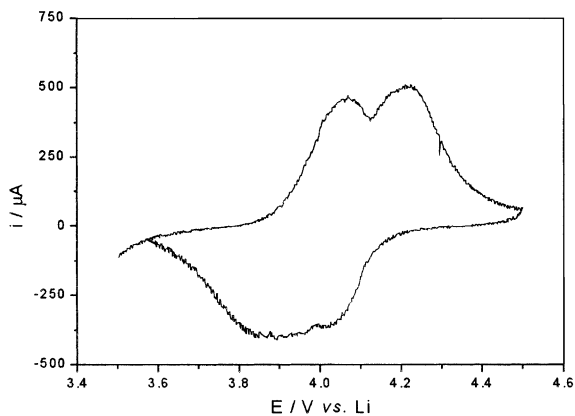


Fig. 1. Cyclic voltammogram for LiMn_2O_4 electrode in EC:DMC (50:50% v/v), 1.0 M LiClO_4 solution. Potential scan rate: 0.1 mV s^{-1} .

3. Results and discussion

The cyclic voltammogram for the LiMn_2O_4 electrode at a scan rate of 0.1 mV s^{-1} is presented in Fig. 1 and shows two reversible processes, which is characteristic of LiMn_2O_4 systems. The electrochemical Li^+ deinsertion from the tetrahedral sites of LiMn_2O_4 is reversible and occurs near to $+4.0 \text{ V}$ [4], represented by the two anodic peaks in Fig. 1. The two-step process indicates a phase transition, which is associated with an ordering of lithium on the tetrahedral 8a sites. The first and second anodic processes, at $+4.05$ and $+4.2 \text{ V}$, are related to the oxidation of Mn^{3+} to Mn^{4+} , followed by the lithium ion deintercalation, leading to the $\lambda\text{-MnO}_2$. During the charge and discharge process, the cubic symmetry of the structure is maintained [5], being observed a minimal contraction of the unit cell over a wide composition range. The electrochemical reversibility of the system can be observed by the similar anodic and cathodic charge values ($Q_a \sim 17 \text{ C}$ and $Q_c \sim 17 \text{ C}$) determined in Fig. 1.

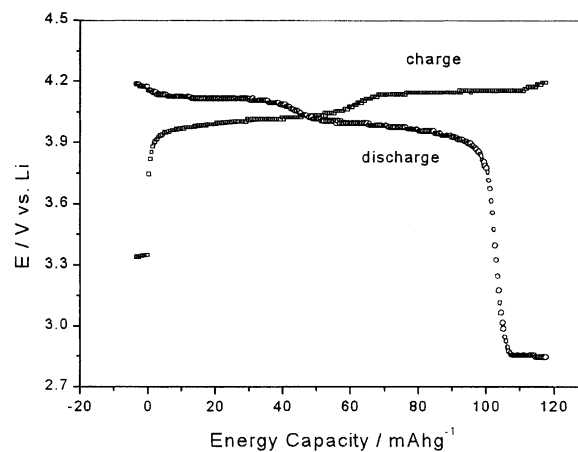


Fig. 2. Charge–discharge for LiMn_2O_4 electrode in EC:DMC (50:50% v/v), 1.0 M LiClO_4 solution. Discharge rate $C/30$ ($70 \mu\text{A}$).

In Fig. 2 is depicted the charge–discharge curves of the LiMn_2O_4 electrode. The energy capacity obtained at the first discharge is 107 mAh g^{-1} , which is in agreement with other reported data for LiMn_2O_4 electrodes obtained from different synthesis methods [6–10]. Two plateaux can also be observed associated with the processes observed in the cyclic voltammogram. The reversibility of the electrochemical process is also observed in the charge–discharge curves.

In order to characterize the mass transport in this system, the electrochemical impedance data were obtained at potentials close to the redox couples observed in the cyclic voltammogram. In Fig. 3, the typical impedance spectra at $+4.05$ and $+4.2 \text{ V}$ are presented in which two overlapped arcs are noticed at high and at intermediate frequencies (Fig. 3(a) and (b), respectively). At low frequency a linear diffusion impedance behavior is observed and can be represented as a Warburg impedance, that is associated with the lithium intercalation/deinsertion. The apparent chemical

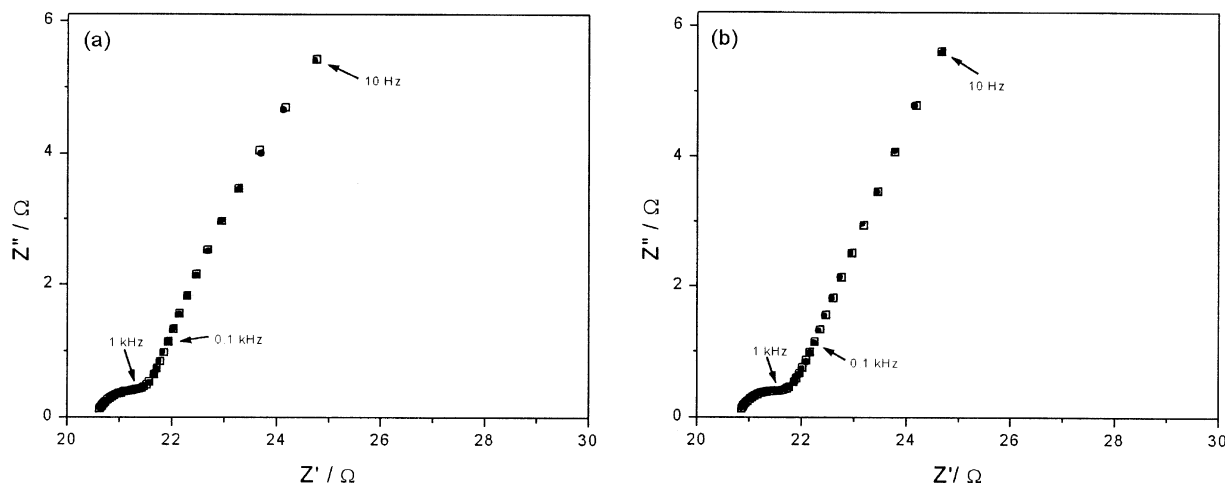


Fig. 3. EIS data for LiMn_2O_4 electrode in EC:DMC (50:50% v/v), 1.0 M LiClO_4 solution at (a) 4.05 V and (b) 4.2 V .

diffusion coefficient (D_{Li}) for lithium in porous LiMn_2O_4 can be calculated using the relation [11]

$$D_{\text{Li}} = \frac{f_{\text{T}} r^2 \pi}{1.94}$$

where f_{T} is the frequency at which the impedance spectrum shows a transition from semi-infinite diffusion behavior to finite-diffusion behavior. The average radius r was obtained from scanning electron microscopy photomicrographs of LiMn_2O_4 powder. The calculated D_{Li} values at 4.05 and 4.2 V dc potential are 7.7×10^{-11} and 4.9×10^{-11} cm^2/s , respectively. These results are in agreement with the solid state diffusion in porous materials.

4. Conclusion

A modified combustion route was used to synthesize pure LiMn_2O_4 phase spinel powders, as revealed by X-ray diffraction. An electrochemical reversible process was observed during the oxidation and reduction of the electrode. From the charge and discharge data, an energy capacity of 107 mAh g^{-1} was determined. The analysis of electrochemical impedance data indicate the porous nature of the electrode.

Acknowledgements

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