$LiMn_2O_4$ COMPOSITE AS AN ACTIVE MATERIAL CATHODE IN LITHIUM BATTERIES

Silmara Neves, Sérgio Dalbon and Carla Polo Fonseca
LCAM – Lab. Caracterização e Aplicação de Materiais
Universidade São Francisco – 13251-900, SP - BRAZIL
cfonseca@saofrancisco.edu.br

Due to their remarkably high voltage or high energy density lithium ion batteries were recently incorporated into cellar, clock radios, portable fluorescent lamps, compact disc, players electronic games, powered toys, cameras, calculators and notebook, etc.

Numerous cathode compounds have been used in lithium batteries, e.g. metal oxide such as CuO, MnO_2 MoO_3, V_2O_5 and recently the lithium metal oxide $LiMO_x$.

This work presents preliminary results a low temperature synthesis of a $LiMn_2O_4$ and $LiMn_2O_4$/Pani/PVDF composite and their electrochemical characteristics as a new cathode material to lithium batteries.

In the XRD analysis, $LiMn_2O_4$ formation was observed. All diffraction peaks for this material are assigned to the diffraction indices of $LiMn_2O_4$ single-phase spinel (Fig1.).

The intercalation/de-intercalation process from the system $LiMn_2O_4$/Pani/PVDF composite film was analyzed by cyclic voltammetry technique (Figure 2). Li extraction is accompanied by an oxidation of Mn^{3+} to Mn^{4+}; repeated charge/discharge cycles can lead to collapse of intercalation sites of the lithium ion decreasing charge capacity of material, due to, a high volume reduction of approximately 7.5% between the starting material and the full extracted spinel. Two-phase intercalation/de-intercalation process illustrated by two pairs of redox peaks at high potential range in the cyclic voltammogram, Li de-intercalation at 4.0 e 4.2 V *vs.* Li and Li-intercalation at 3.9 e 4.1 V. The presence of PAni stabilized electrochemically the system acting as electronic conductor and electroactive material. The 3.1 / 2.8 V peak showed in both films was related to coexistence of cubic and tetragonal phase of manganese oxide

The impedance spectra of the $LiMn_2O_4$ pure film consists a not very well defined semicircle in a high frequency range, a line inclined at a constant angle (45^o) to the real axis in the low frequency range (Fig.3). The semicircle in the high frequency range is due to “charge transfer reactions” at the interface of the electrolyte /oxide electrode, and the inclined line in the low frequency range is attributable to ‘Warburg impedance’ that is associated with lithium diffusion through the oxide electrode. Impedance of pure system is higher than the composite film 23 and 14 $k\Omega cm^2$, respectively. This fact was attributed the Pani presence in this composite which increase the electronic conductivity of the film.

$LiMn_2O_4$ film and $LiMn_2O_4$/Polyaniline (PAni) /PVDF composite films were fabricated by a precipitation method using a spin-coating and annealing at low temperature. The $LiMn_2O_4$ powder showed high specific surface and the composite film showed homogeneous. The electrochemical properties of the two films were compared and the composite showed the best performance due to presence of the PAni that act as electronic conductor improving the electronic conductivity of $LiMn_2O_4$ beside to be a electroactive material increasing charge /discharge capacitivity of film. The PAni presences increase discharge capacity of the composite film in approximately two times in relation to $LiMn_2O_4$ pure film. This composite film showed good electrochemical performance as a cathode for application in lithium batteries.

Acknowledgements

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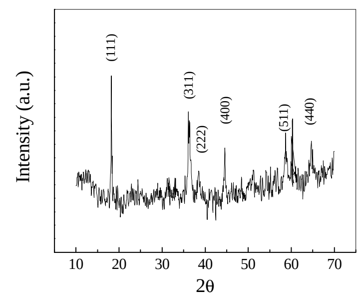

Fig. 1 – XRD data of the $LiMn_2O_4$ counting time = 10 s in the range $15^o \leq 2\theta \leq 65^o$.

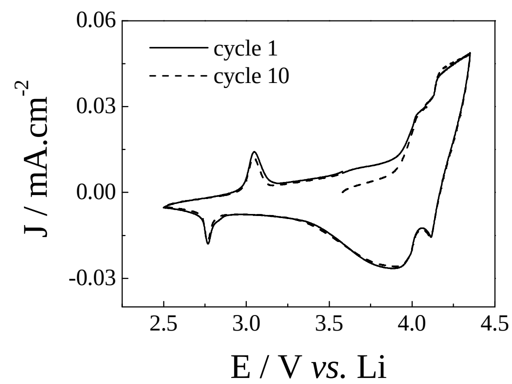

Fig. 2 – Steady state cyclic voltammogram of $LiMn_2O_4$ composite film in PC/EC/1.0 $mol.L^{-1}$ $LiClO_4$; at $5mV.s^{-1}$

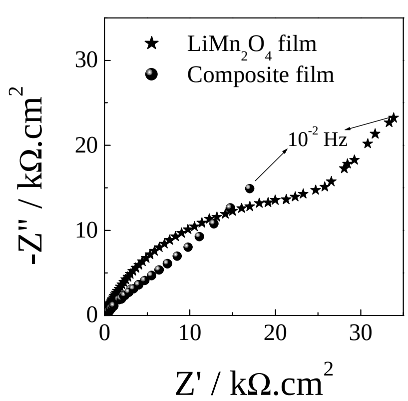

Fig. 3 – Nyquist diagram of the $LiMn_2O_4$ pure film and $LiMn_2O_4$ composite at OCP. Perturbation amplitude 0.01 V and frequency range from 10^{-2} to 10^5 Hz.

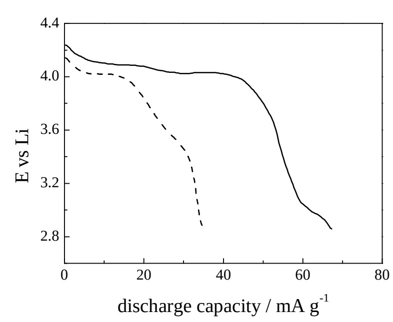

Fig. 4 –Specific discharge curves 30^a discharge cycle of composite film (full line); and $LiMn_2O_4$ pure film (dash line), J = 10 $\mu A.cm^{-2}$.