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EPD of thick films for their application in lithium batteries

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Abstract

Electrophoretic deposition (EPD) is an appropriate tool to prepare thick film electrodes of lithium batteries, once optimized the different factors that affect to this coating method. Compared with other deposition methods, EPD has the ability to allow the simultaneous deposition of the active material, an additive conductor such as carbon black (CB) and a binder to improve the plastic properties of the deposit. However, for obtaining an appropriate electrochemical response they need so far to be compressed. With this simple process, the electrode performance is excellent in terms of the delivered capacity by the cell and the capacity retention on cycling.

Keywords: Suspensions; Shaping; Transition metal oxides; Spinels; Batteries

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1. Introduction

The lithium-ion batteries have been widely adopted as the most promising portable energy source in electronic devices, thanks, among other actions, to the preparation of the electrodes in the form of films.[1–4] Chemical vapour deposition and sputtering have so far been the most frequently used deposition techniques,[5,6] and $LiCoO_2$ and $LiMn_2O_4$ the cathodic materials most commonly tested[7,8] for this purpose. These materials can afford potentials below 4.5 V. The partial replacement of manganese in $LiMn_2O_4$ with various transition metals is known to endow this compound with the ability to deliver a substantial capacity at voltages above 4.5 V.[9,10] $LiNi_{0.5}Mn_{1.5}O_4$[11,12] is the doped spinel exhibiting the best electrochemical properties and opens up prospects for a new generation of Li-ion batteries of higher energy than those commercially available at present.

The EPD has demonstrated to be a useful and simple deposition method. A difference with other coating techniques is that the material to be processed by EPD does not require defined properties and hence, there is a broad variety of materials that could be coated and deposited. The aim of this work was to obtain controlled deposits of a well-crystallized spinel of nominal composition $LiNi_{0.5}Mn_{1.5}O_4$ onto aluminium electrodes by EPD.

2. Experimental

Spinel of nominal composition $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) was prepared from appropriate amounts of Li_2CO_3, $Mn(Ac)_3{\cdot}2H_2O$ and $Ni(Ac)_2{\cdot}4H_2O$ (Ac = acetate) (Merck, Gemany) by using a conventional ceramic method as described elsewhere.[13] Synthesized powders have octahedral or pseudo-polyhedral forms with an average particle size of ~3 μm and a small specific surface area of $1.3\,m^2\,g^{-1}$. Spinel powders are mixed with carbon black (CB) to shape the cathode of the lithium battery. CB has a large specific surface of $275\,m^2\,g^{-1}$. The particle size distributions were determined by laser diffraction analysis and by dynamic light scattering (Mastersizer S and NanoZS, Malvern, UK), and the surface area by one-point N_2 adsorption, BET method (Monosorb, Quantachrome, USA).

Citric acid and polyvinyl pyrrolidone (PVP) were used to stabilize LNMO and CB particles in acetone. Electrophoretic mobility of $0.1\,g\,l^{-1}$ suspensions of LNMO in acetone was determined by laser Doppler velocimetry (Zetasizer, NanoZS, Malvern, UK). Polyvinyl butyral (PVB) was used as a binder in order to increase the films density.

LNMO and CB suspensions were separately prepared and optimized for EPD tests. In both cases, powders were added to citric acid and/or PVP acetone solutions and ultrasonicated with a 400 W sonicator probe (Hielscher UP400S, Germany) for 1 min. Suspensions were prepared to solids loadings of 2 and $10\,g\,l^{-1}$. Mixtures with 80/20 (w/w) LNMO/CB composition

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were prepared by mixing the desired volumes of the corresponding LNMO and CB suspensions and later homogenized by mechanical stirring for 30 min.

LNMO and LNMO/CB coatings were shaped by EPD on aluminum discs (1.29 cm^2). The work electrode and the counterelectrode were parallel aluminum and graphite foils, respectively, separated a distance of 2 cm in the electrophoresis cell. Aluminum deposition discs were anchored to the aluminum work electrode before the test.

EPD was performed under potentiostatic conditions using a high voltage power source (Labconco, mod. 433-3250, USA). The voltage applied in all cases was 100 V during times up to 300 s. After EPD, samples were withdrawn at a constant rate of 7.5 mm s^{-1} and left to dry for 5 h at room conditions. The dry deposits were then weighted.

Electrochemical measurements were carried out with two-electrode Swagelock-type cells, using Li (supplied by Strem) as anode and a piece of Whatman paper was employed as a spacer. The electrolyte, supplied by Merck, was 1 M anhydrous $LiPF_6$ in a 1:1 mixture of ethylene carbonate and dimethyl carbonate. Cells were assembled in an M-Braun glove-box. Step potential electrochemical spectroscopy (SPES) curves were recorded at 2.5 mV/0.06 h per step. Galvanostatic tests were conducted under a C/6 charge/discharge regime (C representing 1 Li^+ ion exchanged in 1 h). Both types of electrochemical measurements were performed on a McPile II (Biologic) potentiostat–galvanostat system.

3. Results and discussion

The evolution of the electrophoretic mobility of the LNMO in acetone and the suspension specific conductivity as a function of the amount of citric acid are shown in Fig. 1. The more significant change in the conductivity of the LNMO suspensions was observed for small amounts of citric acid (by 1 wt.%). This value is maintained constant for higher acid concentrations. The surface charge of the particles was negative and the mobility achieves a maximum for 1 wt.% citric acid.

Different spinel suspensions with a solid loading of 2 g l^{-1} were prepared, adding 1, 15 and 30 wt.% of citric acid. Another suspension with 10 g l^{-1} of powder and 15 wt.% of citric acid was also prepared. Deposition kinetics of the suspensions was evaluated applying 100 V up to 300 s. Table 1 summarizes the most important parameters that determine the conditions to obtain the LNMO films. Suspension solids loading and citric acid concentrations are related with the suspension conductivity, the maximum value achieved by the current density and the current loss measured after a deposition time of 300 s.

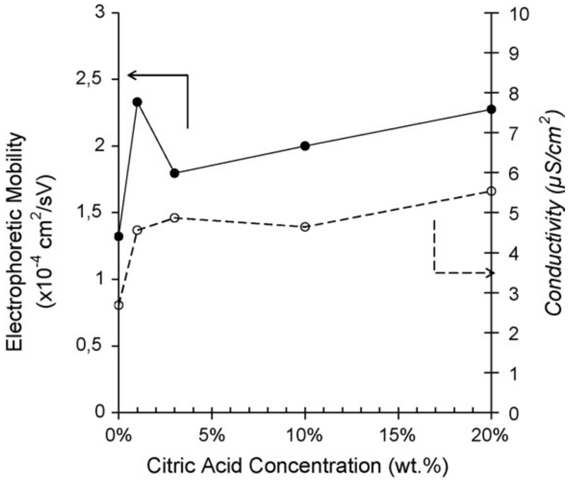

Fig. 1. Evolution of electrophoretic mobility and conductivity of 0.1 g l^{-1} LNMO suspensions with citric acid concentration.

The evolution of conductivity for 2 and 10 g l^{-1} suspensions differs from that of 0.1 g l^{-1} suspensions (Fig. 1). Depending on the amount of citric acid added, differences between conductivities become significant. The 2 g l^{-1} LNMO suspension with 1 wt.% of citric acid has the lowest conductivity, while it increases considerably for a 15 wt.%. However, the conductivity slightly decreased with further addition of this component. The conductivity also increases when increasing the solids concentration to 10 g l^{-1}, which means that the citric concentration in acetone increases to 7.1 × 10^{-3} N. Considering that a particles-free 10^{-2} N citric acid solution in acetone has a conductivity of 0.1 μS cm^{-1}, it could be assumed that charging of particles is the main contribution to the suspension conductivity, even in acetone. Consequently, suspension conductivities measured in this work mainly depend on the solids loading and the efficiency of the dispersant agent, and it should vary during the deposition process.

When working under potentiostatic conditions, the evolution of the current density with time affects directly to the films formation, since it is the current which provides the particles motion. Current density achieves its maximum value after 30 s of deposition time for all the suspensions used to obtain the spinel films. The different maximum values of current density registered for the same applied potential (100 V) depend on the suspensions conductivities. So, the highest conductivity

Table 1
Suspension parameters and electric conditions

Solids loading (g l^{-1})	Citric acid concentration		Conductivity (μS cm^{-1})	Current (mA/cm^2)	
	Related to dry powder (wt.%)	Related to acetone volume (N)		Maximum value	Current loss (%)
2	1	0.1 × 10^{-3}	3.5 ± 0.1	0.20 ± 0.03	27
	15	1.5 × 10^{-3}	5.7 ± 0.1	0.39 ± 0.03	17
	30	10^{-2}	5.2 ± 0.1	0.36 ± 0.03	11
10	15	7.1 × 10^{-3}	8.0 ± 0.1	0.42 ± 0.03	19

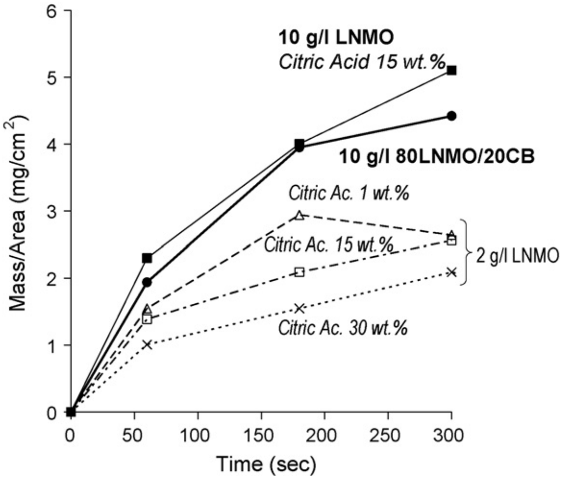

Fig. 2. EPD kinetics of the mixture 80LNMO/20CB compared to that of differently prepared LNMO suspensions.

and hence, the highest current density correspond to the 10 g l^{-1} LNMO suspension dispersed with 15 wt.% of citric acid. In all cases during the film consolidation, the current density decreases with deposition time, being the 2 g l^{-1} suspension with 1 wt.% of citric acid, the one having the highest current loss after 300 s (27%).

The EPD kinetics of the films obtained from the prepared suspensions is plotted in Fig. 2. A higher addition of citric acid leads to a lower deposition rate. In all cases kinetics is not linear with time, influenced by the evolution of the own system in which the current decreases with time. Homogeneous films covering the aluminium substrates were obtained in all cases, except from suspensions with a 30 wt.% of citric acid. Suspensions dispersed with 15 wt.% of acid showed a more stable kinetics, however, the increase of solids loading from 2 to 10 g l^{-1} did not promote the increase of the deposited mass than that predicted by the theoretical equations.[14] Otherwise, SEM studies verified that deposits of 10 g l^{-1} suspensions were denser.

Several CB suspensions with solids loading from 0.01 to 1 g l^{-1} were prepared with different PVP concentrations (1, 1.5, 2 and 5 wt.%), and ultrasonicated for 1 min. The particle size distribution of these suspensions was measured by laser diffraction analysis. Particle size measurements are not stable for solids concentrations higher than 0.1 g l^{-1} and PVP contents lower than 1.5 wt.%. Specifically, adding 1.5 wt.% of PVP to the suspension, the mean particle size of the distribution was 900 nm, while the addition of 2 wt.% or more of PVP decreased the mean size value to 250–200 nm. So, the addition of PVP amounts higher than 2 wt.% promotes an effective deagglomeration of the CB particles that hinders sedimentation. Below this concentration, CB clusters were maintained and suspensions sediment in few minutes. CB deagglomerated suspensions, with a similar main particle size (270 nm), were also obtained from the suspension dispersed in a citric acid solution.

A suspension with a solids loading of 10 g l^{-1} with a composition of 80 wt.% of LNMO and 20 wt.% of CB (80LNMO/20CB) was prepared mixing the CB suspension in a citric acid solution in acetone (30 wt.% related to the solids content), also deagglomerated by the addition of 2 wt.% PVP, and the LNMO powders suspended in a citric acid solution of 1.5×10^{-3} N (15 wt.% related to the solid content) in acetone. Fig. 2 also shows the deposition kinetics of the 80LNMO/20CB suspension. The deposits prepared from the mixture were less dense than those obtained from the suspension of pure LNMO due to the lower density of the CB powders. Fig. 3 shows a detail of the 80LNMO/20CB film surface in which the spinel particles appear surrounded by the CB powder.

The addition of PVB as a binder to the 80LNMO/20CB suspension was also studied, verifying that PVB improves shaping performance while maintaining the formation characteristics of the deposit.

The optimized deposits prepared with CB and PVB were chosen to analyze their electrochemical properties in lithium cells. Step potential electrochemical spectroscopy, a related cyclic voltammetry (CV) technique, was first used as the characterization method owing to its ability to provide information on the different electrochemical reactions responsible of the charge/discharge processes. CV curves of $LiNi_{0.5}Mn_{1.5}O_4$ have been repeatedly reported[15,16] and the anodic scan is characterized by a double and intense peak in the 4.7–4.9 V region, associated to the $Ni^{2+} \rightarrow Ni^{4+}$ process. This reaction is reversible and the double peak is also observed in the cathodic scan. Fig. 4 shows the SPES curves for some deposits prepared by EPD. The shape of the voltammetric curve of as-prepared deposits, independently on the deposition conditions, significantly differs from that reported for $LiNi_{0.5}Mn_{1.5}O_4$ as the strong double peak in the high voltage region is absent. Instead, a weak and broad peak is observed together with a signal of similar characteristics in the 4.0–4.5 V region, this latter associated to the $Mn^{3+} \rightarrow Mn^{4+}$ conversion.

The reduced electrochemical response was also found in deposits prepared without adding binder agent, PVB. A limited connectivity between the coating and the substrate and

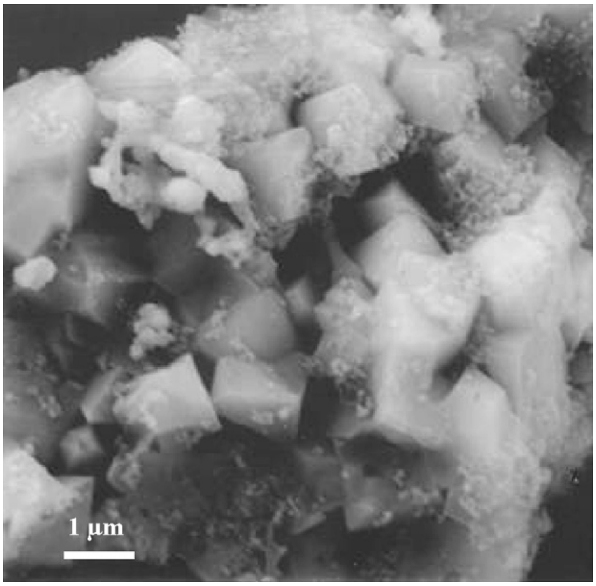

Fig. 3. SEM microstructure of 80LNMO/20CB films obtained by EPD.

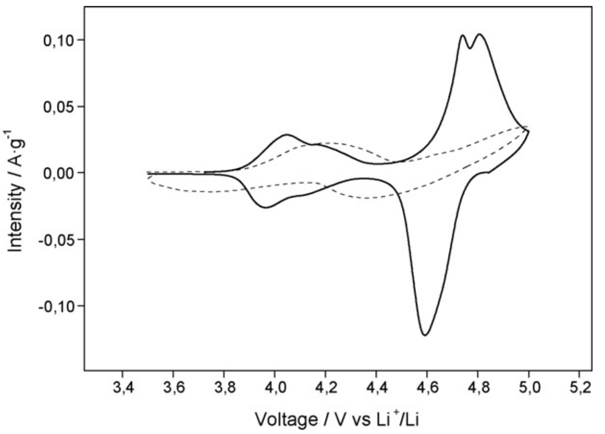

Fig. 4. SPES curves for 80LNMO/20CB EPD films prepared with 2 wt.% of PVB. Unpressed (dashed line) and pressed at 517 MPa (solid line) deposit.

also between the own particles was suggested as the reason of this inconvenience, otherwise easily overcome by pressing the deposit.[16] By applying this procedure to the composite deposits, the shape of the CV curve was clearly modified, Fig. 4, and consistent with that expected for the spinel. Thus, the properties of the electrode made from the as-prepared deposit is improved by pressing it, probably because the resistance created at the coating/substrate interface is significantly reduced, thereby improving conductivity in the electrode. Our results depart from those of Kanamura et al.,[17] who found an acceptable electrochemical behavior for $LiCoO_2$ and $LiMn_2O_4$ electrodes obtained by EPD in the absence of pressure, no reference to electrode compression was made.

Based on the above considerations, the cycling tests were performed on electrodes made from pressed deposits. Fig. 5 shows the discharge capacity delivered by the cell, made from an electrode prepared from a 80LNMO/20CB deposit with 2 wt.% PVB, on prolonged cycling. Data were recorded at a charge/discharge rate of C/6 and over the voltage window 3.5–5.1 V. For comparison we have also included the capacity of three cells made from the following electrodes, namely: (i) the same deposit without pressing; (ii) the deposit pressed but without binder PVB; and (iii) bulk spinel mixed with 20 wt.% CB and 2 wt.% PVB. Consistent with CV curve, the cell made from the unpressed deposit delivered a low capacity (below 40 mAh/g for the first discharge) and slowly faded with cycling. At the 40th cycle, the capacity barely exceeded 10 mAh/g. The electrochemical response of the same electrode pressed at 517 MPa suffered a drastic change and the capacity delivered increased above 130 mAh/g, closed to the theoretical value of the spinel (148 mAh/g). Moreover, the capacity retention of the electrode was really good, capacity loss per cycle <0.2 mAh/g. The performance of this cell was better than that made from bulk spinel, the initial capacity of which was lower (124 mAh/g), and faded faster with cycling. The electrode made from a deposit pressed at 517 MPa but prepared without PVB also showed a good performance but the capacity delivered was about a 7% lower than that measured for the deposit with binder.

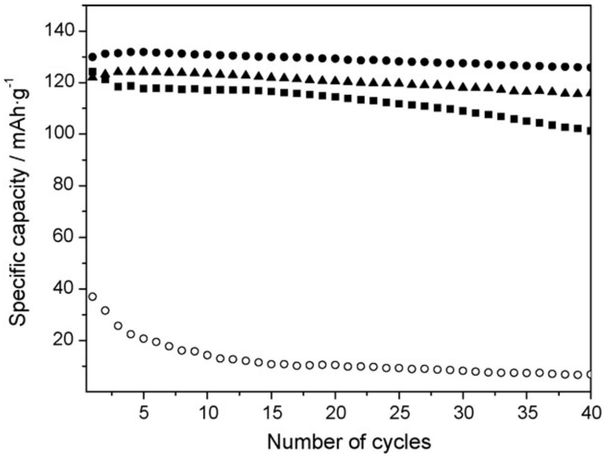

Fig. 5. Variation of the specific discharge capacity of Li/Li–Ni–Mn–O cells cycled over the voltage range 3.5–5.0 V. (■) Bulk material in pellet form; 80LNMO/20CB deposits pressed at 517 MPa: (●) (2 wt.% PVB), (▲) (without PVB); (○) unpressed deposit (2 wt.% PVB).

4. Conclusions

LNMO and CB powders were stabilized in acetone suspensions, and homogeneous films have obtained on aluminum substrates from a mixture suspension composed by 80 wt.% of LNMO and 20 wt.% of CB. The suspension conductivity was the key factor to control the electrophoretic deposition kinetics in acetone suspensions. The film density increased with the solids content of the suspension and the addition of PVB, but connectivity between the deposited particles and between the coating and the substrate is not complete. However, the capacity delivered by uniaxially pressed films obtained by EPD (130 mAh/g) was higher than that obtained from cells prepared by pressing mixture of LNMO, CB and PVB in a similar proportion.

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