



Preparation and Electrochemical Characterization of High-Stability MnO Anodes for Li-Ion Batteries



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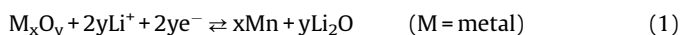
ABSTRACT

The article deals with the optimization of an anode based on commercial manganese oxide. Several parameters are considered in order to enhance capacity, rate capability and long-term cycleability. Particularly, Polyacrylic Acid as a green binder with enhanced mechanical features is proposed, while Vinylene Carbonate is added to a standard carbonate-based electrolyte system in order to enhance the stability of passivation layer and of electrode/electrolyte interface. The role of a reversible “gel-like” layer toward interfacial stability is investigated as well. Several structural, morphological and electrochemical investigation techniques are applied in order to fully characterize the behavior of baseline and modified electrodes and cells. This process results in an optimized system able to deliver, in a half-cell vs. metal Li, specific capacity values up to 725 mAh g⁻¹ at 1C-rate, stable for 100 cycles, and relevant rate capability, confirming a major influence of electrode and electrolyte formulation toward electrochemical performance.

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1. Introduction

In recent years, secondary Lithium-Ion batteries (LIBs) have become one of the most used power devices for portable electronic products and electric vehicles (EVs) [1]. This strong interest is mainly due to long cycle life, high energy density, low self-discharge and a wide operational temperature window. With the aim to further enhance energy density, innovative electrode materials, able to store lithium by mechanisms alternative to intercalation, are currently investigated [2,3]. Among favorable candidates, transition metal oxides (TMOs) generally have large theoretical capacities. The reaction between lithium and TMO-based anodes is the so-called ‘conversion reaction’ reported in Equation (1).

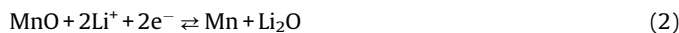


Lithium ions uptake proceeds through the formation of metallic nanoparticles (NPs) embedded in an amorphous lithium oxide matrix, usually involving a huge volume expansion. Applying a reverse polarization, lithium release takes place and the nanometric nature of particles is maintained [4]: this special feature allows a good reaction reversibility since the transition metal

nanoparticles catalyze the dissolution of the lithium-based matrix. Despite these good premises, conversion materials are affected by an initial high coulombic inefficiency (above 40%) attributable to the solid electrolyte interphase (SEI) formation, low conductivity and poor cycle life, often due to the continuous volume changes during charge/discharge cycles. Between them, manganese oxides have been extensively studied over the years, thanks to their high theoretical specific capacity, low reaction potential, lower voltage hysteresis than other TMOs and higher safety compared with carbonaceous materials [5]. As already mentioned, manganese oxides have a very low electronic conductivity that hinders a complete active material utilization ($10^{-7} \sim 10^{-8} \text{ S cm}^{-1}$ for Mn₃O₄) [6]. This behavior is mainly due to the insulating nature of metal oxides, but also to the formation of the lithium oxide matrix. The formed Li₂O phase can reversibly store and release Li thanks to the catalytic activity of dispersed metal NPs [4]. Manganese oxides have several structures and stoichiometries, which include MnO₂, Mn₂O₃ (hexagonal corundum), Mn₃O₄ (inverse spinel) and MnO (cubic rock salt) [2]. Among these oxides, MnO (theoretical specific capacity of 756 mAh g⁻¹) is believed to be one of the most promising anode materials for Li-ion batteries. However, it exhibits an initial coulombic efficiency lower than 60%, a low electronic conductivity and it suffers from big volume changes during Li uptake/release, which can eventually lead to active material pulverization and decohesion from current collector [7–9].

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In order to buffer the volume changes, the technical feasibility of using poly(acrylic acid) (PAA) as a binder alternative to the traditional poly(vinylidene fluoride) (PVdF) is here evaluated. Thanks to its superior mechanical properties, such as low swellability in carbonate-based electrolytes and high elastic modulus [10], PAA has already demonstrated to be a viable substitute of PVdF for electrode materials prone to volume changes, such as those working by Li alloying [11,12]. Moreover, PAA is soluble in environmental-friendly organic solvents, such as water and ethanol, allowing the replacement of the toxic and expensive solvent N-Methyl-2-pyrrolidone (NMP). Further improvements are also shown, obtained by acting on the electrode working potential range, the conductive additive amount and the use of electrolyte additives [13].

2. Experimental

Commercial MnO (Alfa Aesar, 99%, 200 mesh) was used as received. The commercial material was characterized by X-Ray diffraction (XRD) using a Philips diffractometer equipped with a Cu-K α source ($\lambda = 1.504 \text{ \AA}$) and Bragg-Brentano geometry in the $20^\circ < 2\theta < 80^\circ$ range. In order to prepare electrodes, slurries containing MnO as active material, Super C65 (SC65, Timcal Ltd.) as conductive additive, and PVdF (Sigma Aldrich, $M_w \sim 534,000$) dissolved in N-methyl-2-pyrrolidone (NMP) or PAA (Sigma Aldrich, $M_w \sim 450,000$) dissolved in ethanol as polymeric binder, were casted onto a $10 \mu\text{m}$ thick copper foil. Circular electrodes were cut and dried at $T = 120^\circ \text{C}$ under vacuum overnight. The loadings of the electrodes resulted in the order of $1 \sim 2 \text{ mg cm}^{-2}$. The morphological characterization was performed with a ZEISS Sigma Series 300 field emission scanning electron microscope (FE-SEM). Electrochemical performances were investigated using Swagelok-type three-electrode T-shaped cells, assembled in an argon-filled glove box, using Li foil as counter and reference electrodes. Circular Whatman GF/A glass fiber 12 mm diameter disks were used as separators. Either a 1 M solution of LiPF_6 in ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1 (v:v) mixture or a 1 M solution of LiPF_6 in EC:DMC 1:1 + 2% vinylene carbonate (VC) additive were used as electrolytes (Solvionic, France). Electrochemical characterizations were performed using a VMP3 galvanostat/potentiostat (Bio-Logic, France). All the tested cells were kept at open circuit potential (OCV) for 12 h before the electrochemical measurements. Galvanostatic charge/discharge cycles were performed at several specific currents (1C rate calculated as 756 mA g^{-1}) in different working potential ranges. Cyclic voltammetry (CV) experiments were performed at a 0.3 mV s^{-1} scan rate. Electrochemical impedance spectroscopy (EIS) measurements were recorded at $E = 0.6 \text{ V}$ bias potential in the 200 KHz to 100 mHz frequency range, applying a $\Delta E = \pm 5 \text{ mV}$ sinusoidal perturbation. Potential values

are reported versus the Li^+/Li redox couple ($E = -3.04 \text{ V}$ vs. SHE). The characteristics of electrodes and cells have been progressively tuned in order to evaluate the parameters affecting the electrochemical behavior and to optimize charge/discharge performances. The experiments carried out are summarized in Table 1.

3. Results and discussion

3.1. Sample characterization

XRD pattern of commercial MnO powder is shown in Fig. 1a. The characteristics peaks are in good agreement with the cubic crystal structure (cF8, space group: Fm3m) and match the JCPDS card No. 07-0230. No other crystalline phases were observed in the as-received MnO. As shown in the SEM micrographs of MnO anodes, PAA-based pristine electrode (Fig. 1c) shows a lower tendency to aggregation with respect to PVdF-based pristine electrode (Fig. 1b), highlighting a better dispersion and a more uniform morphology.

3.2. Electrochemical characterization

In order to characterize the redox processes involved in reversible Li storage, Cyclic Voltammetry (CV) has been performed for the initial three cycles of a PVdF-based MnO electrode (A) in the 0.005 V to 3 V potential range and at a 0.3 mV s^{-1} scan rate (Fig. 2). The first cathodic scan is characterized by three main features: the large shoulder labelled as (A) at $E \sim 0.8 \text{ V}$, related to the solid electrolyte interphase (SEI) formation; a peak at $E = 0.32 \text{ V}$ labelled as (B), related to MnO to Mn reduction and Li_2O formation; a low-potential peak, labelled as (C), which can be attributed to reversible Li storage by the amorphous carbon used as conductive additive. In the anodic scan a first peak (D) is related to reversible Li release from carbon, while the large peak located at $E = 1.23 \text{ V}$ and labelled as (E) can be attributed to the re-oxidation of Mn nanoparticles to MnO with concurrent Li_2O dissolution. From the second cycle on, the reversible couple (C,D) and the anodic peak (E) do not change their position throughout the voltammetric experiment, meanwhile the cathodic peak (B) is shifted toward higher potentials, most likely due to a lower electrode resistance, a behavior typical of conversion-enabled TMOs [14–16].

PAA-based electrodes have been tested in order to evaluate the possibility of replacing PVdF/NMP system with a more environmental-friendly formulation, and to assess its compatibility with morphological and mechanical features of conversion anodes. For sake of comparison, the PAA- and PVdF-based electrodes underwent galvanostatic cyclations in the 0.005 V to 2 V potential window. Fig. 3a shows the comparison between the discharge capacity values of the two electrodes. The large irreversible capacities in the first cycle are mostly related to the SEI formation, together with the first MnO conversion of Mn^{2+} into Mn nanoparticles. During the following cycles, the anodes show decreasing

Table 1

Summary of experiments carried out for performance optimization: electrode label (A-I), slurry composition (MnO:binder:carbon mass ratio), pressure applied upon electrode manufacture, electrolyte formulation, techniques applied, potentials investigated. CV = Cyclic voltammetry; GC = galvanostatic charge/discharge cycles at 1C; Rate Cap. = rate capability test; EIS = electrochemical impedance spectroscopy.

Electrode	MnO %	Binder/%	SC 65%	P/tons cm^{-2}	Electrolyte	Technique	E/V
A	80	PVdF/10	10	0	LiPF_6 1 M EC:DMC 1:1	CV, GC	0.005–2
B	80	PAA/10	10	0	LiPF_6 1 M EC:DMC 1:1	GC	0.005–2
C	80	PAA/10	10	8	LiPF_6 1 M EC:DMC 1:1	GC	0.005–2
D	80	PAA/10	10	8	LiPF_6 1 M EC:DMC 1:1	GC	0.005–3
E	70	PAA/10	20	8	LiPF_6 1 M EC:DMC 1:1	GC	0.005–3
F	70	PAA/10	20	8	LiPF_6 1 M EC:DMC 1:1 + 2% VC	GC	0.005–3
G	70	PAA/10	20	8	LiPF_6 1 M EC:DMC 1:1 + 2% VC	Rate Cap.	0.005–3
H	70	PAA/10	20	8	LiPF_6 1 M EC:DMC 1:1	EIS	0.6
I	70	PAA/10	20	8	LiPF_6 1 M EC:DMC 1:1 + 2% VC	EIS	0.6

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