CATHODE MATERIALS FOR HIGH ENERGY DENSITY LITHIUM BATTERIES

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ABSTRACT

Two classes of cathode materials have been developed for high energy density applications. The Li-rich layered oxide material with the general formula $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ($\text{M} = \text{Ni}, \text{Mn}, \text{Co}$) and the lithium manganese silicate $\text{Li}_2\text{MnSiO}_4$. Both materials have theoretical capacities higher than commercialized ones, which may give rise to higher energy density batteries.

Li-rich materials have been prepared by solid state and co-precipitation routes. Transmission Electron Microscopy (TEM) characterization showed an irreversible evolution of the structure through a spinel phase during the first charge. Electron Energy Loss Spectroscopy (EELS) also showed a continuous cation migration during cycling of the material leading to charge/discharge voltage decay. The redox process has been studied by X-Ray Diffraction (XRD) in synchrotron facilities (ESRF, Grenoble, France). Ni/Mn ratio has been identified to have a great role on capacity fading of the material. Finally, a Li-rich optimized composition has been prepared and stable reversible capacity of 250 mAh.g^{-1} has been obtained.

$\text{Li}_2\text{MnSiO}_4$ has a large theoretical specific capacity (333 mAh/g) through exchange of 2 lithium ions per formula unit. The thermal stability due to strong Si-O bonds makes $\text{Li}_2\text{MnSiO}_4$ a very promising material for future energy storage in space applications. Preparation in inert atmosphere showed beneficial improvements of LMSO's electrochemical properties. Nano-sizing and carbon coating have been effective ways to improve electronic conductivity and therefore electrochemical performance. Up to 1.66 Li per formula unit can be re-inserted in the 1st cycle. XRD analysis showed complete amorphization of $\text{Li}_2\text{MnSiO}_4$ after the 1st charge at 4.8 V with complete modification of the charge/discharge curves in the next cycles. Increasing the carbon coating ratio limits capacity loss during cycling but did not avoid amorphization. Finally influence of voltage window on structure stability was investigated. Careful choice of upper limit voltage has been showed to stabilize $\text{Li}_2\text{MnSiO}_4$ structure but for now is still limited to low Li^+ insertion/extraction from the host material.

1. INTRODUCTION

Driven by recent deployment of electric vehicles, researches on new lithium-ion battery technologies are constantly increasing. To meet demands of automotive/aerospatial sector, new cathode materials targeting high energy density, low cost, eco-friendliness and safety are investigated. Aerospace sector requests state-of-the-art lithium-ion batteries to supply electrical power when solar energy is not available, for emergency cases and during high-power pulsed payloads. Both terrestrial and space transportation are benefiting to this R&D rising.

Layered lithiated transition metal oxide material such as LiMO_2 ($\text{M} = \text{Ni}, \text{Mn}, \text{Co}$) represents the most commercialized class of cathode for Li-ion secondary batteries. Since few years, a polyanionic compound - LiFePO_4 - gains market shares because of its high structural stability leading to higher safety properties. These materials are all limited in term of specific capacity in their domain of stability ($150\text{-}200 \text{ mAh/g}$). However, aerospace applications require batteries with more and more power and embedded energy, at lower cost. In this frame, recent developments on Li-rich layered oxides and upstream research on polyanionic lithium manganese silicate ($\text{Li}_2\text{MnSiO}_4$) have been carried out by CEA.

Li-rich materials have very high practical energy densities and very high specific capacities ($>250 \text{ mAh/g}$). It is economically attractive due to its composition mainly rich in manganese which is cheaper than cobalt. From a structural point of view, the lithium-rich layered materials can be regarded as a composite material built of LiMO_2 and Li_2MO_3 domains ($\text{M} = \text{Mn}, \text{Ni}$) [1]. The high specific capacity ($> 250 \text{ mAh.g}^{-1}$) of Li-rich materials is attributed to the reversible capacity coming from the redox activity of cations in the LiMO_2 component and to an additional capacity corresponding to the electrochemical activation of the Li_2MO_3 component above 4.4 V [2]. This activation process

involves oxidation of oxygen from the structure but the process is not really understood, especially the reversibility is not clear.

Since 2005 [3] researchers work on silicate cathodes. $\text{Li}_2\text{MnSiO}_4$ shows a theoretical high specific capacity of 333 mAh/g through exchange of 2 lithium ions by formula unit. 1st and 2nd lithium extraction has been computed to occur at high voltage of 4.1 and 4.5V respectively [4] leading to high energy density. Covalent Si-O bonds avoid oxygen release in excessive conditions [5], which improves battery safety. Absence of Ni and Co enables low cost and eco-friendliness. In addition to these characteristics, well spread-out raw materials occurrence is a key-factor for strategic sectors like space. As for polyanionic phosphates [6] low electronic conductivity is counterbalanced by size decrease and coating with conductive agent like amorphous carbon. Effect of particle size, atmosphere preparation, carbon coating and voltage window on electrochemical performance and structural stability will be discussed.

2. RESULTS AND DISCUSSION

2.1. Li-rich materials; recent developments

Li-rich materials with general formula $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$ ($\text{M} = \text{Ni}, \text{Mn}, \text{Co}$) were investigated in CEA in 2007. In early developments, Li-rich materials were prepared by solid state route. Lately, the use of co-precipitation synthesis allowed higher performances (stable 250mAh/g capacity and higher tapped density) and a better control of its morphology (Fig.1). Such properties are desirable for the realization of high energy density electrodes. The synthesis has been scaled-up in a pilot co-precipitation equipment, with 1 kg batch size.

Figure 1. Evolution of the discharge energy and capacity of Li-rich material obtained in half cells (vs. Li) using [2.5 – 4.8] V vs. Li^+/Li cut-off voltages.

Despite very interesting high capacities and attractive price due to its high content in cheap manganese, some challenges still have to be overcome (a large irreversible capacity during the first cycle and the fade of the

average cell voltage during the cycle life)

Our group worked simultaneously on Li-rich synthesis development and on its structure evolution understanding. The results from TEM (Fig. 2), Scanning Electron Microscopy (SEM), in-situ synchrotron diffraction measurements (ESRF, Grenoble, France) and electrochemical measurements have been analyzed in parallel to get better understanding of the voltage decay and capacity fading mechanisms.

Figure 2. TEM image and chemical composition of Li-rich material (a) before cycling and (b) after 50 cycles.

First, *in situ* X-Ray diffraction study combined with a transmission electronic microscopy study led to the identification of an irreversible structural change during first charge, accompanied with the formation of a secondary phase with spinel structure at the surface of the particle, which can be the origin of the irreversible capacity observed in the first cycle [7].

According to the coupled EELS/TEM study, the voltage decay is due probably to the continuous cationic migration during cycling [8] (Fig.2 and 3).

Figure 3. Illustration of the structural instability of the Lithium-rich layered materials.

Finally an *in situ* X-ray Absorption Spectroscopy (XAS) study at ESRF coupled with fine electrochemical analyses gave the identification of the different electrochemical processes and of the link between high and low potential processes in the material [9]. These conclusions were completed and confirmed by a composition study with different Mn/Ni ratios in the aim to understand the Mn role on the voltage decay [10].

Solve this structural instability leading to voltage fading during cycle life is the priority.

As a result, CEA strategy is now to work on a modified Li-rich structure stopping voltage decay. The first results are very promising (Fig.4). Synthesis optimizations are ongoing.

Figure 4: Electrochemical performances of the new generation of Li-rich cathode developed by CEA. Capacity (a), average potential (b) and specific energy (c) as a function of the cycle number.

2.2. $\text{Li}_2\text{MnSiO}_4$ material study

Four polymorphs have been reported in literature [11]. The two firsts, $\text{Pmn}2_1$ and Pmnb , are usually obtained at lower temperature and have orthorhombic lattice related to $\beta\text{-Li}_3\text{PO}_4$. The two others, $\text{P}2_1/\text{n}$ and Pn are monoclinic and are formed at higher temperature.

Figure 5: XRD patterns of $\text{Li}_2\text{MnSiO}_4$ (a), $\text{Li}_2\text{MnSiO}_4/\text{C}$ with 3wt.% of C (b) and $\text{Li}_2\text{MnSiO}_4/\text{C}$ with 8wt.% of C (c); x: MnO ; #: Li_2SiO_3 ; \$: Mn_2SiO_4 .

$\text{Li}_2\text{MnSiO}_4$ samples were prepared by sol-gel process. Carbon coating (C-coating) was obtained in a second step, by pyrolysis of the polymer (P123) at 650°C for 30 minutes under Ar. The carbon coating ratio was

controlled by the quantity of polymer added in solution. Three samples have been prepared having 0; 3 and 8 wt.% C-coating ratio, as determined by ThermoGravimetric Analysis (TGA). Fig. 5. shows the powder XRD of the three samples.

All XRD patterns correspond to $\text{Li}_2\text{MnSiO}_4$ material with orthorhombic phase with $\text{Pmn}2_1$ space group. However, cubic MnO impurity was also observed for all synthesis. Furthermore, Li_2SiO_3 and Mn_2SiO_4 impurities have been found for two samples (0 and 3wt.% carbon content). These impurities have been regularly reported in different papers [12, 13]. Carbon-coated materials have broader diffraction peaks than uncoated one. It shows that the coherence length is smaller in the C-coated samples. This is probably due to the action of P123 copolymer in solution, which inhibits growth and crystallization of particles [14]. However, SEM picture showed similar particle size in samples with and without C-coating (Fig.6). The primary particles were spherical with a mean diameter of 50 nm. The primary particles are agglomerated together to form micrometric size secondary particles.

Figure 6: Scanning Electron Microscopy images of $\text{Li}_2\text{MnSiO}_4$ (a) and $\text{Li}_2\text{MnSiO}_4/\text{C}$ with 8wt.% of C (b).

Electrochemical performance have been studied in coin cells vs. Li counter electrode, in galvanostatic mode, between 1.5 and 4.8 V.

Fig. 7 shows the 1st cycle obtained at C/20 ($1\text{C} = 333\text{ mA/g}$) for $\text{Li}_2\text{MnSiO}_4$ without C-coating, after a 48h exposition to air or full preparation in Ar.

Figure 7: Galvanostatic charge and discharge between 1.5 and 4.8V of $\text{Li}_2\text{MnSiO}_4$ which was exposed to air 48h (a) and prepared in argon (b).

Charge capacity was two times higher when storage of $\text{Li}_2\text{MnSiO}_4$ took place in Ar atmosphere. Actually, charge capacity increased from 76 mAh/g in air to 156 mAh/g in Ar. Discharge capacities were respectively 56 mAh/g in air and 97 mAh/g in Ar. It has been shown by XRD that $\text{Li}_2\text{MnSiO}_4$ reacts with air to form Li_2CO_3 .

Formation of Li_2CO_3 is most probably due to combined oxidation of Mn^{2+} and lithium extraction at the surface, followed by reaction of lithium with CO_2 from air to form Li_2CO_3 [15]. The presence of such isolating material explains lower performance of $\text{Li}_2\text{MnSiO}_4$ electrodes exposed to air. We also showed by XRD that the presence of carbon-coating slows down the reactivity of $\text{Li}_2\text{MnSiO}_4$ in air. However, the carbon layer does not completely protect the material.

Figure 8. Galvanostatic curves between 1.5 and 4.8V of $\text{Li}_2\text{MnSiO}_4/\text{C}$ prepared in argon with 0wt.% (a), 3wt.% (b) and 8wt.% of carbon (c).

In the next part of this study, all materials from pyrolysis to coin cells were prepared in inert atmosphere to avoid lithium extraction and insulating Li_2CO_3 at surface of particles. Fig. 8 shows the influence of carbon-coating (0; 3 and 8 wt.% of carbon) on the 1st cycle. Charge capacities reached 277, 242 and 77 mAh/g; discharge capacities reached 197 mAh/g, 161 mAh/g and 97 mAh/g for samples with respectively 8, 3 and 0 wt.% of carbon. Higher C-coating ratio clearly increased kinetics of the composite $\text{Li}_2\text{MnSiO}_4/\text{C}$ materials. Extraction and insertion of lithium superior to 1 per formula unit is achieved for 8wt.% of carbon.

Figure 9. XRD patterns of $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrodes, after 20 cycles at C/20 1.5-4.0V (a), after 20 cycles at C/20 1.5-4.8V (b), after 1 charge at C/20 until 4.8V (c) and pristine (d) ; x: MnO ; +: Al current collector.

1st and 2nd galvanostatic cycle of $\text{Li}_2\text{MnSiO}_4/\text{C}$ with 8wt.% of C between 1.5 and 4.8V are plotted on fig. 10. Shape of charge and discharge of cycle 2 were completely different from cycle 1. A steep polarization is observed during 2nd charge supposing a probable major change in the $\text{Li}_2\text{MnSiO}_4/\text{C}$ composite material during the first galvanostatic cycle. XRD measurements on $\text{Li}_2\text{MnSiO}_4/\text{C}$ electrode before and after the first oxidation are shown in Fig.9c and d. After the first oxidation, all the diffraction peaks from $\text{Li}_2\text{MnSiO}_4$ vanished. Thus, a complete amorphization of the material occurred during 1st charge. Amorphization might limiting lithium diffusion. Capacity loss due to this phenomenon has been reported in the literature [16].

Figure 10. First and second galvanostatic cycles of $\text{Li}_2\text{MnSiO}_4/\text{C}$ (8wt.% of C) with a voltage window of 1.5-4.8V.

Figure 11. First and second galvanostatic cycles of $\text{Li}_2\text{MnSiO}_4/\text{C}$ (8wt.% of C) with a voltage window of 1.5-4.0V.

One major hypothesis is the instability of Mn at oxidation state (III) and (IV) obtained during lithium extraction, which causes major distortion and finally loss of long range order into structure [17]. Actually, deep charge i.e. deep lithium extraction irreversibly damaged $\text{Li}_2\text{MnSiO}_4$ structure and led to gradual capacity loss. On the opposite, the shape of the charge/discharge curves was really similar in the two first cycles when the upper cut-off voltage was limited to 4.0 V vs. Li^+/Li (fig. 11). As a consequence, the capacity was stable upon cycling, as shown in Fig. 12d. However only 0.3 lithium per formula unit was exchanged, greatly limiting the capacity of the material.

Figure 12. Relative discharge capacity loss versus cycle number of $\text{Li}_2\text{MnSiO}_4$ (1.5-4.8V) (d); $\text{Li}_2\text{MnSiO}_4/\text{C}$ (3wt.% of C, 1.5-4.8V) (c); $\text{Li}_2\text{MnSiO}_4/\text{C}$ (8wt.% of C, 1.5-4.8V) (b); $\text{Li}_2\text{MnSiO}_4/\text{C}$ (8wt.% of C, 1.5-4.0V) (a).

XRD showed that the structure was maintained in this narrower voltage window, even after 20 cycles (Fig. 9a). It is a clue that structure is maintained. However only 0.3 lithium per formula unit is exchanged. Nevertheless XRD on electrodes after 20 cycles of charge-discharge (10 cycles at C/20 followed by 10 cycles at C/10) is performed on both voltage window to assess structure preservation. No peaks of $\text{Li}_2\text{MnSiO}_4$ remained in electrode cycled until 4.8V, which is

supported yet by XRD pattern after one charge (Fig.9b). To the contrary structure of $\text{Li}_2\text{MnSiO}_4$ is kept in electrode cycled until 4.0V. It is source of good cyclability for silicates.

3. CONCLUSION

Li-rich and Lithium manganese silicate have been studied as cathode material for lithium-ion batteries. Spherical particles of Li-rich have been synthesized by co-precipitation route. TEM and in-situ diffraction measurements analyses have been performed to understand structural modifications of the structure during cycling. The formation of an irreversible spinel phase and cation migrations upon cycling are probably responsible for performance loss of the material. Control of the Mn/Ni ratio lead to stable and reversible discharge capacity of 250 mAh/g.

$\text{Li}_2\text{MnSiO}_4$ was prepared by sol-gel synthesis. Careful preparation in inert atmosphere improved its electrochemical performance avoiding insulating layer of lithium carbonate around particles and lowering polarization. Up to 1.66 Li^+ ions can be reinserted in 8% carbon coated $\text{Li}_2\text{MnSiO}_4$ composite during the 1st discharge. Amorphization during its first charge was probably responsible for capacity loss upon cycling. Stabilization of the structure was observed using appropriate voltage window. However, only 0.3 Li^+ ions can be reversibly extracted from the structure. A new path of investigation is open and will lead to better understanding of lithium manganese silicate and maybe will provide solutions to counterbalance its structural instability.

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