Searching for new anode materials for the Li-ion technology: time to deviate from the usual path

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Abstract

A brief review of our fundamental studies of the reversible reactivity mechanism of vanadates towards lithium is presented. This mechanism totally differs from the classical one based either on reversible insertion/deinsertion of lithium into host structures or on Li alloying reactions, and has led to the thought of using nanosized transition metal oxides as possible negative electrode materials for rechargeable Li-ion batteries. Electrochemical capacities, as high as 700 mAh/g with a 100% capacity retention up to 100 cycles and high rates, can be achieved with optimized metal oxides (MO, M = Co, Cu, Ni, Fe, etc.) powders. By combining transmission electron microscope (TEM), infrared (IR) and magnetic measurements we directly proved the formation of 10–50 Å metal nanoparticles dispersed into a lithia (Li_2O) matrix during the reduction step of MO with Li. Upon oxidation, the metal nanoparticles were shown to convert back to MO while Li_2O was decomposed. The new opportunities provided by these metal oxides systems based on the reversible formation/decomposition of Li_2O are discussed together with the positive attributes that nanoparticles could have to the field of energy storage. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Today's research on negative electrodes for the Li-ion technology is mainly split between (1) enhancing the electrochemical characteristics of the carbonaceous negative electrode by chemical (pyrolytic processing of organic materials) or physical (mechanical milling of carbons) means, and (2) finding alternative materials to substitute for the presently used carbonaceous negative electrode composites. The second approach has sequentially led to the discovery of new oxides ternary vanadates (R–V–O) [1], amorphous tin composite oxides (ATCO) [2,3] or composite negative alloy electrodes [4,5] that can display large electrochemical capacities versus Li at low voltages. Therefore, the poor capacity retention of these new materials upon cycling is limiting their use in practical cells.

Fundamental studies, directed towards a better understanding of the Li reactivity mechanism, were undertaken to solve these materials electrochemical limitations. For the ATCO's or alloys electrodes, once the first discharge is

achieved, it is believed [6] that the Li uptake/removal proceeds in accordance with a classical Li–Sn alloying mechanism that is reversible over limited amounts of cycles because of cycling-driven aggregation issues. While the ($SnFe_2 + SnFe_3C$) system studied by Dahn and Mao [4,5], or the Cu_6Sn_5 system studied by Thackeray [7,8] belongs to the negative composite electrode class, there are subtle differences in their Li reactivity mechanism. For the former, as Li reacts there is a decomposition into ($Fe + SnFe_3C$) together with a Li alloying (Li–Sn) reaction, while for the latter, the decomposition into Cu together with a "Li–Sn" reaction is preceeded by an insertion reaction leading to a $LiCu_2Sn$ phase [8,9].

Interestingly, while the unusual low voltage and large Li uptake/removal with the vanadates were discovered first, the Li reactivity mechanism in this system still remains very disturbing. The non-transparency of oxygen to the Li mechanism as previously proposed by Denis et al. [10] was later supported by RMN measurements [11], and more recently confirmed by the existence of an experimental correlation between the oxygen content and the measured capacity in Fe-based hydrated vanadates series [12]. However, the way the oxygen was participating in the process

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was still speculative. To shed some light on this issue we embarked, a few years ago, in a fundamental study of the Li reactivity in such vanadates by means of in situ X-rays, XANES, Mössbauer and microscopy studies, with a special attention to the Fe and Co-based vanadates [13]. Several trends were deduced with (1) a full amorphization of the vanadate powders during their first electrochemical reduction versus Li (e.g. first discharge), (2) the formation of a composite matrix consisting of Li_2O, M–O and Li–V–O nanoparticles as deduced from transmission electron microscope (TEM) studies, (3) the reduction upon discharge of the vanadium state from +5 to +2 and its reoxidation up to +4 on the subsequent oxidation state (as deduced from XANES in situ measurements), and (4) the reduction of the ternary cation M^{n+} to metallic element and its reoxidation up to a $+n$ state on the subsequent charge as again deduced by XANES at metal K-edge or as deduced by Mössbauer measurements for M = Fe [14]. Among all these results, the most intriguing one was the possibility to fully reduce and oxidize 3d-metal cations. Thus, could such a reaction be linked to the electrochemically driven nanosized character of the composite matrix? As an attempt to provide an answer to this question we deviated from the usual path, and embarked in a complete study of 3d-metal oxides, previously disregarded as energy storage materials due to the lack of right conditions (open framework structure, etc.) for the classical Li insertion/deinsertion process. To our surprise, several 3d-metal oxides turned out to be attractive electrode materials to be used in Li-ion cells as reported herein.

2. Experimental

Metal oxides powders used in the present study came from commercial sources unless otherwise specified. They were characterized for phase purity by means of X-ray diffraction (XRD) using a SCINTAG diffractometer having a Cu Kα radiation, and for morphology by a Philips TEM CM12 instrument equipped with a home designed sample holder for moisture sensitive samples.

Swagelok-type cell configurations using 3d-metal oxide powders (MO) as the positive electrode, lithium metal as the negative electrode and a borosilicate glass fiber sheet saturated with a 1 M $LiPF_6$ electrolyte solution in 1-1 dimethyl carbonate:ethylene carbonate in weight as the separator were assembled, and then electrochemically tested using a ''Mac-Pile'' automatic cycling/data recording system operating both in galvanostatic or potentiostatic modes.

The MO composite electrode was made using either Bellcore plastic PLiON technology or simply by mixing the MO powder with 10% SP, and placing the loose powder mixture on top of the positive electrode Swagelok plunger. Tests were ususally made on electrodes ranging from 7 to 10 mg/cm^2. Li-ion cells were made from 1 cm^2 plastic disks of $Li_{1+x}Mn_2O_4$ and MO with a weight ratio of 6.5. In situ X-ray electrochemical measurements were done by means

of an electrochemical cell assembled similarly to our swagelok cell but having a Be window as current collector on the cathode side.

3. Results

Li/MO cells using various metal-oxide electrodes were tested between 0.01 and 3 V and the voltage-composition traces are shown in Fig. 1. Despite the 20% irreversible loss usually observed between the first discharge and charge, these materials can reversibly cycle over two lithiums leading to capacities ranging from about 600 to 700 mAh/g with the capacity retention being dependent on the material morphology as will be discussed elsewhere [15].

During the first discharge, all the Li/MO cells show a plateau beginning at the early stage of the reduction process, and followed by a continuous voltage drop down to 0.01V. The voltage at which this plateau occurs changes, and its amplitude depends on the nature of the 3d-metal as well as on its initial oxidation state. For instance, this plateau was found to be longer for Co_3O_4 than for CoO. In situ X-ray measurements have shown that it is through this plateau that the full amorphization of the sample occurs. Furthermore, from TEM measurements on electrochemically reduced metal-oxide electrodes (Cu_2O was taken as an example herein [16]), we first evidenced that the material habitus (e.g. the global shape of the particle) was preserved but we also noted that besides amorphization, the material was undergoing a decomposition reaction leading to metallic M nanoparticles embedded into a Li_2O polymer matrix with, in addition, the growth of a passivating layer (mainly organic since it was decomposing under a long beam exposure) around the particle (Fig. 2). Interestingly, while qualitative only, we noted that the particle SEI layer was drastically evolving between charge and discharge (a point that will be discussed in details in a forthcoming paper).
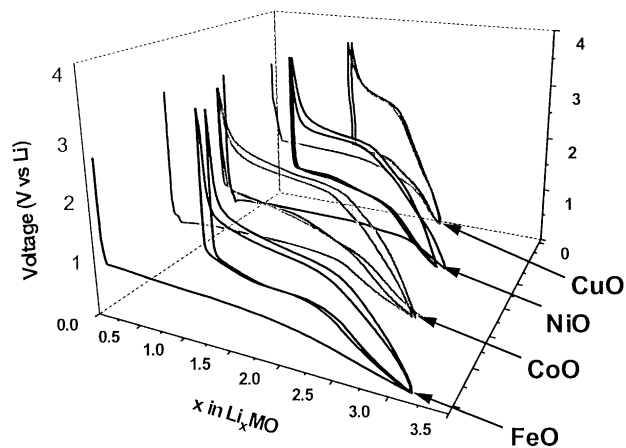

Fig. 1. Voltage-composition profile for various MO/Li cells. The cells were cycled at C/5 rate (e.g. 1 lithium per formula unit in 5 h) in the 3–0.01 V range.
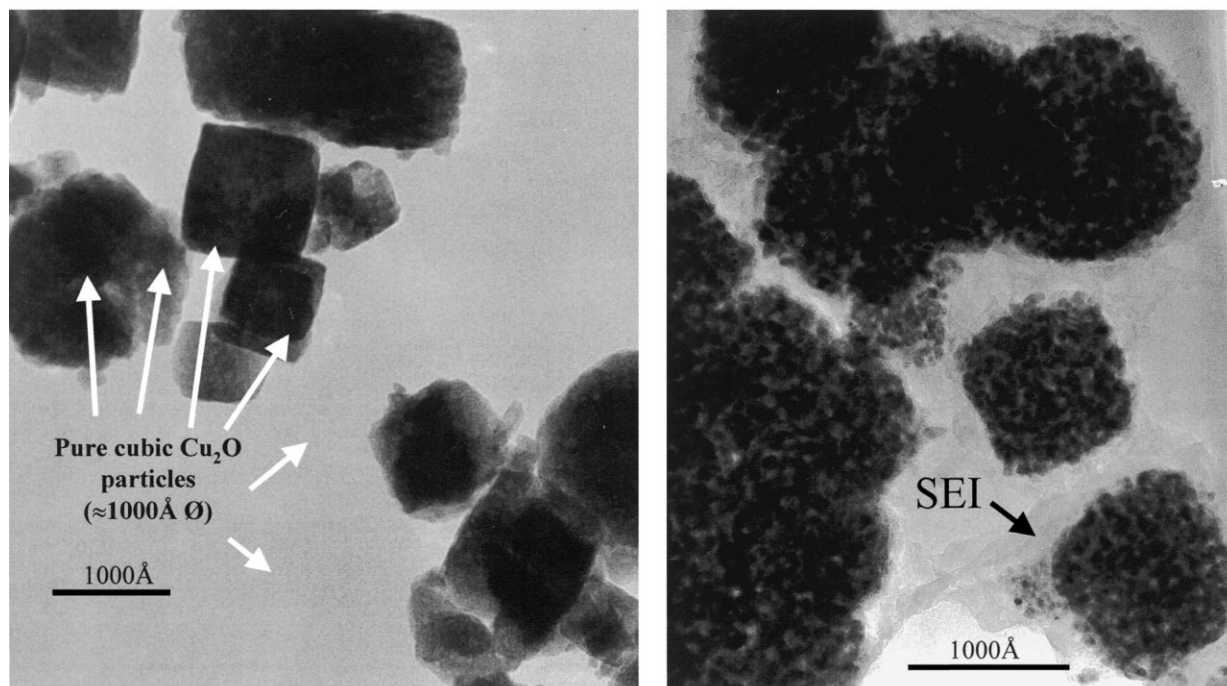
Fig. 2. TEM observations realized on a Cu_2O electrode recovered from a fully discharged Cu_2O/Li cell. The micrograph of the starting Cu_2O electrode composed of 1000 Å particles is shown on the left with the micrographs of the fully lithiated Cu_2O electrode on the right. Initial particles are transformed in 20 Å particles agglomerates. The global shape is kept; a white triangle indicates the ''inorganic'' SEI layer surrounding the agglomerates.

For all these Li/MO cells, the shape of the following charge totally differs from that of the first discharge, with namely a round-off of the charge voltage-composition curve instead of well pronounced plateaus. The oxidized electrode composite matrix was found (as deduced by TEM measurements not shown herein) to have a similar texture to the reduced material but with a different composition, with usually the presence of MO instead of M and the disappearance of Li_2O. In terms of magnetic properties, the MO phases are antiferromagnetic (no saturation magnetization) while the M phases are ferromagnetic (existence of saturation magnetization). We took advantage of such a drastic difference to directly follow the electrochemical reactivity of MO towards Li during cycling. Fig. 3 shows, for example, the evolution at 4.2 K of the saturation magnetization for CoO electrodes recovered from CoO/Li cells stopped at different states of discharge and charge. Note that the saturation magnetization increases as the reduction proceeds to reach its maximum value for the fully reduced sample, and then diminishes to reach values close to 0 as the sample is charged (e.g. oxidized), thus confirming the CoO $\rightarrow$ Co reversible process earlier sensed from XANES [17], and evidenced by TEM measurements. In addition, magnetic measurements as a function of temperature have revealed, for our reduced samples, the super paramagnetism phenomena (i.e. appearance of a compensation temperature) inherent to fine particle systems and consistent with the nanosized character of the matrix electrode revealed by our TEM results.

Besides their large initial capacity, a key figure of merit in selecting new electrode materials is their ability to sustain their capacity over several cycles. Various MO/Li cells were tested and their capacity retention evaluated as a function of both the morphology and nature of the 3d-metal oxides. The effect of the particle size was conveyed by showing that the capacity of Cu_2O/Li cells after seventy cycles is only 35% of the initial capacity instead of 100% when the Cu_2O
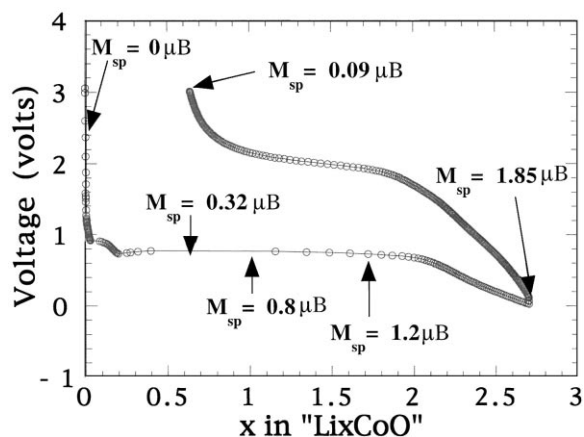

Fig. 3. Variation of the room temperature remnant aimantation for CoO electrodes recovered from CoO/Li cells that were stopped at various states of discharge or charge. The aimantation increases during the reduction step, and then converts back to its initial value on the subsequent charge implying a reversible CoO $\rightarrow$ Co redox reaction (see text).

precursor powders composed of 1 μm instead of 0.15 μm particles are used. Among the various investigated metal-oxide powders with particle sizes ranging from 1 to 5 μm, we found, independently of the cycling rate, the best capacity retention to be in order of merit for CoO, Cu_2O, NiO and FeO. Finally, as expected and based on the SEI layer formation evidenced by TEM, we experienced a strong dependence of the life cycle of the MO/Li cells on the nature of the electrolyte (salt + solvent). However, it is beyond the scope of this paper to further dwell on this issue that will be highly documented in a forthcoming paper.

Electrochemically optimized CoO powders were then used in conjunction with $LiCoO_2$ and $LiMn_2O_4$ for the assembly of Li-ion cells. For cell balancing, the $LiMn_2O_4$ and $LiCoO_2$ capacities were taken as equal to 120 and 140 mAh/g, respectively, while CoO's was taken as 800 mAh/g so that the weight ratios of positive to negative be taken as 6.4 and 7.5, respectively. The behavior of a three-electrode $LiCoO_2$/CoO cell assembled with a ratio of 6.4 is shown in Fig. 4. Note that the cell can deliver its total capacity between 1.2 and 4 V. A penalty inherent in the use of CoO as the negative electrode is its 20–25% capacity loss between the first discharge and charge cycles. As a way to compensate for such a loss we used, in accordance with our previous studies, the lithiated spinel $Li_{1+x}Mn_2O_4$ in which x can be considered as a lithium reserve. Using a chemically lithiated spinel phase with $x = 0.3$, the ratio of positive to negative can be lowered, and the overall cell capacity enhanced. The voltage profile of such a cell is shown in Fig. 5a and b; the capacity retention of both cells over the first few cycles. The positive capacity attributes of such CoO-based Li-ion cells over commercial $LiCoO_2$/C ones reside in the fact that CoO has twice the capacity of carbon and about three times its density.
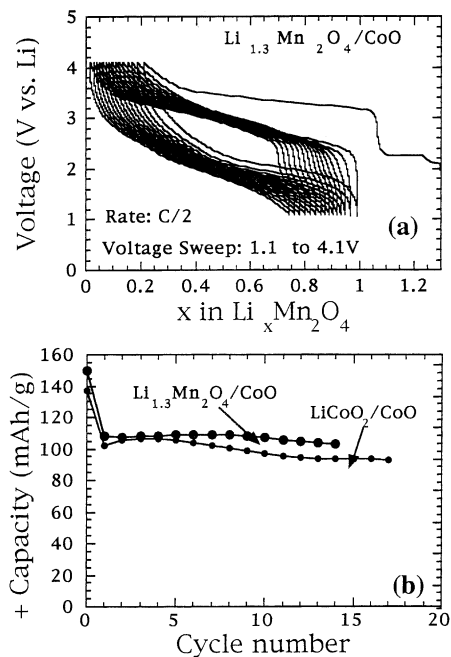
Fig. 5. The output voltage of a $Li_{1+x}Mn_2O_4$/CoO cell cycled at a C/5 rate is shown in (a) and (b) its capacity retention together with that of the cell presented in Fig. 4.

4. Discussion/conclusions

We have reported on the electrochemical performances of 3d-metal oxides and on their attractiveness with respect to their use in Li-ion batteries. Indeed, such MO materials (M = Cu, Co, Ni, Fe) can show reversible capacities as high as 700 mAh/g. The mechanism by which these metal oxides react with lithium totally differs from the classical Li insertion/deinsertion process or Li-alloying reactions since none of the 3d-metals investigated alloys with lithium. From TEM, magnetic and XANES measurements (not shown here), we deduced a novel Li reactivity mechanism that consists of the reduction of MO into M (first discharge) and the oxidation of M into MO (first charge), concomitant with the formation/decomposition of Li_2O, with the complete process being favored by the nanosized character of the composite matrix formed during the first discharge.

The capacity retention for these new oxides was found to worsen with decreasing the precursor particle size, an opposite trend to what was reported for either the ATCO's or composite negative electrodes alloys. This difference is nested in the way that Li reacts in both materials. For the ATCO's and negative composite alloys, the Li reactivity mechanism boiled down to phase decomposition, and finally to the formation of an electrochemically active "Li-alloys" matrix dispersed into an electrochemically inactive matrix (Li_2O or M), and the cycle life failure was associated to metal particles agglomeration issues. X-ray as well as TEM measurements failed in evidencing metal particle agglomeration in our metal-oxide composite electrodes after more
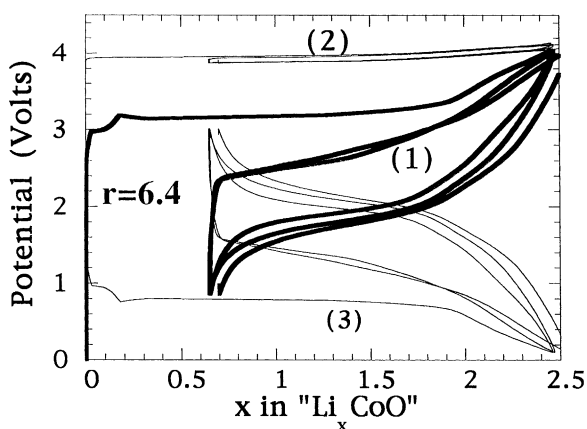
Fig. 4. The first few cycles of a $LiCoO_2$/CoO cell cycled between 4.1 and 1.1 V, as measured with the three-electrode configuration, are shown. The curve denoted '1' represents the output voltage of the cell while the curves denoted '2' and '3' represent the voltage of the $LiCoO_2$ and CoO electrodes vs. Li, respectively.

than 50 cycles, suggesting that the cycle life failure mechanism must be different in our system. However, these measurements, namely TEM, revealed the appearance and partial vanishment around the initial particle of the SEI layer upon cycling. The formation of an SEI layer usually originated from a catalytic-driven electrolyte reduction. Based on the observed experimental link between the capacity retention and the nature of the electrolyte used, we believe that the origin of our cell lifetime failure is rooted in the SEI formation layer that, if too large, will block the metal-oxide particle reactivity towards lithium. So, why is such an effect worse for smaller MO precursor particles? Or why does the size of the precursor particle seem to govern the SEI layer formation despite the nanosized character of our electrode?

Both questions can be answered as follows. As lithium reacts with MO particles and the particle habitus (e.g. shape) is totally preserved, a phase demixion occurs with particle free active metal sites at the surface, and core metal particles being surrounded by Li_2O. It is well known that highly divided metal particles have enhanced catalytic properties, and therefore will favor the decomposition of the electrolyte they will come in contact with. It is then obvious that the number of surface active sites (surface to bulk ratio) will be greater for small particles than for large ones, the reason why the formation of this SEI layer will appear to become more rapidly detrimental to small particles rather than large particles. In contrast, within the core material, the metal nanoparticles enhance the formation/decomposition of Li_2O that they are surrounding by favoring the Li_2O formation/decomposition reversible process rather than the electrolyte decomposition, with which they have no contact. Hence, the very different roles of surfacic and core metal nanoparticles. Within the context of this work, it is interesting to recall that a similar type of electrochemically driven reaction was reported to occur at high temperature (420°C) in LiAll-LiCl·KCllα-Fe$_2$O$_3$ cells [18].

$$MO + 2Li \Leftrightarrow Li_2O + M$$
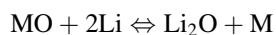
We have also shown that Li-ion cells using 3d-metal oxides as negative electrodes can deliver 100% of their capacity at voltages >1.2 V, a voltage anticipated to be the cut off discharge voltage of tomorrow's electronics. This exercise was done only to stress the new opportunities that such cells could present with respect to the field of energy storage. However, it should be realized that a few issues must be resolved prior to being implemented. The most urgent one resides in a better understanding of the chemical reactions involved in the growth of the SEI layer so that we can better control its formation, and therefore extend the lifecycle of these electrodes beyond a few hundreds cycles.

There is a large amount of literature work dealing with nanometric oxides of a few hundreds nanometers. In contrast, very little exists about synthesizing 1–5 nm free non-agglomerated oxide nanoparticles. The reason being that producing real nanometric clusters is not an easy task, and generally requires sophisticated methods. The electrochemical approach described here provides then an easy and costless synthesis alternative enabling to explore totally new phenomena beyond the field of energy storage, namely, the field of magnetism. Following these findings, the observed low voltage and large Li reactivity of numerous 3d-based chalcogenides materials, vanadates and borates can now be explained.

Acknowledgements

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