

Protocols for studying intercalation electrodes materials :

Part I: Galvanostatic cycling with potential limitation (GCPL)

I – Introduction

The basic characteristic of an electroactive intercalation compound is the thermodynamic voltage-composition relation, that corresponds to the equilibrium phase diagram of the system. See for example Armand [1] for detailed description of the various behavior that can be encountered, which depends on the changes in electronic and structural properties upon intercalation/deintercalation.

Basically a continuous dependence of the potential vs. composition corresponds to a solid-solution single-phase domain whereas a potential plateau corresponds to a two-phase domain.

Other properties of interest, particularly in view of possible applications as active electrode in a battery are the potential window of electrochemical stability, kinetics and reversibility of the intercalation process.

The voltage-composition relation can be determined either in a current controlled mode or in a potential controlled mode. These two techniques are usually referred to as "Galvanostatic Intermittent Titration Techniques" [2] and "Potentiostatic Intermittent Titration Techniques" [3] respectively.

The first method corresponds to performing successive charge increments by applying from a galvanostat a constant current for a given time ($\Delta Q = I \cdot \Delta t$), then switching to open circuit for determining the corresponding equilibrium potential. The results is a set of $V(Q)$ values, at periodic intervals in Q . The time dependence of the potential when switching the current on and off (chronopotentiometry) can give information on the kinetics of the process, more or less accurately depending on the conditions of the

experiment (duration of the current-on period and geometry of the electrode particularly).

The second method corresponds to applying to the electrode, from a potentiostat, a potential equal to its initial equilibrium potential. Then a step is applied to a potential value close to the initial one whereas recording of the chronoamperometric response is performed for a given time. This method is described in the second application note.

At that time it is important to note that diffusion coefficient values in solids are about 4 to 8 orders of magnitude lower than in liquids (usually in the range of 10^{-8} to 10^{-12} cm^2/s for materials of practical interest for batteries). With a diffusion coefficient value of 10^{-10} cm^2/s it takes hours to be close to equilibrium in grain of material with a 20 μm diameter after a change of surface concentration related to the potential step. Consequently the potential scan rates to be used will be in the range of a few mV per hour ($\mu\text{V}/\text{s}$).

One can take advantage of this slow kinetics and of the large possibilities of the digital systems presently available, for recording systematically the chronoamperometric responses at every potential steps. Using this "Step Potential Electrochemical Spectroscopy" it is possible to discriminate easily the various processes that can be involved in intercalation electrode materials, and to observe intermediate metastable redox states too [4-6].

Thus the potential controlled methods, that corresponds to looking at the extensive response of a system (charge variations) to the application of an intensive perturbation (applied potential changes) appears particularly suitable for basic studies of the

behavior of intercalation electrode materials, whereas galvanostatic method are much more devoted to long term behavior of systems under cycling.

In the EC-Lab software all these types of measurements can be performed through two protocols, the Galvanostatic Cycling with Potential Limitation (GCPL) and the Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA) respectively.

In addition to the basic parameters that makes possible to perform the measurements presented above, these protocols have many additional parameters and facilities related to the specificity of intercalation electrodes and their uses in batteries. This can be seen on the various windows of the flow diagrams of the protocols. One can mention the fact that the progress of the redox reactions can be controlled and monitored either in term of charge, or in term of molar amount of the active electrode material once given its molar mass, its amount, the molar mass the intercalated species and its change of ionization degree upon intercalation; the determination of equilibrium potential as reaching a preset slope for the open circuit potential vs. time; the possibility of preparing extensive cycling studies with various loop conditions, etc...

II – Galvanostatic Cycling with Potential Limitation (GCPL)

This protocol corresponds to the most standard for studying the behavior of batteries upon cycling. The performance of a battery is determined as a function of its charge and discharge conditions: a given rate, within a given potential range mainly.

When concerning a battery the galvanostatic rate is usually expressed as C/h , h being the number of hours at which the nominal charge of the battery (which involves both positive and negative electrode) will be passed

through. When studying a given electrode material, then C is in general the charge corresponding to the total expected reduction/oxidation of that electrode. Often one considers the specific capacity of an intercalation electrode material per weight (mA.h/g for example) and the galvanostatic rate can be expressed in current per active mass (mA/g).

In the battery protocols, entering the electrode characteristics in the corresponding window gives access to the theoretical capacity of a given electrode, from which the charge/discharge currents can be determined depending on the rate to be applied.

The figures below (Figs. 1 and 2) correspond to the study of a LiMn_2O_4 / graphite battery, with such a GCPL protocol, in a work undertaken for optimization of this system [7].

It is a good example of the interest of such galvanostatic intermittent techniques in Li-Ion (or rocking chair) batteries, using three electrodes cell: monitoring the potentials of the positive and negative electrode vs. a reference (a piece of lithium metal), it was possible to follow independently the behavior of each electrode material under cycling.

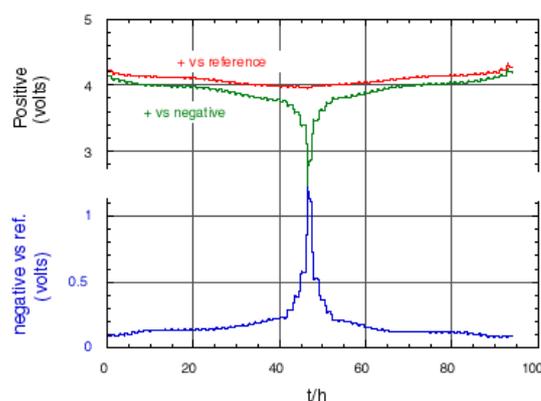


Figure 1: $\text{Li}_x\text{Mn}_2\text{O}_4$ graphite cell with Li reference electrode: Potential variation for each electrode as a function of time. (intermittent galvanostatic cycling ($C/15-0.5h$; OCV-1h) with positive to negative voltage limitations).

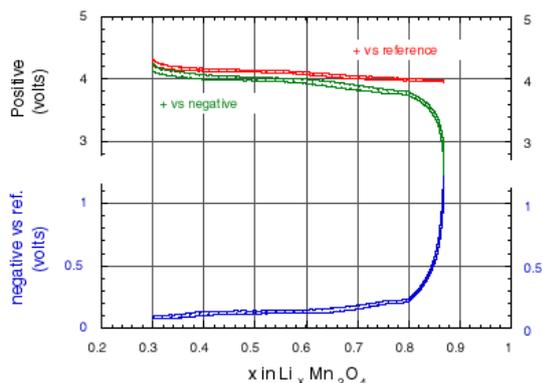


Figure 2: Potential variation for each electrode as a function of composition x in $\text{Li}_x\text{Mn}_2\text{O}_4$.

At $t = 0$ the battery was in a charged state, with the negative electrode at the potential of the LiC_6 - LiC_{12} two phase equilibrium, whereas the positive electrode was in an oxidized state of LiMn_2O_4 at 4.2 V close to $\text{Li}_{0.3}\text{Mn}_2\text{O}_4$. The discharge corresponds to reduction of the positive electrode with insertion of lithium coming from the negative electrode (and electrons coming through the external circuit). The corresponding oxidation of the negative electrode is seen on the increase of its potential vs. the reference: a plateau of potential is observed close to 120 mV which is the next equilibrium potential of the Li_xC_6 system (LiC_{12} - LiC_{18}) and to 0.220 V which is the next one. Then the potential increases rapidly which means that all the lithium has been deintercalated. At that time the potential of the negative electrode is still close to 4 V and corresponds to a non completely intercalated $\text{Li}_x\text{Mn}_2\text{O}_4$. Thus this battery appears charge limited by the negative electrode characteristics.

Looking at the details of the potential evolution when the current is switch on/off (Figs. 3 and 4), one can see that the polarization is larger at the positive electrode. The potential recovery appears also faster on the negative graphite electrode at the switch off. This means that the power capability of this battery is governed by the characteristics of the positive electrode material.

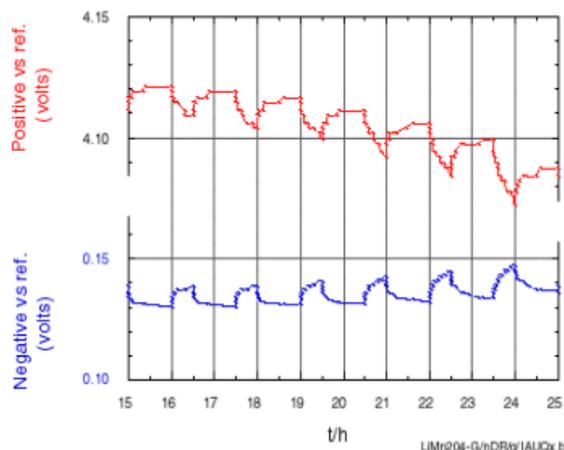


Figure 3: Expanded view of the potential variation of the positive and negative electrodes over a narrow domain of time. (intermittent galvanostatic cycling (C/15-0.5h ; OCV-1h) with positive to negative voltage limitations).

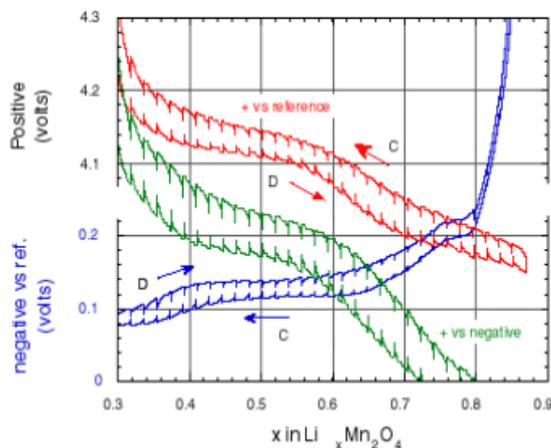


Figure 4: Potential vs. composition x in $\text{Li}_x\text{Mn}_2\text{O}_4$ for each electrode.

Note that in the PCGA protocol, one has the possibility to switch from a constant current mode to a constant potential mode upon reaching a predefined limit of potential.

This applies to the electrode which is connected to the Working electrode terminal relatively to the reference electrode. This potential controlled mode (referred to in the battery domain as "Floating") prevents the corresponding electrode material to be over-oxidized (or over reduced), whereas the current can continue to flow (for a given time, or up to a predefined current limit) as long the electrode material has not reached its equilibrium in the bulk. This mode is very important for studying Li-Ion batteries, for

limiting oxidation of the positive electrode material for which complete oxidation/de-intercalation is detrimental to the reversibility.

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