

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, which corresponds to the equilibrium phase diagram of the system. See for example Armand [1] for a detailed description of the various behaviors that can be encountered, depending on the changes in electronic and structural properties upon intercalation/deintercalation.

In short, 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 with regards to possible applications for active electrodes 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 a constant current from a galvanostat for a given time ($\Delta Q = I \cdot \Delta t$), then switching to open circuit to determine the corresponding equilibrium potential. The result 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 first a potential equal to its initial equilibrium potential using a potentiostat. At this point, a potential 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.

It is important to note that, at this time, 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 with a 20 μm diameter grain material 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 the slow kinetics and of the large possibilities of the digital systems presently available, to systematically record the chronoamperometric responses at every potential step. Using this "Step Potential Electrochemical Spectroscopy" it is possible to easily discriminate the various processes involved in intercalation electrode materials, and to observe intermediate metastable redox states too [4-6].

Thus, the potential controlled methods, that correspond to looking at the extensive response of a system (charge variations) to the application of an intensive perturbation (applied potential changes) appears particularly suitable to the basic studies of the behavior of intercalation electrode materials, whereas galvanostatic methods are much

more devoted to the long term behavior of systems being cycled.

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

In addition to the basic parameters that make the measurements presented above possible, these protocols have many additional parameters related to the specificity of intercalation electrodes and their use in batteries. This can be seen on the various windows of the protocols.

One can mention the fact that the progress of the redox reactions can be controlled and monitored either in terms of charge, or of the active electrode material's molar amount, or once given its molar mass, of its amount, of the mass of the intercalated species and of its change of ionization degree upon intercalation.

II – Galvanostatic Cycling with Potential Limitation (GCPL)

Galvanostatic Cycling with Potential Limitation (GCPL) is the most standard protocol for studying the behavior of batteries being cycled. The performance of a battery is determined as a function of its charge and discharge conditions, which are generally a given rate and a potential range.

With regards to batteries, the galvanostatic rate is usually expressed as C/h , h being the number of hours needed for the nominal battery capacity (which involves both positive and negative electrodes) to pass through. When studying a given electrode material, then C is in general the charge corresponding to the total expected reduction/oxidation of the intercalation species in 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 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 which needs 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 an experiment undertaken for optimization of this system [7].

This 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 independently follow the behavior of each electrode material being cycled.

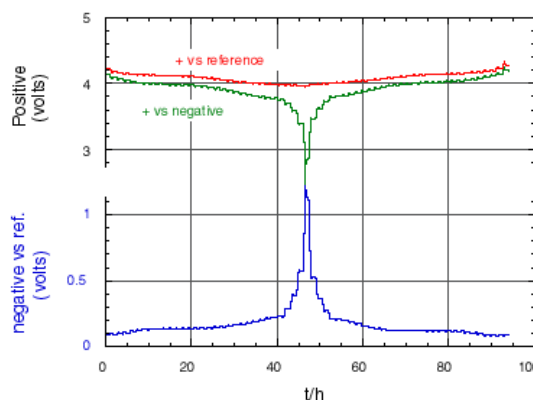


Figure 1: $\text{Li}_x\text{Mn}_2\text{O}_4$ graphite cell with Li reference electrode: Potential variation for each electrode as a function of time. (intermittent galvanostatic cycling $C/15-0.5h$; OCV-1h with positive to negative voltage limitations).

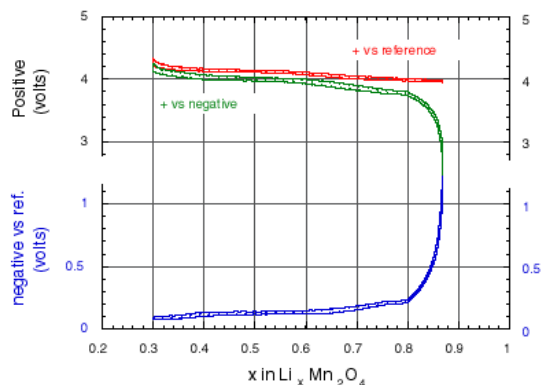


Figure 2: Potential variation for each electrode as a function of x in $\text{Li}_x\text{Mn}_2\text{O}_4$.

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 the reduction of the positive electrode with the 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 this point, the potential of the positive electrode is still close to 4 V and corresponds to a partially 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 switched on/off (Figs. 3 and 4), one can see that the polarization is larger at the positive electrode. The potential recovery appears faster on the negative graphite electrode than on the positive electrode. This means that the power capability of this battery is governed by the characteristics of the positive electrode material.

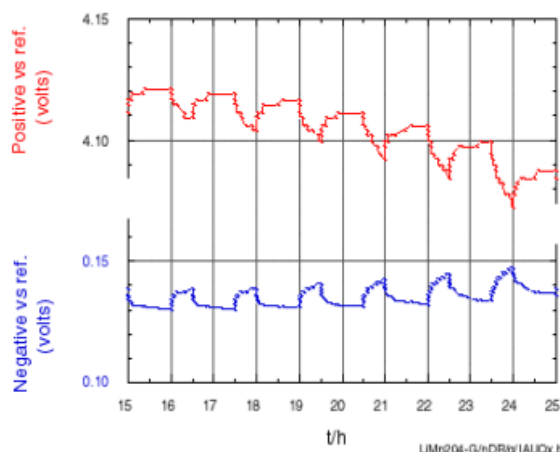


Figure 3: Expanded view of the potential variation of the positive and negative electrodes over a narrow domain of time. (intermittent galvanostatic cycling (C/15-0.5h ; OCV-1h) with positive to negative voltage limitations).

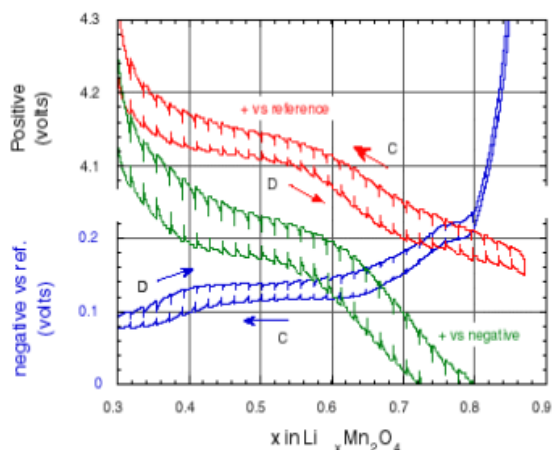


Figure 4: Potential vs. composition x in $\text{Li}_x\text{Mn}_2\text{O}_4$ for each electrode.

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 potential limit.

This applies to the electrode connected to the working electrode terminal relatively to the reference electrode terminal. This potential-controlled mode (referred to in the battery domain as "Floating") prevents the corresponding electrode material from being 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 as the electrode material has not reached its bulk equilibrium. 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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