

## Protocols for studying intercalation electrodes materials: Part II: Potentiodynamic Cycling with Galvanostatic Acceleration (PCGA)

### Available instruments for the PCGA protocol

Instrument	MPG	VMP	VMP2	BiStat
Used	✓			
Alternative		✓	✓	✓

### 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 (1980) 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"

(GITT, Weppner and Huggins, 1977) and "Potentiostatic Intermittent Titration Techniques" (PITT, Wen et al., 1979) respectively.

The first method corresponds to performing successive charge increments by applying from a galvanostat a constant current for a given time. It has been developed and explained in the first application note.

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. Then switching to open circuit makes possible the recording of the equilibrium potential, which will be as close to the previously applied potential as the final current was negligible at the cut-off. Integration of the chronoamperometric response gives the charge increment ( $\Delta Q = \int i(t).dt$ ), whereas its shape can give information on the kinetics of the process at that potential levels. Repeating the experiment, one get a set of "incremental capacity" values,  $\Delta Q$  (V), with corresponding kinetic information, with a resolution in potential better than the potential step amplitude.

An extension of this PITT protocol was proposed by A.H. Thompson (1979) as Electrochemical Potential Spectroscopy. In this mode, the successive steps of potential are applied, without going through an open circuit period, every times the reduction (oxidation) current has reached a predefined value which is considered as negligible compared to the capacity of the system. One gets

in this way a set of quasi-equilibrium incremental capacities values, at periodic potential intervals corresponding to the potential step amplitude. When reported as  $\Delta Q$  vs. the potential, the results of such an experiment is the incremental capacity voltammogram of the reduction/oxidation, that is a spectrum of the redox states of the system, obtained with the resolution of the potential step amplitude.

This can be compared to a linear sweep cycling voltammetry, with the difference that instead of performing a linear potential sweep ie. a sweep either continuous or stepwise but periodic in time, and recording the current, the duration of a potential level will depend on the kinetics of the process at that level. This is justified by the fact that the various redox processes that can occur successively in an intercalation electrode material, usually have very different kinetics. For example, it may be controlled by the kinetics of the phase transformation in the two phase domains whereas it is diffusion controlled in the single-phase solid-solution domains. By comparison with usual voltammetric studies of species solvated in a supporting liquid electrolyte, using a blocking electrode, the kinetics is governed by the diffusion coefficient of the species in the electrolyte, which does not depends much on the potential.

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  $10^{-12}$   $\text{cm}^2/\text{s}$  for materials of practical interest for batteries). With a diffusion coefficient value of  $10^{-10}$   $\text{cm}^2/\text{s}$  it takes hours to be close to equilibrium in grain of material with a  $20\mu\text{m}$  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 (Chabre, 1991, 1992; Chabre and Pannetier, 1995).

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 behaviour of intercalation electrode materials, whereas galvanostatic method are much more devoted to long term behaviour 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...

## RESULTS

The following example deals with an accurate determination of the phase diagram of the  $\text{LiCoO}_2$  system upon lithium deintercalation, using the PCGA protocol.

This compound is presently the active material of the positive electrode of several commercial "Lithium-Ion" batteries, the negative electrode material being carbon, either as graphite or as a coke. The initial  $\text{LiCoO}_2$  / C couple is the

discharged state of the battery. Charging the battery corresponds to oxidation of the  $\text{LiCoO}_2$  by lithium removal, with concomitant reduction of the negative carbon electrode, by formation of well defined intercalation compounds in the case of graphite (lithium goes between the graphene layer in several steps with final formations of  $\text{LiC}_{12}$  below 120 mV vs.  $\text{Li}^0\text{-Li}^+$  and then  $\text{LiC}_6$  below 80 mV). As the potential of the negative electrode depends on its degree of reduction, a basic study of the positive electrode material requires either the use of a reference electrode (a piece of lithium in the electrolyte as indicated previously, Blyr et al., 1998) or designing a battery with metallic lithium as negative electrode.

Upon lithium deintercalation,  $\text{LiCoO}_2$  experiences several structural phase change and reaches a state which is not thermodynamically stable at high oxidation level. Thus its use as reversible electrode in batteries is limited to partial deintercalation. This limit appears as a limit potential upon charge, usually close to 4.1 V between positive and negative terminals in commercial batteries (the reason for the floating mode at the end of a galvanostatic charge).

The first steps of these structural changes have been studied for long (see for example Reimers and Dahn, 1992). Works have been performed for looking at the structural changes above the reversibility limit (Ohzuku and Ueda, 1994, (Amatucci et al., 1996) which was still an open

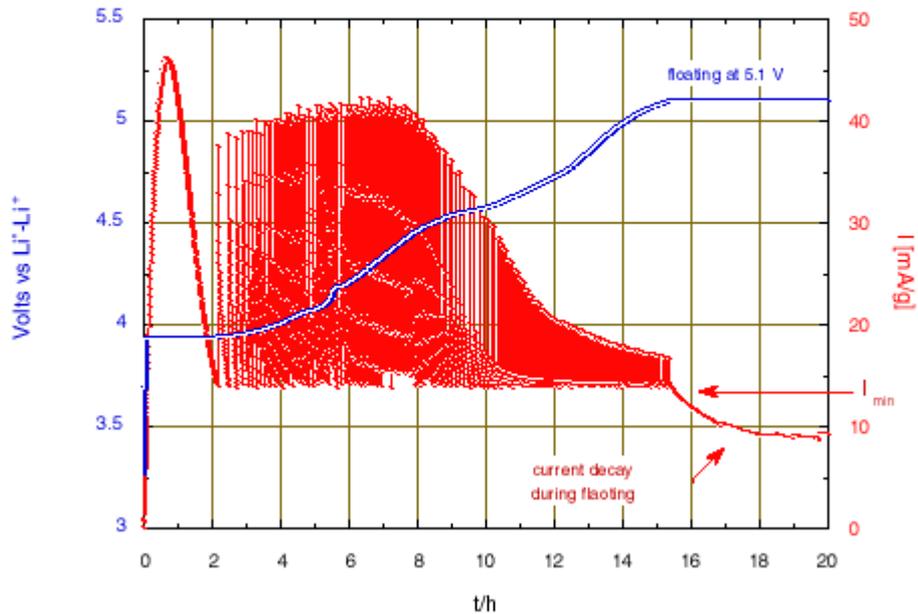
question and studies have been performed to look at its dependence with alloying the Co (Tarascon et al., 1999).

The experiment presented here has been done on a small  $\text{LiCoO}_2$  / Li metal cell , in thin foils form, using an electrolyte that resists to oxidation up to about 5 volts vs  $\text{Li}^0\text{-Li}^+$  (Morcrette et al., 2000). The positive electrode contained 9.8 mg of active material, corresponding to a nominal charge of 2.684 mA.h for complete lithium removal (the theoretical capacity of total Li removal is 274 mA/g for  $\text{LiCoO}_2$ ). Setting a very long duration for the potential levels (100h) occurrence of the steps of potential were in fact governed by reaching the current value that was set as "acceleration" current, here  $I_{\min} = 0.135$  mA, corresponding to a galvanostatic regime close to C/20 (13.7 mA/g). We choose a potential step amplitude of 5 mV to get a high resolution on the incremental capacity voltammogram. The potential limit of the first sequence was initially set to 5.245 V. There was no acceleration current in the second sequence, which means that the potential will then be kept to 2.250 V for the duration that was set to 100h too.

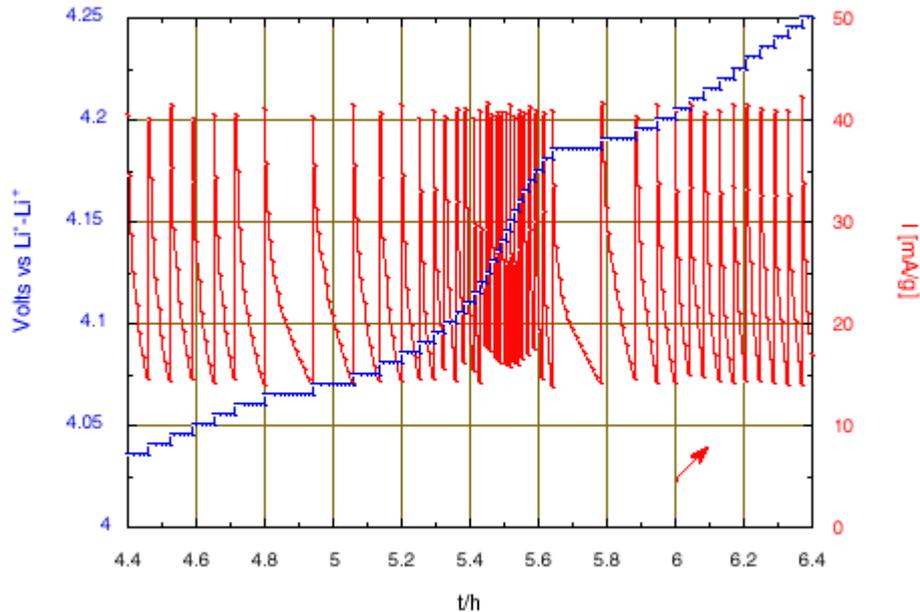
All these conditions lead to the chronoamperometric response reported in the figure below:

Li deintercalation from  $\text{LiCoO}_2$   
using step potential electrochemical spectroscopy

+5 mV potential steps with C/20 equivalent  $I_{\min}$



zoom on the chronoamperometric responses  
when crossing the intermediate phase domain  
around 4.15 V and  $x=0.5$



LiCoO2-Li\_1\_9-11b\_13\_IGx.rpk

The large peak of current that initiate when reaching 3.935 V is due to the nucleation and growth of the new phase under the driving force of the over voltage from the equilibrium two-phase potential. After 2 hours, once the transformation is

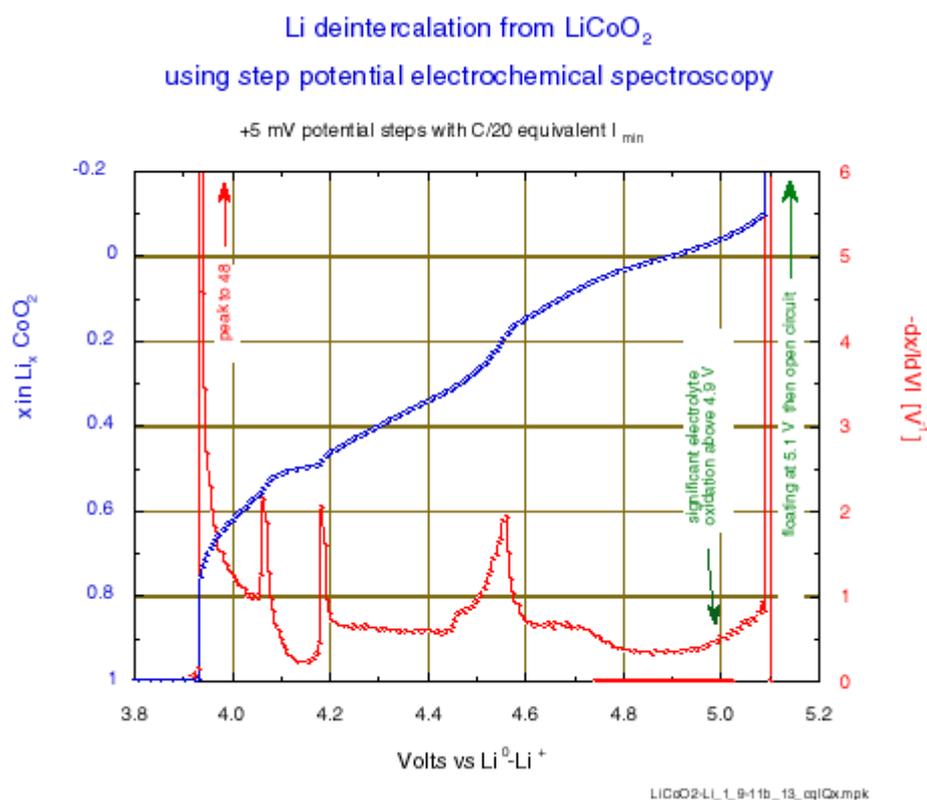
almost completed the potential scan continues. A change of scanning rate is observed after almost 5 hours, when reaching 4.05 V. due to crossing the domain of existence of an intermediate phase. Then much smaller changes of slope were

observed. The slope increase from 4.8 V is attributed to parasitic current due to oxidation of the electrolyte, becoming large at higher potential. Thus the condition has been modified to limit the final floating potential to 5.1 V. The current decay observed during the floating corresponds to a tendency towards equilibrium, but with a constant current contribution due to the progress of the electrolyte oxidation.

The incremental capacity is reported as  $-dx/dV$  per volt, for sake of comparison with others experiments; ie. the charge increments values, obtained by integration of chronoamperometry for each potential level ("Process Data" function, selecting "Compact" option) have been normalized

to the total charge for  $x = 1$ , taking also into account the potential step amplitude.

This representation gives clear evidences of the limits of the various domains of the phase diagram. The first phase transition occurs close to 3.935 V, then entering and leaving the existence domain of the intermediate is observed at 4.060(2) and 4.180(2) V respectively (the potentials where the oxidation peaks initiate). Note that in this domain the minimum of incremental capacity occurs exactly for  $x = 0.5$  which corresponds to perfect lithium ordering. Finally the last phase changes which are still discussed occur in the 4.45 to 4.6 V range, before the last increase of  $-dx/dV$  due to occurrence of the electrolyte oxidation above 4.8 V.



Compared to an incremental capacity determination made by differentiation of the content vs. the potential ( $-dx/dV$ ) from a galvanostatic experiment at a C/50 rate (Reimers and Dahn, 1992), such a step potential electrochemical spectroscopy determination give better results, with narrower and higher peaks of incremental capacity at every transition ( $48 \text{ V}^{-1}$

compared to 29 at the first transition, and above 2 compared to 1.5 at the domain limits of the ordered phase).

And this is obtained in a much shorter time: the effective duration of the total lithium removal was reached in less than 13.5 hours in this experiment. The effective average rate of a step potential spectroscopy experiment with a current

acceleration is effectively of the order of 50% to 70% larger than the rate corresponding to the acceleration current.

This time saving was emphasized by Thompson (1983) and can be understood easily: assuming that for a diffusion controlled process the decay of the current after a potential step is close to an exponential decay (that is true for a RC), within one time constant of duration of the potential level the current decays to about 37% of its initial value whereas the charge that has been passed is close

to 63% its limit value. Thus the effective equivalent rate is 1.7 times larger than the rate corresponding to the current reached before a new potential step.

All these results emphasize the interest of the "GCPL" and "PCGA" protocols, for studying batteries and battery electrode materials.

Note : The figures presented in this section are not issued from the EC-Lab graphic application, but have been done with the Kaleidagraph™ application, from EC-Lab exported Text files.

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