

Hysteresis observed in quasi open-circuit voltage measurements of lithium insertion in hydrogen-containing carbons

Tao Zheng, J.R. Dahn *

Department of Physics, Dalhousie University, Halifax, NS, B3H 3J5 Canada

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Abstract

High capacities with large hysteresis were observed during lithium insertion in hydrogen-containing carbons heated at temperatures near 700 °C. Quasi open-circuit voltage (OCV) measurements were used to study these materials. Using a simple model developed previously [1], we can qualitatively model the result of the OCV measurement. It is believed that the lithium atoms bind near aromatic hydrogen at edge of each graphene layer in the materials. This activated process involves a carbon-carbon bonding change from $(sp)^2$ to $(sp)^3$ leading to large hysteresis during lithium insertion. © 1997 Published by Elsevier Science S.A.

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1. Introduction

Lithium can be inserted reversibly in most carbonaceous materials for lithium-ion battery applications. Recently, we and others, studied lithium insertion in carbons prepared from organic precursors heated from 500 to 1100 °C [2–8]. High capacities for lithium were found in samples pyrolyzed near 700 °C, which contain substantial hydrogen (H/C atomic ratio > 0.1). The majority of this capacity showed large hysteresis—the lithium was inserted near 0 V and removed near 1 V. The capacities exhibiting large hysteresis have been shown to be proportional to the hydrogen content of the samples [2,4]. It is believed that the inserted lithium in hydrogen-containing carbon may bind to a carbon atom which also binds a hydrogen atom [9]. Therefore, a corresponding change to the carbon-carbon bond from $(sp)^2$ to $(sp)^3$ occurs [1]. Bonding changes in the host have been previously shown to cause hysteresis in such electrochemical measurements [10].

In Ref. [1], a simple qualitative model was developed to understand the hysteresis during lithium insertion in hydrogen-containing carbons. This model predicts current and temperature dependent behavior for the electrochemical cells with hydrogen-containing carbon as the cathode and metallic lithium as the anode. We believe there is an activated barrier between the sites for intercalated lithium and the sites near

aromatic hydrogen for bonded lithium. The height of the barrier, E_a , varies linearly with the chemical potential of intercalated lithium in the carbon sample, μ , that is $E_a = E_{a0} + r\mu$, where E_{a0} is a constant and r is an unitless parameter [1]. We also assume that energy of bonding site for lithium near the aromatic hydrogen atoms, E_b , does not change during charge and discharge of the cell. Predictions of this model show that the hysteresis loop closes (or hysteresis is reduced) as the environmental temperature increases or as the discharge/charge current is reduced for Li/carbon cells [1]. Here, we used the quasi OCV measurement to help understand the hysteresis during lithium insertion in hydrogen-containing carbons ever better.

2. Experimental

A typical hydrogen-containing sample made from polyvinyl chloride (PVC) pyrolyzed at 700 °C [2] was chosen to study in this work [2]. Other samples reported in Refs. [1,2] display similar behavior. We called the sample PVC700 (the H/C atomic ratio was 0.2). Electrochemical cells were made with lithium foil as anode electrodes and with cathode electrodes of the carbon samples [2]. Two electrochemical cells made from PVC700 were tested in thermostats at 30 °C.

Quasi OCV measurements were carried out using a MacPile Multichannel galvanostat/potentiostat (Bio-logic,

* Corresponding author.

France). The cell is charged or discharged for a while, then the current is stopped and the cell is allowed to relax, before it is charged or discharged again. Here, cells are charged or discharged for 2 or 4 h with a constant current before the current is stopped. Then the cell is left in the open-circuit state until the magnitude of the change in the voltage with time, dV/dt is less than 0.3 mV/h.

3. Results and discussion

A coin cell containing the PVC700 sample was studied with the MacPile charger at 30 °C. The cell was first cycled once to eliminate the irreversible capacity prior to the relaxation study. The cell was discharged for 2 h with a constant current (CC) corresponding to a 40 h rate before its relaxation. After the cell was tested for about 700 h, a 4 h discharge period was used for the CC discharge instead of a 2 h period. During the charge, the cell was charged with CC for 4 h before relaxation. Fig. 1 shows the voltage plotted versus time for the OCV measurement. The inset in Fig. 1 is the ‘boxed portion’ during discharge in the plotted voltage curve. The inset is divided into two parts by a straight line, which labels when the CC segment was changed from 2 to 4 h long. It is clear that this change does not affect the relaxation data collected for the voltage profile of the OCV measurement.

The voltage profile for the OCV measurement of the PVC700 sample is shown in Fig. 2 compared with that measured with a 40 h rate CC. The voltage profile of the OCV measurement in Fig. 2 is approximately equivalent to that of a CC measurement with a very small CC. The estimated magnitude of this current will be considered later below. In this figure, the low voltage plateau during discharge moves upward by about 0.10 V compared with the CC data, and the

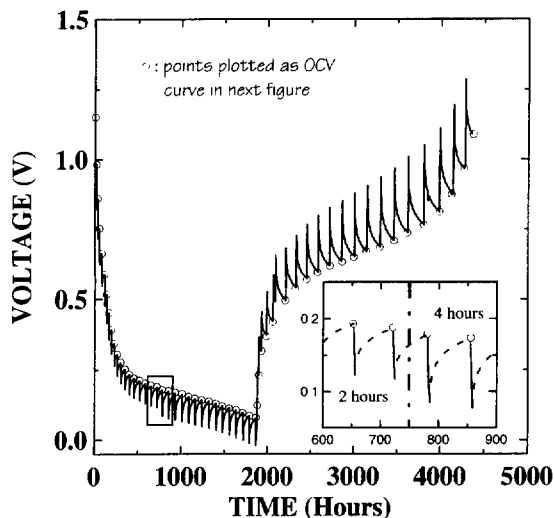


Fig. 1. The voltage is plotted vs. real time for the MacPile experiment on the sample PVC700. The inset enlarges the boxed portion at the left-hand side of the figure. The solid lines in the inset show the CC discharge segments, and the dashed lines show the relaxation parts. The vertically dashed line in the inset labels where the CC segment was changed from 2 to 4 h long. This one-cycle test took about six months.

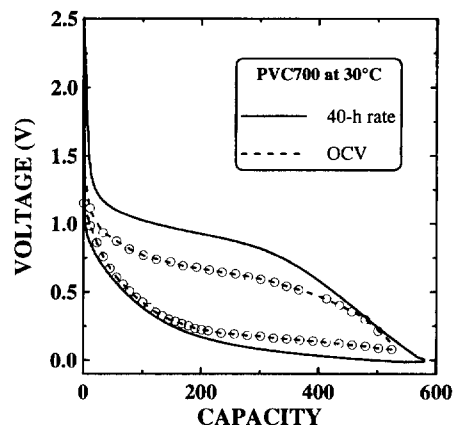


Fig. 2. Voltage profiles for the OCV measurement and for a normal 40 h rate measurement with CC. Open circles show recorded points, as shown in Fig. 1

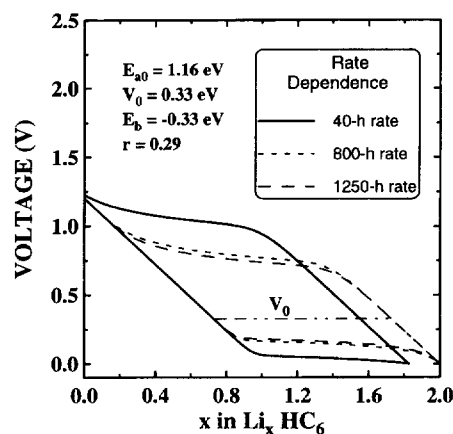


Fig. 3. Cell voltage profiles calculated at 303 K for $r=0.29$, and $E_{a0}=1.16$ eV, $\nu=1.0 \times 10^{15}$, $V_c=1.2$ V, $E_b=-0.33$ eV (or equilibrium voltage $V_0=0.33$ V). Three discharge/charge rates corresponding to $C/40$, $C/800$ and $C/1250$ are shown. The calculations are detailed in Ref. [1].

1 V plateau during charge moves downward by 0.25 V. The plateaus move with different speed. The ratio of the shifts of two plateaus satisfies $r/(1-r)=0.10/0.25$ as described in Ref. [1]. Therefore, $r \approx 0.29$, in approximate agreement with $r \approx 0.33$ which was obtained in Ref. [1]. The hysteresis loop is not symmetric when $r \neq 0.5$. When $r < 0.5$, the charge plateau moves more rapidly towards the equilibrium voltage than the discharge plateau as the current decreases.

Fig. 3 shows calculated cell voltage profiles for CC measurements at 30 °C, based on the model developed in Ref. [1]. The parameters used in this figure are $r=0.29$ (as obtained above), $E_{a0}=1.16$ eV, $\nu=1.0 \times 10^{15}$ /s (during discharge, ν is the rate that lithium crosses from the activated sites to the bonding sites), and $E_b=-0.33$ eV. We also assume that unintercalated carbon has a voltage $V_c=1.2$ V in the model calculation. The meanings of these parameters were carefully described during the derivation of the model in Ref. [1]. The three discharge/charge rates shown correspond to $C/40$, $C/800$ and $C/1250$, respectively. The low voltage plateau moves up about 0.10 V for the $C/800$ case, and the 1 V plateau moves down about 0.25 V for the $C/1250$ case.

Therefore, we expect that the OCV measurement approximately corresponds to a CC measurement with a 1000 h rate.

The quasi OCV measurement in Fig. 1 took about six months, and still the voltage curve displays substantial hysteresis. The model developed in Ref. [1] is capable of explaining this as shown in Fig. 3. We believe this is further confirmation of the success of the model for hysteresis in hydrogen-containing carbons.

4. Conclusions and practical considerations

Carbons heated around 700 °C show large capacities for lithium with significant hysteresis. The OCV measurement showed a current-rate dependence of the hysteresis, which is consistent with the prediction of the simple model we proposed in Ref. [1]. This model suggests an activated process for lithium insertion in hydrogen-containing carbons.

Although the hydrogen-containing carbons show higher capacities, the large hysteresis will affect the efficiency of a real lithium-ion cell during charge and discharge. For example, the cell may charge at 4 V and discharge at 3 V. Therefore, efforts to produce industrially useful hydrogen-containing

carbons for lithium-ion batteries should focus on reducing the activation energy for the lithium bond near hydrogen, for it controls the size of the hysteresis. If the activation energy can be reduced, then excellent carbons for lithium-ion cells can be obtained.

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