

Great reversible capacity of carbon lithium electrode in solid polymer electrolyte

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Abstract

The reversible storage capacity of lithium in a mesophase-derived semi-coke, heat-treated (HTT) below 700 °C, was found by far exceeding the theoretical value corresponding to the LiC_6 composition. A capacity as high as 1660 mAh/g was obtained in the case of carbon, heat-treated at ~450 °C, when poly(ethylene oxide)-based electrolyte is used in lithium cells operated at 100 °C. This great capacity is discussed on the basis of a model where lithium forms multilayers on the external basal surfaces of the nanometric size mesocarbon domains. © 1997 Elsevier Science S.A.

Keywords. Lithium; Semi-coke; Capacity; Polymer electrolytes; Electrodes, Carbon

1. Introduction

Several papers report on carbonaceous materials used as the negative electrode in lithium-ion-type batteries yielding a reversible specific capacity higher than the theoretical 372 mAh/g of LiC_6 [1–4]. Most of these studies were performed in a liquid electrolyte at ambient temperature. The lowest temperature for heat treatment of these carbons was ~700 °C. In this work, we used pitch coal derived semi-coke with low HTT and solid-state polymer electrolyte (POE– LiClO_4) in cells operated at 100 °C. The dimensionally stable interface between lithiated carbon and POE provides a more favorable condition to explore a larger part of the carbon surface which potentially may store lithium.

2. Experimental

Mesocarbon from pitch coal (CP) of ~6 µm in grain size was heat-treated at 450, 500, 700 and 1000 °C under vacuum for several hours. Accordingly the samples are designed as CP450, CP500, CP700 and CP1000. The CP powder was then mixed with carbon black (CB), poly(ethylene oxide) (POE) and LiClO_4 with a weight composition of: CP(60wt.%):CB(10wt.%):POE(23.1wt.%): LiClO_4 -(6.9wt.%). Acetonitrile was added to form a slurry. The

mixture was ground for 1 h into a hermetically closed glass holder filled with zircon beads of 1.5 to 2 mm in diameter. The dispersed slurry was spread onto a stainless-steel disc of 16 mm in diameter. The film was dried in air and under primary vacuum at 120 °C for 5 h. The total weight of the film is 2 to 3 mg and the estimated thickness is 10 µm/mg.

The solid-state test cell consisted of a button type 2430, where a metallic lithium foil with a diameter of 20 mm was used as the negative and reference electrodes. $\text{P}(\text{OE})_8$ – LiClO_4 film of 20 mm (diameter) was pressed onto the carbon electrode at ~80 °C in order to enhance the contact surface. The cell was then assembled and sealed in dry box filled with argon. The test cells were operated at 100 ± 1 °C under a galvanostatic regime (74.4 mA/g of carbon, theoretical C/5 regime) between 5 mV and 1.5 V, or 4 V as the upper potential limit.

3. Results and discussion

In order to evaluate the effect of the upper limit of the voltage applied to the cell on the faraday efficiency (γ_F) (capacity 'out'/capacity 'in') and the reversible capacity Q_{rev} of the active carbon electrode, two potential ranges have been used: (i) 5 mV–1.5 V range, and (ii) 5 mV < E < 4 V.

3.1. 5 mV–1.5 V range

Typical charge/discharge curves are shown in Fig. 1. During the first carbon reduction (lithium 'in'), a semi-plateau

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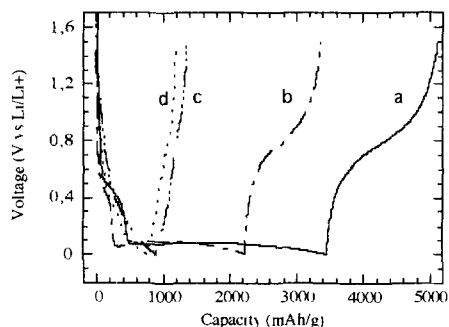


Fig. 1. First galvanostatic discharge/charge cycles ($i = 74.4$ mA/g active carbon) $5 \text{ mV} < E < 1.5 \text{ V}$, $T = 100$ °C obtained with pitch coal heat-treated at: (a) 450 °C; (b) 500 °C; (c) 700 °C, and (d) 1000 °C.

appeared in the 1–0.8 V range, not anymore observed during the following cycles. A great capacity is consumed during this first carbon reduction especially with the CP450 sample. Nevertheless, when the current is reversed, the restored capacity (lithium ‘out’) is also very high. Table 1 gives for each heat-treated carbon, the amount of electricity consumed and restored together with the capacity corresponding to the first 1–0.8 V semi-plateau. The Faraday yield of the first cycle and 10th cycle are also reported.

The most outstanding result is the ultrahigh q_{rev} (charge capacity) value over 1600 mAh/g reached with the semi-coke CP450 sample. With increasing HTT, the capacity decreased to 430 mAh/g for the coke CP1000.

The anisotropic part of soft carbon precursors are essentially composed of basic structure units (BSUs) of small polyaromatic flat layers of ~ 10 Å in size [4]. At HTT < 500 °C, BSUs are randomly distributed in the isotropic mesophase. As the HTT increases, BSUs arrange in plus or minus straight columns. The coherence length in the perpendicular direction to the basal layers (L_c) tends to increase, while hetero-atoms (such as oxygen and nitrogen) evolve in gaseous forms. At 800 °C, the carbon content is greater than 96%, the remaining atom being mainly hydrogen. Such nanoscopic carbon has a very high surface/volume ratio. Therefore, lithium should be stored mainly on the surface since the intercalated part would account for 372 mAh/g. It is known from the reactivity of polyaromatic molecules with strongly electron donors species such as alkali metals, that the stabilizing reaction results from the electron transfer to delocalized π electron clouds. Such a phenomenon is well documented in graphite-intercalation compounds as in the MC_{6n} and MC_{8n} staging phases with alkali metals M.

Table 1

Characteristic data of the galvanostatic discharge/charge cycling of the Li/POE–LiClO₄/CP cells operated at 100 °C, $5 \text{ mV} < E < 1.5 \text{ V}$

Sample	1 V–0.8 V semi-plateau capacity (mAh/g)	First discharge capacity (mAh/g)	Charge capacity (mAh/g)	Faraday yield of first cycle (%)	Faraday yield of tenth cycle (%)
CP450	460	3457	1660	48.2	93
CP500	270	2229	1138	51.1	95
CP700	No	895	460	51.4	99.6
CP1000	No	754	438	58.1	99.9

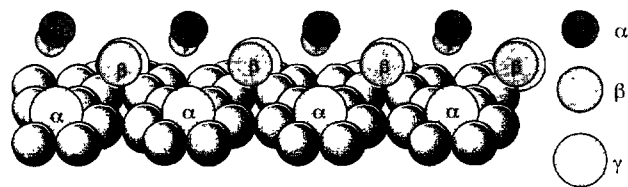


Fig. 2. Schematic representation of the lithium multi-layer formation on the external basal carbon planes

In order to stabilize lithium on the (a, b) layer with help of the charge transfer we suggested that tri-metal layers α , β , γ might be formed with an epi-taxial arrangement as shown in Fig. 2. Multi-layer formation on the graphite external layers has been reported with several organic molecules [5]. In the case of highly electron donor species such as lithium, a charge transfer should be expected between each lithium and the facing carbon hexagon. However, due to increased distances between lithium and the carbon sheet, the charge transfer should decrease from the first (closest: α) to the second (medium: β) and the third (external: γ) layers.

The ionicity of lithium should then decrease which means that the external layer should have a stronger metallic character. The Li–Li distance between adjacent layers is that which minimize the total energy being is the sum of an attractive term (Li–C) and a repulsive term (Li–Li). Following this model, if excess lithium is deposited on the previously formed α , β , γ layers, it should have a stronger metallic character; the carbon hexagons being screened by the three layers, leaving no possibility to a further charge transfer.

At low HTT, BSUs arrange in one to three stacking layers [4]. If a total of six lithium layers are formed (three on each face), the theoretical composition is respectively Li_6C_6 , Li_6C_{12} and Li_6C_{18} . The corresponding capacity is 2232, 1116 and 744 mAh/g. Therefore, assuming the multi-layer model, BSUs here could be composed of 43% of monolayers and 57% of bi-layers to achieve 1660 mAh/g.

3.2. $5 \text{ mV} < 4 \text{ V}$

When the upper voltage limit is extended to 4 V with CP450, an additional capacity is restored as shown in Fig. 3. A second semi-plateau appeared in the 3.5–4 V range during the oxidation step extending the restored specific capacity to 2210 mAh/g to be compared with 1666 mAh/g for the previous section. As a consequence, the faraday yield γ_{F1}

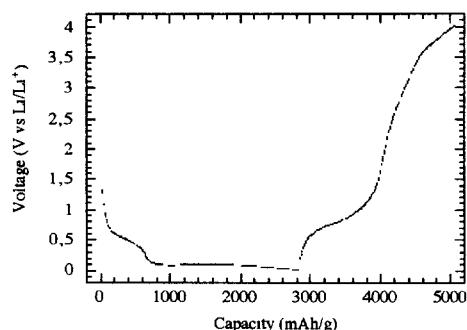


Fig. 3. First galvanostatic discharge/charge cycle of pitch coal heat-treated at $= 450\text{ }^{\circ}\text{C}$, $i = 74,4\text{ mA/g}$ active carbon and $5\text{ mV} < E < 4\text{ V}$, $T = 100\text{ }^{\circ}\text{C}$.

reached 78% instead of 48.2%. The lithium restored in the 3.5–4 V segment should partially account for the loss capacity during the first cycling. Because of the differences in energy needed to re-oxidize lithium, a stronger binding energy should be built up. In a recent paper, we have showed by impedance measurements that during the first reduction, the interfacial impedance tends to decrease as the amount of transferred lithium increased. We attributed such a result to the increased wetting of the carbon surface by the ionically conducting polymer. Such a phenomenon was addressed to as the ‘Zipper model’ where lithium tends to bind carbon to

the polymer through the formation of C–Li–O surface bonding. Lithium involved in such a bonding should be energetically more stable than the transfer-charge type lithium. We attribute the 3.5–4 V semi-plateau to the removal of the binding lithium at the carbon–polymer interface. As a matter of fact, if after re-oxidation at 4 V a following cycle is performed between 5 mV and 1.5 V, a part of lithium is lost again as a result of reformation of the surface binding lithium in a similar way as for the virgin state. Therefore, lithium used as the interfacial binder (Zipper model) is reversible only between 1.5 mV and 4 V which obviously is not of interest in practical lithium-ion batteries.

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