

# A new approach for the preparation of anodes for Li-ion batteries based on activated hard carbon cloth with pore design

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## Abstract

We demonstrate herein the possibility to prepare carbon anodes for Li-ion batteries using simple carbonized polymeric precursors such as cotton and phenolic cloths. Activation by controlled oxidation forms highly porous carbons whose electrochemical activity in Li salt solutions is mostly an irreversible reduction of solution species and double layer charging. Treating these porous carbons by chemical vapor deposition (CVD) of carbon on their surfaces, closes the pores in a way that they can insert Li-ions, but not solution species. These general carbon engineering processes form new carbons with nanoscopic, selectively closed pores, which can serve as highly reversible anode materials for Li-ion batteries, with relatively low irreversible capacity. The capacity of these electrodes depends on the nature of the carbon CVD process. This paper describes the scheme for carbon engineering, gas adsorption measurements that demonstrate the impact of the carbon CVD process, and the relevant changes in the structure of the pores and some preliminary electrochemical measurements in non-aqueous Li salt solutions.

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## 1. Introduction

The most commonly used anode material for Li-ion batteries is graphite, which can insert lithium reversibly at an initial capacity of 372 mAh/g. Graphite as an electrode material has some drawbacks, such as limited stability due to its fragile structure, high sensitivity to the electrolyte solutions, and, of course, limited capacity (only about 10% of that of Li metal anodes) [1].

Over the years, many research groups and industries tried to develop alternative carbons that can insert Li at higher capacity compared to graphite, and that can be more robust during repeated Li insertion–deinsertion in a wide spectrum of Li electrolyte solutions [2]. A large variety of disordered, soft and hard carbons that can insert Li reversibly at capacities twice as high as the capacity of graphite were tested in recent years [3,4]. Another direction in the fabrication of improved carbon anodes for Li-ion batteries relates to surface treatments of graphite materials (e.g. a mild oxidation of graphite particles which makes their surface to be slightly porous [5], surface treatment of graphite particles by surfactants [6] and metallic particles [7], which improve the electrodes'

passivation). In this work, we developed methods of carbon engineering that can produce highly porous carbons that can insert Li-ions reversibly and very specifically while screening out solution species. Simple polymeric species such as cotton cloth can be easily carbonized, thus forming monolytic, integral conductive carbon electrodes. Furthermore activation (mild oxidation) produces highly porous carbons whose major electrochemical activity in non-aqueous Li salt solutions is an irreversible reduction of solution species. However, by treating these porous carbons by chemical vapor deposition (CVD) of carbon on their surface [8], it is possible to partially close the pores in a way that they can insert lithium, but not solution species (i.e. low irreversible capacity), as is illustrated in Fig. 1. This paper describes such efforts. The properties of the carbonaceous materials produced were studied by both gas adsorption techniques [9] and voltammetry, in non-aqueous Li salt solutions. The morphology of the electrodes was explored by atomic force microscopy (AFM).

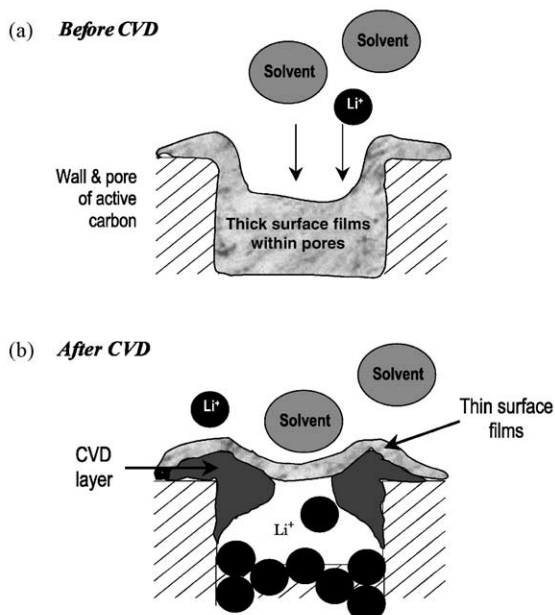
## 2. Experimental

We used highly activated carbon cloth, based on a phenolic precursor (type SC2225, distributed by Spectracorp, USA). It has a surface area (BET model) of 1650 m<sup>2</sup>/g, and

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### A porous carbon electrode



Superficial CVD enables stereo-selective Li insertion into closed pores on the carbon after formation of thin passivating surface films.

Fig. 1. (a) An illustration of a pristine porous active carbon whose pores are filled by insoluble reduction products of solution species, which form surface films. (b) An illustration of the desired Li insertion process into a porous carbon whose pores were partially closed by carbon CVD. Only Li ions can be inserted (reversibly) into the pores.

a pore size far larger than that of the usual non-aqueous solvent molecules ( $>5 \text{ \AA}$ ). The CVD process was carried out by saturating a stream of Argon (80 ml/min) with toluene at  $0^\circ\text{C}$ . The gas blend was passed over the sample in a rotary oven ( $0.15\text{--}0.35 \text{ s}^{-1}$ ) after being preheated to  $1000^\circ\text{C}$ .

The sample was first heated to  $1000^\circ\text{C}$  under Ar flow for about 30 min in order to remove the air, water vapor, and various surface groups. Then, Ar flow was bubbled throughout the toluene trap.

We also prepared carbon electrodes based on carbonization of cotton cloth at  $1050^\circ\text{C}$  followed by activation with  $\text{CO}_2$  (mild oxidation) at  $900^\circ\text{C}$  which makes the carbon highly porous. For this purpose, a temperature programmable tubular oven was operated under controlled atmosphere.

The BET area of the carbons before and after CVD was measured using a Gemini 2375 surface analyzer (Micromeritics, Inc.), which employs  $\text{N}_2$  adsorption at 77 K.

Gas adsorption isotherms and kinetics were measured in a standard volumetric vacuum system made of Pyrex glass, for the analysis of the properties of the micro-pores. The gases,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$ , were chosen as molecular probes according to their molecular size ( $\text{N}_2 > \text{O}_2 > \text{CO}_2$ ). Adsorption kinetics were measured by monitoring gas pressure drop versus time in volume calibrated adsorption and admission cells.

The electrochemical behavior of these materials was measured by cyclic voltammetry (PGSTAT Autolabsystem from Ecco Chemie, Inc.) of the carbon electrodes (4 mg) in non-aqueous  $\text{LiAsF}_6$ , EC–DMC 1:1 solutions, under argon atmosphere in three-electrode cells (versus Li reference and counter electrodes). The contact resistance was negligible for the small currents employed.

AFM images of the carbon samples were obtained with the pico-SPM instrument from Molecular Imaging, Inc. (USA).

### 3. Results and discussion

In the carbon studied, there are three locations into which lithium can be inserted: the activated carbon substrate, the

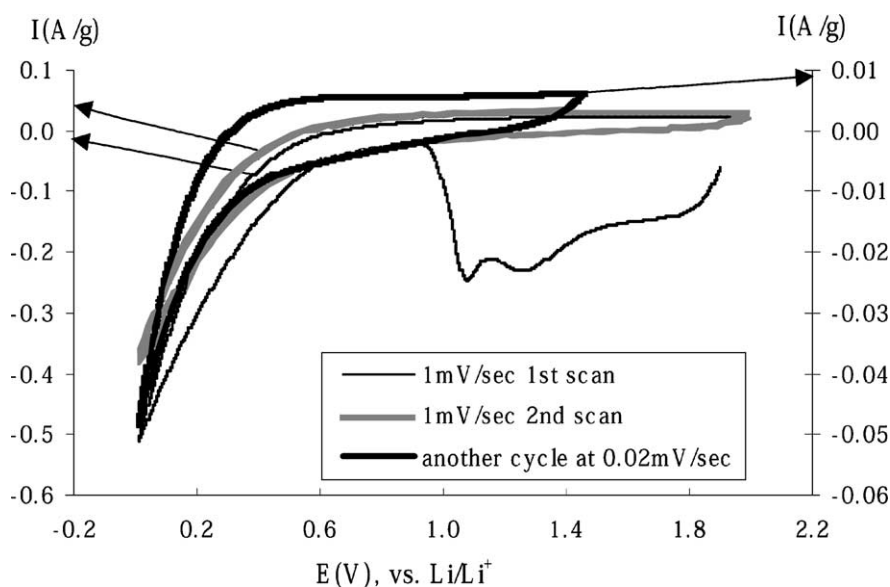


Fig. 2. Cyclic voltammograms of SC2225 activated carbon cloth electrodes after heating in Argon at  $1000^\circ\text{C}$  for 1.5 h (no CVD). Scan rates: 1st and 2nd cycles at 1 mV/s; 8th cycle at 0.02 mV/s.

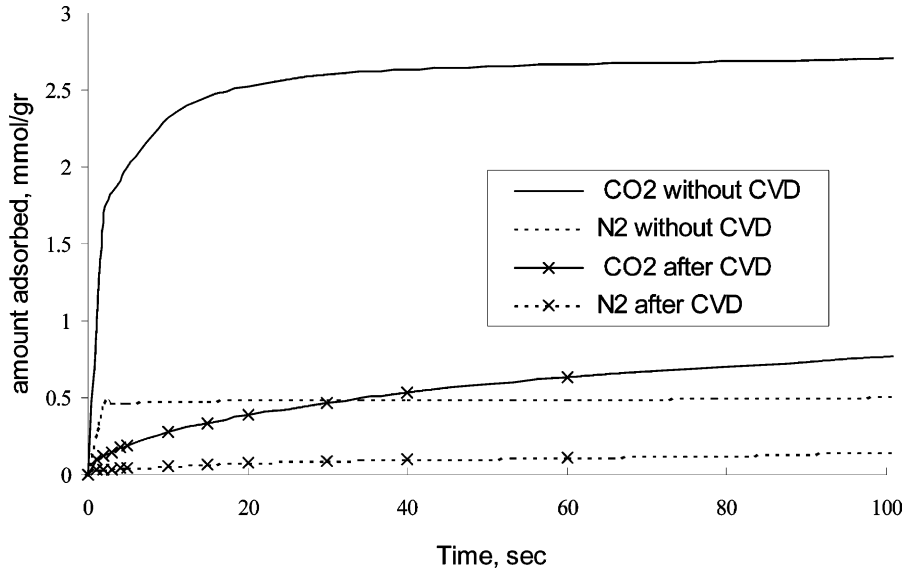


Fig. 3. The adsorption of  $N_2$  and  $CO_2$  on the activated carbon cloth at 298 K before and after CVD of 1 h. The amount of gas adsorbed is plotted as a function of time.

micro-pores and the CVD deposit. The desired effect is the insertion of Li into the micro-pores. Therefore, we performed separate experiments to examine where Li insertion takes place. For this purpose, a layer of carbon was deposited by CVD on glassy carbon rod electrodes at the same conditions selected for the process with the active carbon cloth electrodes. These electrodes were then studied by cyclic voltammetry in a Li salt solution. It did not show any reversible Li insertion capacity, and neither did the pristine glassy carbon electrode (before the CVD process). The glassy carbon electrodes, both treated and untreated, showed an irreversible

voltammetric cathodic wave at potentials below 1.5 V, which relate to reduction of solution species [10].

The typical voltammetric behavior of the active carbon cloth electrodes before the CVD treatment is presented in Fig. 2. The voltammograms of these electrodes show an extensive irreversible cathodic wave, which relates to the reduction of the alkyl carbonate solvent and the  $AsF_6^-$  anion, but not to any process that may be assigned as a reversible Li insertion into the carbon.

The development of a desired pore system by the CVD process is demonstrated in Fig. 3, which show the kinetics of

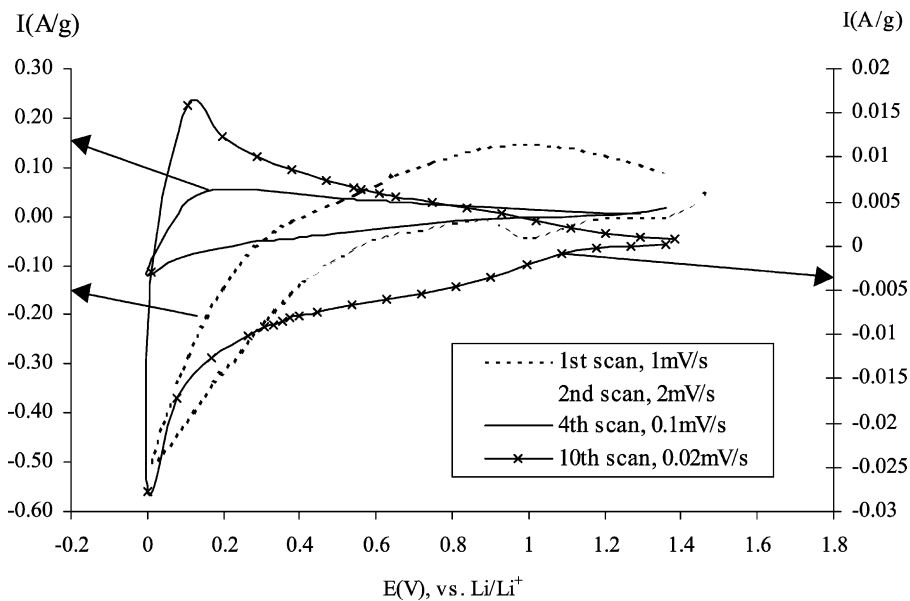


Fig. 4. Cyclic voltammograms of a carbon cloth electrode (SC2225) after being treated by the CVD process for 1 h. Scan rates: 1st and 2nd cycles at 1 mV/s; 6th cycle at 0.1 mV/s; 10th cycle at 0.02 mV/s.

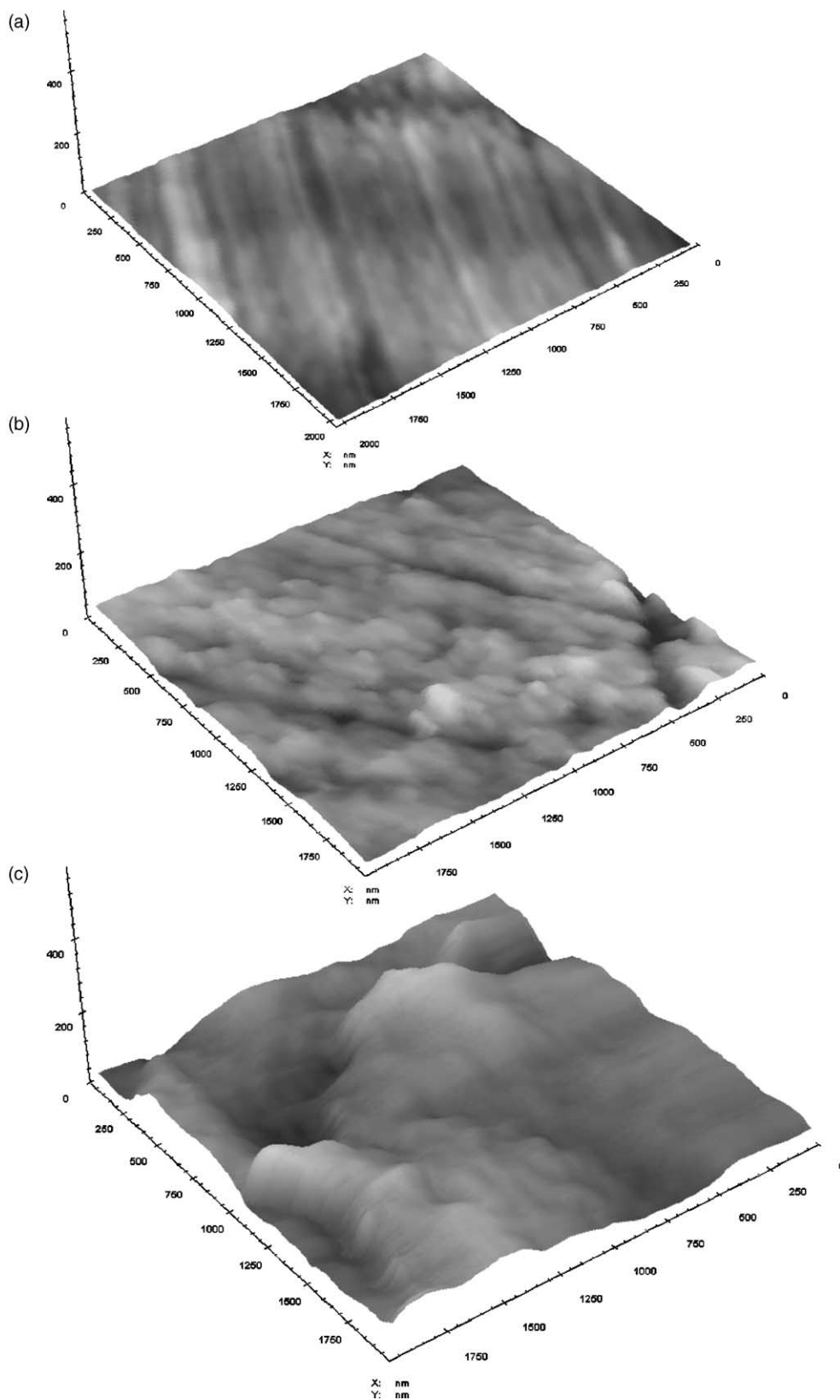


Fig. 5. AFM images ( $2\ \mu\text{m} \times 2\ \mu\text{m}$ ) of the carbon electrodes. The outer walls of fibers are seen: (a) pristine; (b) after 1 h CVD; (c) after 2 h CVD.

adsorption of  $N_2$  and  $CO_2$  at 25 °C into the carbon cloth samples [9] before and after CVD. As a qualitative measure of the adsorption rates, we observe the initial slopes of the curves of gas adsorbed versus time (thereafter, the approach to equilibrium reduces the slope of these curves). The effect of the treatment of the porous carbons by the carbon CVD processes, on the initial slope of the amount of gas adsorbed versus  $t$ -plots is clearly evident. The adsorption of  $CO_2$  is always more intensive than that of  $N_2$  because of stronger and faster interactions with the porous surface due to the smaller effective dimension of  $CO_2$  (compared to  $N_2$ ). However, without a detailed and successful model, it is difficult to tell whether the CVD layer is superficial as desired, or had penetrated into the pores (and to what extent). In any event, from the response of the treated carbons towards gas adsorption it seems clear that a great part of the pores became partially closed due to the CVD process.

Fig. 4 shows cyclic voltammograms of a carbon cloth electrode after a CVD process of 1 h. The build-up of a reversible capacity related to Li insertion at the slow sweep rate is clearly seen. This behavior is totally different from the behavior of the untreated carbon seen in Fig. 2. Of a special interest is the fact that the irreversible process for the CVD-treated electrode is considerably smaller compared with that of the untreated electrode (compare the charges involved in the irreversible peaks around 1.2–0.9 V versus Li/Li<sup>+</sup>, in Figs. 2 and 4). These changes are likely due to clogging the pores with a carbon layer precipitated by the CVD process, which prevents the build-up of the surface films by reduction of solution species within the pores. We could obtain with these electrodes a reversible capacity of Li insertion–deinsertion around 130 mAh/g.

With electrodes treated by CVD processes at longer times, 1.5 h, a similar behavior to that seen in Fig. 4 was obtained, but the irreversible capacity was greater, probably indicating that the CVD layer in this case is porous, and hence more reduction of solution species is required before passivation is reached (by surface films) [11].

The results of CVD processes in which a rotary oven was used, were not remarkably different from those obtained with CVD at a stationary, non-rotating oven. The only difference found in the behavior of electrodes treated by CVD in a rotary oven or in a stationary oven, was a significantly smaller irreversible capacity related to the former case. This can be attributed to the different geometries of the two reactors.

Application of prolonged CVD processes (e.g. >1.5 h) resulted in the preparation of electrodes, which exhibit significantly slower kinetics. It should be noted that when the electrodes were treated by CVD during 2 h, the charging–discharging kinetics were so slow that it was hardly possible to obtain Li insertion and deinsertion. This indicates that an intensive CVD process reduces the Li-ion insertion rates, probably because the CVD layer becomes too thick, and hence, becomes a barrier for Li-ion insertion into the pores.

The structure of the CVD was studied by XRD measurements of the carbon electrodes before and after CVD. In both cases the patterns are those of amorphous carbons.

The electrodes' morphology was studied by atomic force microscopy.

In Fig. 5a, the AFM image of the pristine carbon cloth shows clearly the basic structure of the irregularities of the spinneret holes used to produce the phenol formaldehyde fibers, from which the carbon precursor was prepared.

Fig. 5b shows the irregular growth of the CVD carbon layer which covers the basic structure. Fig. 5c shows the more extensive CVD growth, which yields an irregular, thick carbon layer. The relatively low reversible capacity of Li insertion into the carbon samples can be explained by the morphology of the CVD carbon layers: In spite of the fact that an amount of several monolayers of carbon is deposited in the present processes, the irregular deposition of the carbon layers cannot cover the majority of the wide open pores, thus leading to the deleterious pore filling with solvent reduction products. Hence, in order to obtain high Li insertion capacity with these electrodes, we have to modify the CVD process so as to get a homogeneous, non-penetrating layer.

#### 4. Conclusion

We could obtain a reversible Li insertion into highly activated micro-porous hard carbons by forming a surface layer of carbon on activated carbon by CVD processes. Precipitation on surface carbon layers by CVD on the porous carbon closes the micro-pore openings by forming a stereo-selective Li permeable layer. The theoretical capacity should be that of pore volume filled with metallic Li (about 1400 mAh/g carbon having a specific micro-pore volume of 0.5 ml/g). At present, both pore penetration and incomplete coverage by the CVD material limit the reversible capacity to about 10% of the theoretical value with ~80% efficiency. Optimization of the complex set of CVD parameters should bring about a significant improvement in the reversible capacity of Li insertion into these carbons.

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