

## Improved Carbon Anode for Lithium Batteries Pretreatment of Carbon Particles in a Polyelectrolyte Solution

Miran Gaberscek,<sup>a,\*</sup> Marjan Bele,<sup>a</sup> Jernej Drofenik,<sup>a</sup> Robert Dominko,<sup>a</sup> and Stane Pejovnik<sup>a,b</sup>

<sup>a</sup>National Institute of Chemistry, SI-1000 Ljubljana, Slovenia

<sup>b</sup>Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

A novel approach to reduce irreversible Li loss due to carbon anode passivation is described. The graphite particles for use as anode material are pretreated in an aqueous solution of a polyelectrolyte. The polyelectrolyte (gelatin) molecules adsorb onto the particle surface and have a significant impact on anode passivation, as well as on the binding properties of the carbon particles, *i.e.*, gelatin also serves as a particle binder. The reversible capacity of pretreated electrodes is similar to the reversible capacity of conventional electrodes, but the irreversible capacity losses are much smaller and limited to the first charge/discharge cycle.

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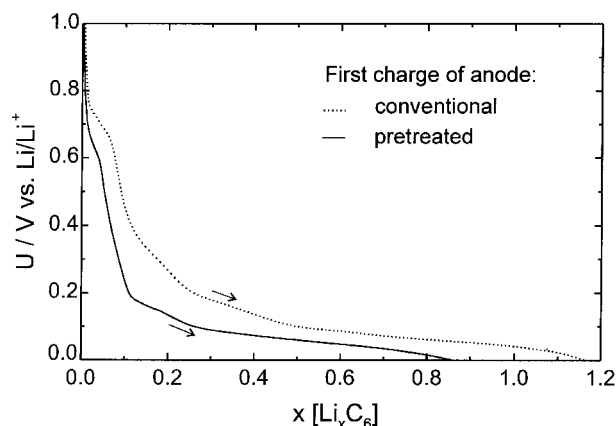
The problem of irreversible capacity losses due to electrolyte degradation and subsequent passivation of the carbon anode during first cycles of Li-ion battery operation has been addressed in several ways. A general approach has been to find an appropriate electrolyte composition for use with the specific type of carbon used.<sup>1-6</sup> Another approach has been the introduction of various electrolyte additives, such as crown ethers,<sup>1,7</sup> phosphorus,<sup>8</sup> CO<sub>2</sub>,<sup>9-11</sup> and N<sub>2</sub>O.<sup>12</sup> In very recent investigations, the pretreatment of carbon particle surfaces has been shown to be an effective way to influence the anode passivation mechanism. The pretreatment may involve procedures such as heating of samples in atmospheres of controlled composition,<sup>13</sup> mild oxidation of graphites,<sup>14-16</sup> silylation of hydroxyl groups,<sup>16</sup> etc.

In this paper, an entirely new approach to the reduction of irreversible lithium losses is described. Carbon particles to be used in the preparation of anodes are pretreated in an aqueous solution of a polyelectrolyte. The polyelectrolyte molecules are adsorbed onto the carbon particle surfaces as a thin uniform layer with individual chains protruding into the solution. As shown in the Results section, such a layer has a remarkable effect on the passivation mechanism. Furthermore, it is shown that the adsorbed polyelectrolyte molecules can serve as a binder between carbon particles so that no traditional binder need be added during electrode preparation. The surface pretreatment procedure is simple and involves inexpensive and environmentally friendly materials only, so it may have potential for use on an industrial scale.

### Experimental

Detailed preparation of the water-based polyelectrolyte solution used in the present study is described elsewhere.<sup>17</sup> The polyelectrolyte used was gelatin no. 48722 (Fluka) with various types of active groups (cationic, anionic, and also nonionic), all capable of serving as nucleation sites for passive film formation. Experimental conditions (concentration, pH, temperature, etc.), under which a maximum adsorption of polyelectrolyte molecules onto the surface of graphite particles occurred, were carefully selected on the basis of many preliminary tests. We have reported that good results can be obtained in the gelatin concentration range 0.01-1%, with  $7 \leq \text{pH} \leq 9$  and temperature from 30 to 100°C.<sup>17</sup> Graphite particles SFG44 as received from Timcal were immersed for about 30 min in the polyelectrolyte solution. The slurry obtained after filtering was partially dried and pressed onto a copper substrate (12  $\mu\text{m}$  thick) at 1000 kPa to obtain a layer of active material  $\sim 50 \mu\text{m}$  thick. Prior to use, the anodes were dried in vacuum at 100°C for 10-12 h.

To evaluate the effect of electrode pretreatment, reference anodes based on the same active material (SFG44 from Timcal) were made. The active material was mixed with a Teflon slurry (Aldrich) and ethanol in such proportions that the final binder content was 6.5 wt



**Figure 1.** First charge of the anode prepared from the polyelectrolyte-pretreated graphite particles and of the conventional graphite anode prepared with Teflon as a binder. The current density was 250  $\mu\text{A cm}^{-2}$  (corresponding to  $\sim C/3$ ).

%. Further treatment of the slurry was the same as in pretreated graphite. In all cases, the electrolyte used was a 1 M solution of LiPF<sub>6</sub> in EC:DMC (1:1 ratio by volume), as received from Merck.

A laboratory-made three-electrode test cell was used to carry out the electrochemical tests. The cell housing was made of Teflon, whereas the electrode holders, which also served as contacts, were made from stainless steel. The sealing was provided using O-rings. Constant pressure on the electrodes was realized through implementation of a relatively large counter electrode holder which was not fixed in the cell but was allowed to press, through its weight, on the sandwiched electrodes. The pressure on the electrodes was  $\sim 5 \text{ N cm}^{-2}$ . The working and counter lithium electrodes were held apart with two separators (Celgard no. 2402) between which a thin strip of lithium serving as a reference electrode was positioned.

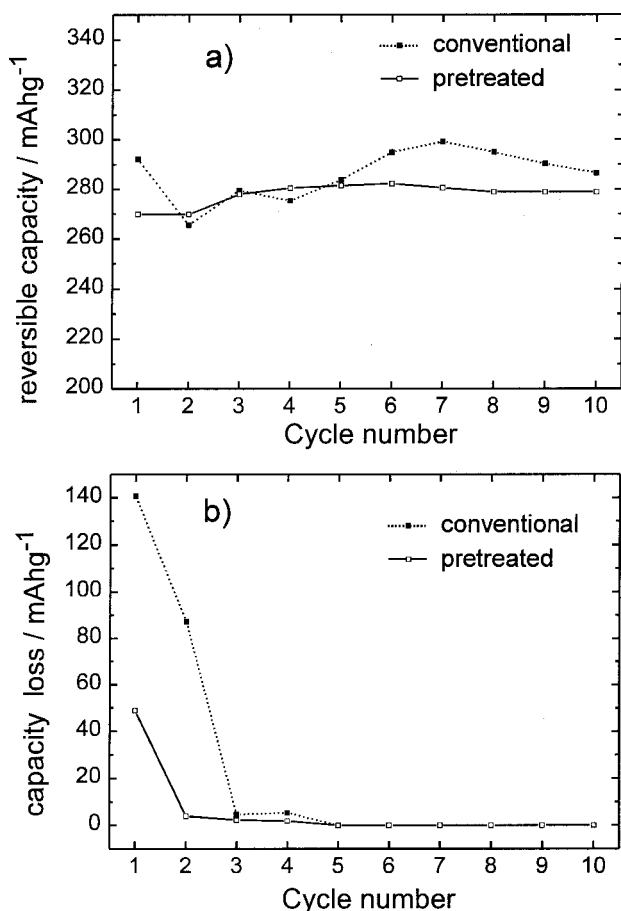
Charge-discharge curves and impedance spectra were recorded using Solartron's 1286 electrochemical interface and 1250 frequency-response analyzer. The constant current during cell cycling was either 50 or 125 mA (corresponding to the C/7 and C/3 rates, respectively), and the geometric surface area of the working electrode was always 0.5 cm<sup>2</sup>. Impedance spectra were recorded at several anode potentials selected on the basis of the shapes of charge-discharge curves.

### Results and Discussion

The first charge/discharge cycles of a conventional anode (CA) prepared using a Teflon binder and an anode prepared from polyelectrolyte-pretreated graphite (PPA) are shown in Fig. 1. In the for-

\* Electrochemical Society Active Member.

z E-mail: miran.gaberscek@ki.si

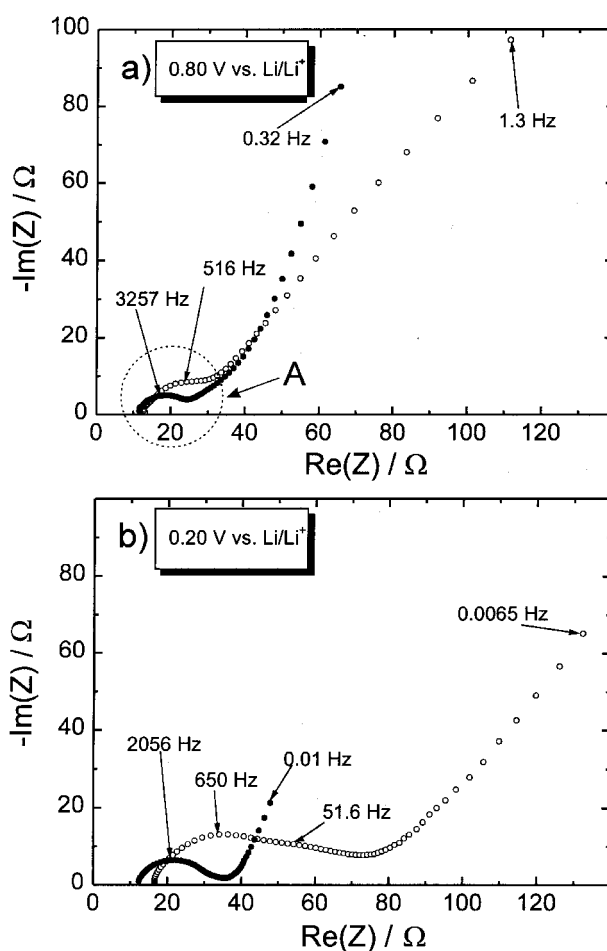


**Figure 2.** (a) Reversible capacity and (b) irreversible capacity loss for the anode prepared from the pretreated graphite particles and for the conventionally prepared anode during first 10 charge/discharge cycles. The current density was 250  $\mu\text{A cm}^{-2}$  (corresponding to  $\sim C/3$ ).

mer case, the irreversible losses are about 32%, whereas the first-cycle losses of the PPA are only about 15%. Both numbers correlate well with the sizes of the “humps” observed during the first charge at potentials between 0.8 and 0.2 V, which are usually related to passive film formation. The humps are much less pronounced in PPA, *i.e.*, much less charge is consumed by the passivation of PPA compared to the passivation of CA.

The values of reversible and irreversible capacity as functions of cycle number for both CA and PPA are displayed in Fig. 2. During the first 10 cycles, the reversible capacity (Fig. 2a) for CA is slightly higher (between 270 and 300 mA h/g) than that for PPA (between 270 and 280 mA h/g). However, the irreversible capacity losses during the first few cycles (Fig. 2b) are much lower for PPA than for CA which, again, indicates that much less charge is lost due to formation of the passive film on PPA.

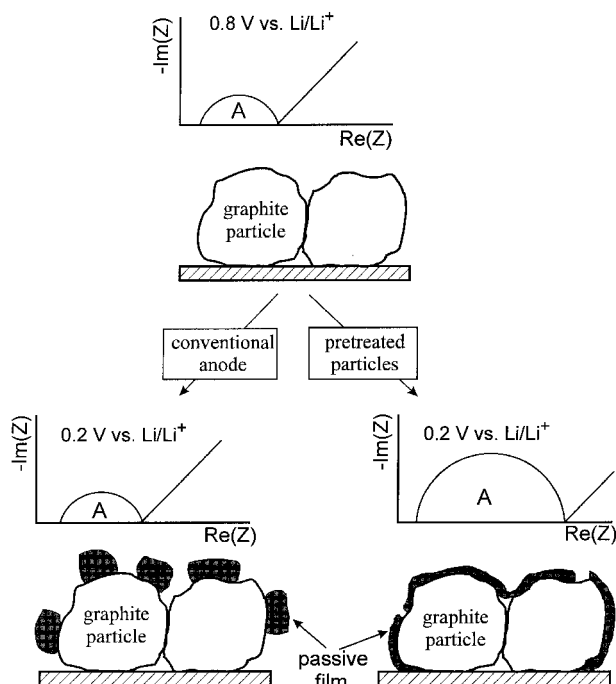
Further information about passive film formation can be deduced by comparing the impedance spectra recorded before and after passivation, in our case at potentials of about 0.8 and 0.2 V, respectively (Fig. 3). It can be seen that in PPA, the magnitude of the impedance arc designated “A” increases significantly during passivation (Fig. 3a). By contrast, the magnitude of arc A changes only slightly in CA (Fig. 3b). According to a generalized passivation model shown in a previous paper,<sup>18</sup> we assume that arc A appearing in the frequency range of about 1000 to 10 Hz represents the overall resistance/capacitance properties of the anode-electrolyte interface. The model considers time variation of impedance spectra from the state



**Figure 3.** Impedance spectra of the pretreated (○) and conventional (●) anode at (a) 0.8 and (b) 0.2 V vs. reference Li electrode. In both cases, the geometrical surface area of anode was 0.5 cm<sup>2</sup>.

before the beginning of passivation to a state of a fully passivated electrode. In this case, the beginning and final states are described as follows: prior to passivation, A represents the resistance of Li<sup>+</sup> insertion/deinsertion process coupled with the double-layer capacitance; if, however, the electrode is completely passivated, A basically represents Li<sup>+</sup> migration coupled with dielectric displacement within the passive film. In terms of such a model, and taking into account the results shown in Fig. 1-3, the passivation schemes shown in Fig. 4 can be proposed. The small changes in A during passivation together with the large irreversible charge for CA (Fig. 2b) is explained by the formation of a relatively small number of large crystallites of passive film which do not completely cover the surfaces of the graphite particles. By contrast, the more pronounced changes in A and the smaller irreversible charge for PPA (Fig. 2b) imply the formation of a relatively large number of smaller crystallites resulting in a thin film covering most of the graphite particle surfaces. The large surface density of crystallites correlates with the large density of active groups on the polyelectrolyte molecules adsorbed on carbon particles.

An important side effect of the polyelectrolyte pretreatment of graphite particles, as proposed in the present investigation, is that no special binder is needed to prepare the anode. Namely, the polyelectrolyte molecules also serve as a glue which binds the carbon particles together in a similar way as does Teflon (PTFE) or poly(vinylidene fluoride) (PVDF). Because the polyelectrolyte content in the anode material does not exceed 1 wt %, in PPA a higher percentage



**Figure 4.** A simple model explaining the results shown in Fig. 1-3.

of anode material is electrochemically active than in CA. The binding mechanism due to the polyelectrolyte molecules is a subject of current investigation.

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