

# Improved carbon anode properties: pretreatment of particles in polyelectrolyte solution

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## Abstract

It is shown that the properties of carbon anode can be significantly influenced if the carbon particles are pretreated in an appropriate polyelectrolyte solution. Various polyelectrolytes, such as gelatine, different polyanilines and cellulose have been tested. The total content of the polyelectrolyte in the final anode is between 1–2 wt.%. No classical binder is needed to prepare mechanically and electrochemically stable anodes. The polyelectrolyte pretreatment decreases the first cycle(s) capacity loss(es), probably due to formation of a more uniform passive film, the growth of which is governed by the presence of polyelectrolyte molecules. It is shown that the efficiency of polyelectrolyte pretreatment depends on the type of polyelectrolyte used, on the concentration, Bloom value, and on pH of the polyelectrolyte solution used in the pretreatment procedure and on the electrolyte used to prepare the electrochemical cell. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Formation of a passive film on carbon anodes depends on various parameters, such as selection of electrolyte composition [1–3], electrolyte modification using additives [4–7], the type of carbon used [4], and on the pretreatment of carbon particles leading to appropriate surface modification [8–10].

Recently [11,12], we have shown that gelatine pretreatment of carbon particles has a significant influence on anode performance. Basically, the pretreatment procedure involves immersion of carbon particles into a gelatine solution of known composition, concentration, pH, temperature, Bloom value, etc. for a known time. The slurry obtained after partial drying is directly pressed on a copper substrate, i.e. no additional binder needs to be added to prepare mechanically and electrochemically stable anodes. During the pretreatment, gelatine is uniformly adsorbed on the surface of carbon particles. The role of adsorbed gelatine is two-fold: it binds the carbon particles together, thus, replacing the conventional binder (PTFE, PVDF) while, at the same time,

it decreases the irreversible loss(es) during the first cycle(s) [11,12]. The latter has been explained through formation of a thin uniform passive film rather than a coarse and porous layer occurring on non-treated particles [11]. Another important point of the proposed gelatine pretreatment procedure is the fact that the final content of gelatine in anode material is not >2%, the rest being the active carbon material.

In the present paper, we show briefly that the efficiency of the new procedure depends on many parameters related to the procedure itself (gelatine type, concentration, Bloom value and pH), on the selection of electrolyte composition and, finally, on the type of polyelectrolyte selected (polyanilines instead of gelatine have been used).

## 2. Experimental

As active anode material, graphite particles SFG44 as received from TIMCAL<sup>®</sup> were used. The particles were immersed into a water-based gelatine solution for known period of time. The detailed composition and treatment of the gelatine solution are described elsewhere [11,12]. The following parameters defining the gelatine solution were varied: type of gelatine (type A and B of DGF STOEES AG

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were used), concentration, Bloom value and pH. During the pretreatment, the solution was mixed and kept at an appropriate temperature.

Several polyanilines were also checked as pretreatment agents. Emeraldine base, emeraldine salt and protonated polyaniline were synthesised at the National Institute of Chemistry, Ljubljana as described elsewhere [13].

The pretreated particles were separated from the rest of solution by filtering. The slurry was partially dried and pressed onto a copper substrate at a pressure to obtain about 50  $\mu\text{m}$  thick layer of active material. Prior to use, the anodes were dried in vacuum at 100°C for 10–12 h and transferred to an Ar-filled glove box.

For comparison, reference anodes based on the same active material (SFG44) were made according to a conventional procedure, i.e. using teflon as a binder, as described elsewhere [11,12].

Two electrolytes were used to test the anode properties: (a) 1 M solution of  $\text{LiPF}_6$  in EC:DMC (1:1 ratio), (b) 1 M solution of  $\text{LiPF}_6$  in EC:DEC (1:1 ratio), both received from Merck.

The electrochemical tests were performed using a laboratory-made three-electrode testing cell as described elsewhere [11]. The working and the counter lithium electrodes were separated with two separators (Celgard No. 2402). Between the separators, a thin strip of metallic lithium serving as a reference electrode was positioned.

Electrochemical measurements were performed using equipment from Solartron: a 1286 electrochemical interface and a 1250 frequency response analyser. The constant current during cell cycling was either 50 or 125  $\mu\text{A}$  (corresponding to  $C/7$  and  $C/3$ , respectively), while the geometrical surface area of the working electrode was always 0.5  $\text{cm}^2$ . The impedance spectra were recorded in the frequency range 65,000–0.01 Hz at selected anode potentials.

### 3. Results and discussion

Typically, gelatine pretreatment of SFG44 particles decreases the first cycle irreversible losses from 30–35% to below 20% [11,14] while the reversible capacity remains over 300 mAh in most cases.

Of the two types, i.e. two different compositions, of gelatine tested in the present investigation, gelatine type A exhibited lower irreversible losses (ca. 18%) than type B (ca. 22%) under the same conditions (Fig. 1). The reason(s) for the different behaviour have not been found as yet.

In a previous paper [14], it was shown qualitatively that a higher gelatine concentration led to higher irreversible losses. Specifically, the following results have been found lately: pretreatment in 15 wt.% aqueous solution of gelatine has yielded a 22.5% irreversible loss, while pretreatment in 0.2 and 0.1 wt.% gelatine solution has led to 18.2% irreversible loss during the first cycle. The highest average reversible capacity in the first 10 cycles (335 mAh) was

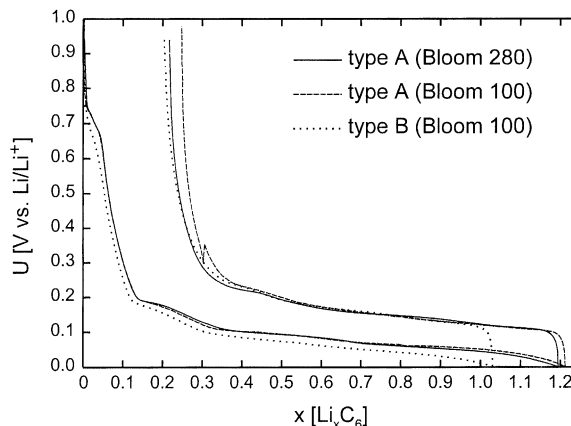


Fig. 1. First charge/discharge of an anode prepared from gelatine-pretreated graphite particles SFG44. Results for two gelatine types of the same producer (see Section 2) and for two Bloom values corresponding to the same time are displayed.

found in the case of the lowest gelatine concentration. Unfortunately, the stability of the anodes pretreated at the lowest gelatine concentration was not satisfactory [14]. After 10 cycles the reversible capacity started to fade significantly. Probably, the amount of adsorbed gelatine was then too low to bind the particles together. We have tried to solve the problem using a gelatine with a higher «gelling power», i.e. a higher Bloom value. As expected, the higher Bloom value means better cycling stability, while the influence of Bloom value on the first cycle(s) irreversible loss(es) is negligible (Fig. 1).

In general, pH of solution is an important factor controlling the amount and also the shape of adsorbed gelatine on substrates [15,16]. Surprisingly, as shown in Fig. 2, the effect of pH of gelatine solution on the first cycle loss is minor in the range from 8 to 12. Only at pH = 5 where the adsorption is considerably lower, a decrease in first cycle capacity was observed.

Several sets of experiment have confirmed our previous investigation [14] where we showed that the gelatine-pretreated anodes are much more stable against cycling and

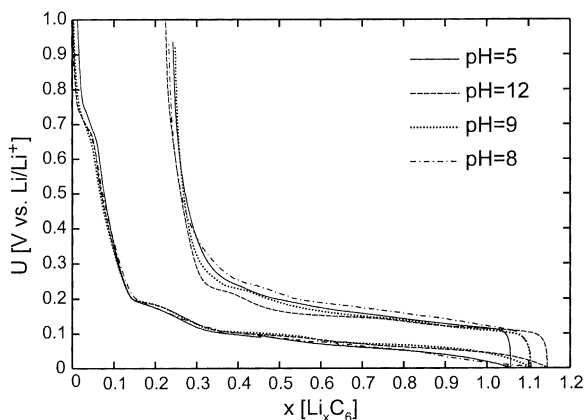


Fig. 2. Effect of pH of the gelatine solution used in the pretreatment procedure on the first cycle behaviour.

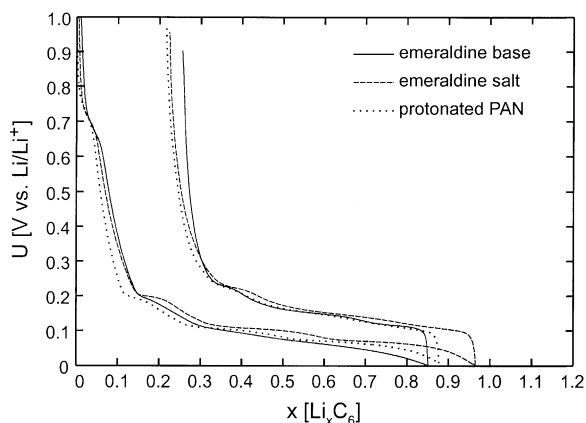


Fig. 3. First charge/discharge of an anode prepared from polyaniline-pretreated graphite particles SFG44. Three polyanilines with different composition were tested.

have significantly lower irreversible losses in EC:DMC than in EC:DEC electrolytes. The reasons for the large differences in pretreated anode behaviour when using similar electrolytes are not known as yet.

The effect of polyaniline pretreatment on first cycle(s) loss(es) (Fig. 3) is comparable to the effect of gelatine. The composition (specific groups) of polyaniline does not to play a significant role. It seems that it is the structure of polyelectrolyte molecules rather than their composition which has a decisive influence on both the electrochemical as well as on the binding properties of pretreated anodes.

Further polyelectrolytes at various conditions are being tested.

#### 4. Conclusions

Appropriate polyelectrolyte (gelatine, polyanilines, etc.) pretreatment of carbon particles used as anode material leads to improvements with respect to the first cycle(s) irreversible loss(es), Coulombic efficiency and reversible capacity. Polyelectrolytes adsorbed on the surface of carbon particles also serve as binders (conventional binders are not needed for preparation of anode). The adsorbed amount of polyelectrolyte is not >2 wt.%. It seems that all these effects should

be attributed to the structure rather than to the composition of the particular polyelectrolyte.

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