Carbon anodes prepared from graphite particles pretreated in a gelatine solution

Jernej Drofenik[a], Miran Gaberšček[a,*], Robert Dominko[a], Marjan Bele[a], Stane Pejovnik[a,b]

[a]*National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*
[b]*Faculty of Chemistry and Chemical Technology, University of Ljubljana, Ljubljana, Slovenia*

Abstract

A new procedure for carbon anode preparation is described. First, carbon (graphite) particles are pretreated in an aqueous solution of gelatine. Then, the slurry is directly pressed on the copper substrate without addition of a special binder. It is shown that such anodes have lower irreversible loss (13–16%) than the classically prepared anodes. Efficiency reaches values close to 100% at latest in the third cycle. Reversible capacity can be as high as 340 mA h g^{-1}. Stability of the new anodes up to 20 cycles is satisfactory only at higher concentrations of gelatine solution used in the pretreatment. Optimization of the new anode is a subject of further investigation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium batteries; Carbon anode; Gelatine pretreatment

1. Introduction

In lithium ion rechargeable batteries, the problem of passive film formation on the surface of carbon anode during the first cycle(s) has still not been solved to a satisfactory degree. On one hand, the passive film formation consumes irreversibly a considerable amount (15–35%) of the lithium present in the cathode upon cell assembly while, on the other hand, the passive film itself represents an additional barrier for lithium ion transfer during cycling. Since the formation of a passive film cannot be avoided due to thermodynamical reasons [1], the reduction of the problem is limited to optimization of the film properties. It can be proposed that an ideal passive film should: (i) be a good ionic conductor (to decrease the polarization during cycling); (ii) be a poor electronic conductor (to have a passivating character); (iii) be very thin (to minimize the irreversible losses of charge); (iv) uniformly cover the surface of each carbon particle (to prevent solvent co-intercalation as well as irreversible losses in later cycles); (v) posses a certain degree of elasticity (to be able to adjust to dimensional changes of anode paricles during cycling).

The film properties can be influenced through selection of the type of carbon used [2], selection of electrolyte composition [3–5], electrolyte modification using additives [2,6–8], and through pretreatment of carbon particles leading to appropriate surface modification [9–11].

In this paper, we present an approach in which carbon (graphite) particles, before being used in the conventional procedure of anode preparation, are pretreated in an aqueous solution of gelatine. The gelatine solution may be modified by appropriate addition of salt(s), surfactant(s), etc. in such a way that a maximum adsorption of gelatine molecules on carbon particle surface occurs. The adsorbed gelatine molecules contain a large number of active groups (cationic, anionic and non-ionic) which may serve as nucleation sites for passive film formation. In a previous paper [12], we showed that the high surface density of nucleation sites should in principle lead to uniform film growth over entire particle surface thus satisfying point (v) stated above. Moreover, the gelatine molecules selected for the present investigation have a sticky character and some of them extend far away from the particle surface (up to 0.5 μm). These special properties might be of considerable help in satisfying point (v) stated above. Even more, the results show that the gelatine-pretreated carbon particles are bound together strongly enough that no conventional binder has to be added to the anode material to prepare mechanically stable anodes.

* Corresponding author. Tel.: +386-61-1760-320;
fax: +386-61-1259-244.
E-mail address: miran.gaberscek@ki.si (M. Gaberšček).

2. Experimental

As active anode material, graphite particles SFG44 as received from TIMCAL® were used. Before use, the particles were immersed into a water-based gelatine solution for 15–30 min. The detailed composition and treatment of the gelatine solution are described elsewhere [12,13]. Three concentration ranges of gelatine have been tested, i.e. medium gelatine concentrations (between 0.1 and 1 wt.%), high concentrations (above 1 wt.%) and low concentrations (below 0.1 wt.%). It seems that the most important properties of gelatine for the present use are: (i) a large number of ionic and/or non-ionic groups, and (ii) presence of long chains some of which extend from the particle surface out into bulk solution. Beyond that, appropriate conditions (pH, temperature, etc.) have to be selected to allow maximum adsorption of polyelectrolyte onto carbon particle surface.

In the present investigation, the pretreated particles were separated from the rest of solution by filtering. The slurry was partially dried and pressed onto a 12-μm-thick copper substrate at a pressure of 1000 kPa to obtain about 50-μm-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 gove 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 [12].

Two electrolytes were used to test the anode properties: (a) 1 M solution of $LiPF_6$ in EC:DMC (1:1 ratio); (b) 1 M solution of $LiPF_6$ in EC:DEC (1:1 ratio), both received from Merck.

The electrochemical tests were performed using a laboratory-made three-electrode testing cell. The cell housing was made of teflon. The electrode holders, which also served as contacts, were from stainless steel. Sealing was provided using O-rings. The working and the counter lithium electrode were separated with two separators (Celgard No. 2402). Between the separators, a thin strip of metallic lithium serving as a reference electrode was positioned. The stainless-steel holder for cathode was enlarged and was slightly smaller than the corresponding compartment. In this way, the holder exerted a constant pressure of ca. $7 \, N \, cm^{-2}$ on the electrodes, regardless of the changes in their dimensions during cycling. The contact between the holder "W" and the upper stainless steel cover was achieved through a thin nickel strip welded onto both sides. Many tests performed in our laboratory have shown that a cell with such construction operates more reliably and gives better reproducibility of electrohemical results than a similar cell in which the electrodes are pressed together using a spring.

Electrochemical measurements were performed using equipment from Solartron: a 1286 Electrochemical Interface and a 1250 Frequency Response Analyzer. The constant current during cell cycling was either 50 or 125 μA (corresponding to C/7 and C/3, respectively), while the geome-

trical surface area of the working electrode was always $0.5 \, cm^2$. The impedance spectra were recorded in the frequency range 65,000–0.01 Hz at selected anode potentials.

3. Results and discussion

In the following, we present some typical electrochemical characteristics of the anodes prepared from gelatine-pretreated graphite particles without addition of classical binders. Note that in most cases shown, the properties are still being optimized by varying experimental conditions, such as gelatine type, gelatine concentration, temperature, pH, etc.

Potential variation during first intercalation and deintercalation of the pretreated (PA) and conventional (CA) anode is shown in Fig. 1. Comparison of the intercalation curves in Fig. 1 shows that in the case of PA, much less charge is consumed to the point when the potential reaches 0.2 V, i.e. when the passivation is considered more or less completed and pure intercalation starts. Furthermore, in the potential range 0–0.2 V, the intercalation curve for PA is smoother than that of CA, i.e. the individual intercalation stages are less pronounced in the former case. The deintercalation curves have similar shapes but, again, the curve for PA is smoother. The most important difference between both systems is in the amount of irreversibly lost charge during the first cycle, i.e. 32% for CA and only 16% for PA. These results can be explained by a simple qualitative model derived from impedance spectroscopy measurements as presented in a previous paper [12]. The model assumes that while in the case of CA a rather thick and porous passive film is formed, the gelatine molecules adsorbed on the surface of PA induce formation of a much thinner and more dense film. It is worth noting that a similar effect of gelatine on formation of carbon black films on printed wiring boards has been reported [14].
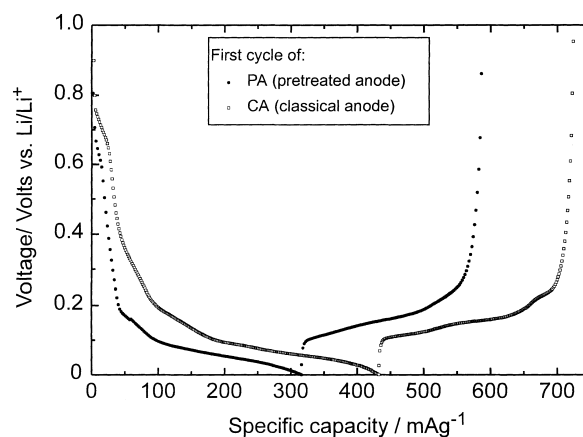

Fig. 1. First charge/discharge of an anode prepared from gelatine-pretreated graphite particles SFG44 without use of a classical binder (PA) and of a corresponding anode prepared according to a conventional procedure (CA) using teflon dispersion as a binder. In both cases, the cycling rate was C/2.
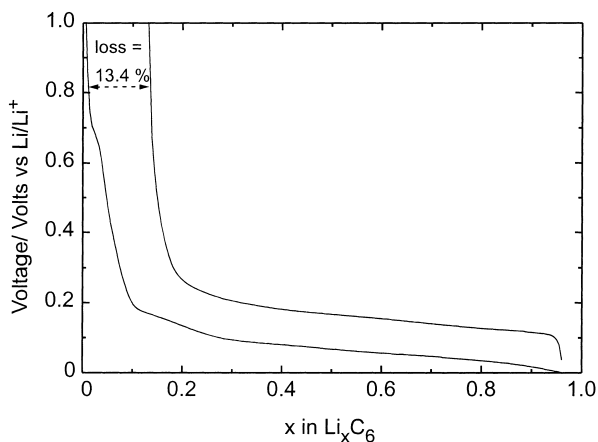
Fig. 2. Minimum irreversible loss of PA. Gelatine concentration during the pretreatment procedure was within the medium range (see Section 2). Cycling rate was C/4.

Fig. 4. Reversible capacity as a function of cycles for PA and CA. The gelatine concentration corresponding to squares was twice lower than that corresponding to circles.

Fig. 2 shows that the irreversible loss in the first cycle using PA can be as low as 13.4%, while the corresponding reversible capacity remains above 300 mA h g^{-1}. The irreversible capacity in several control experiments using CA was between 30 and 35%. Unfortunately, at the present stage of our optimization, the lowest irreversible losses of PAs are still associated with a gradual decrease of reversible capacity due to anode degradation during cycling (not shown in Fig. 2).

From Fig. 3, it can be seen that the efficiency (the ratio between the intercalation and deintercalation charge) of PA increases to over 98.5% already in the second cycle and to more than 99% in the third cycle, while from the fifth cycle on it is effectively 100% (the slight variations are due to the experimental error of charge determination). The problem of this particular set of experiments was that the degree of intercalation was significantly <1 (see the upper curve in Fig. 3). Apparently, this problem can be overcome by decreasing the concentration of gelatine during the pretreatment procedure (see squares in Fig. 4). However, a decreased gelatine concentration results in decreased adhesion between carbon particles and, consequently, in faster anode
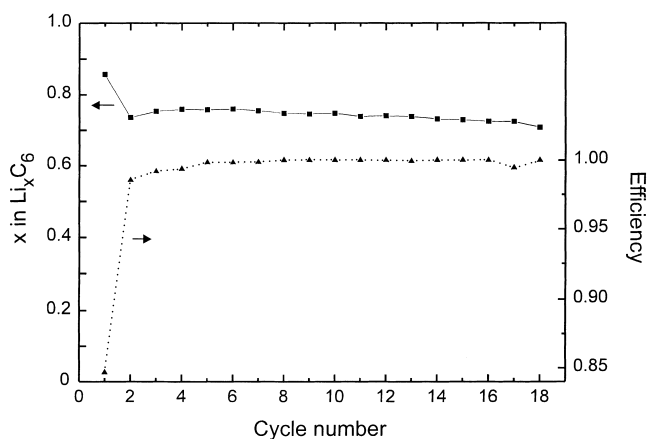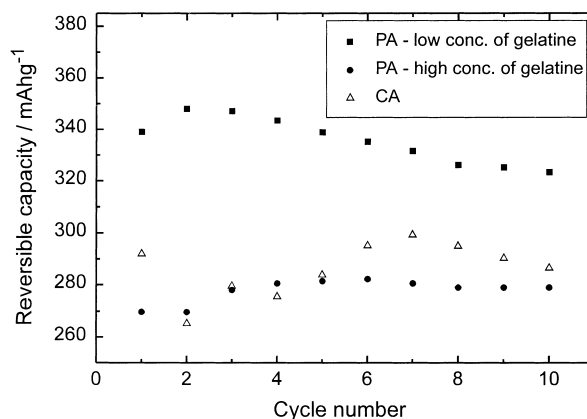
degradation which, in Fig. 4, reflects in a gradual decrease of reversible capacity with the number of cycles. A solution to this problem could be a combination of gelatine pretreatment using small concentrations and addition of an appropriate quantity of classical binder.

The advantage of low gelatine concentration is further illustrated in Fig. 5. Obviously, the higher gelatine concentration leads to higher polarisation. At the same time, the high gelatine concentration leads to lower specific capacity and higher irreversible loss.

The dependence of reversible capacity and efficiency on cycling rate is displayed in Fig. 6. Although the values in both curves show large oscillations, the tendencies are expected and comparable to CAs.

It seems that PA performance depends significantly on the electrolyte composition. Fig. 7 shows that while a change from DMC to DEC does not affect the shape of the first cycle (a), it has a pronounced impact on the efficiency and the reversible capacity as functions of cycle number (b).

Fig. 3. Degree of intercalation (left axis) and efficiency (right axis) as functions of cycle number for a PA anode. Cycling rate was C/2.
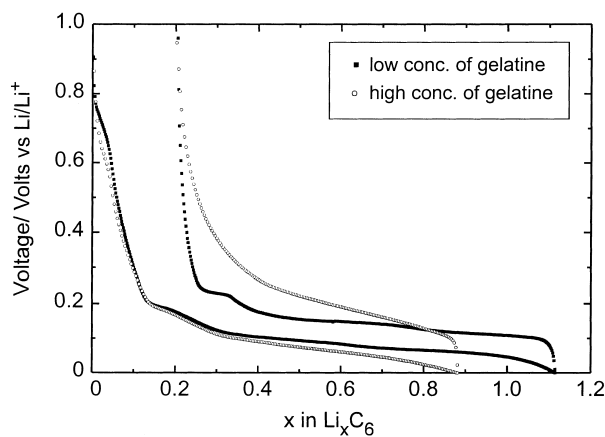

Fig. 5. Influence of gelatine concentration on the shape of the first charge/discharge cycle. The gelatine concentration corresponding to open circles was 10× higher than that corresponding to solid circles (the latter, in turn, corresponded to the medium concentration range — see Section 2).
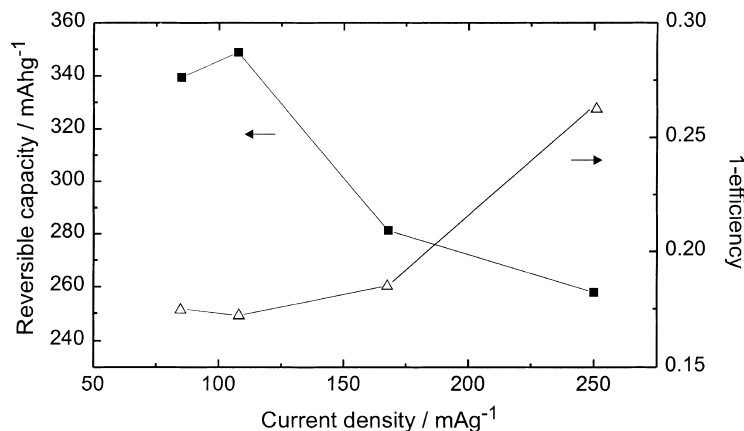
Fig. 6. Reversible capacity and first-cycle loss (given as ''1-efficiency'') of PA as functions of current density.
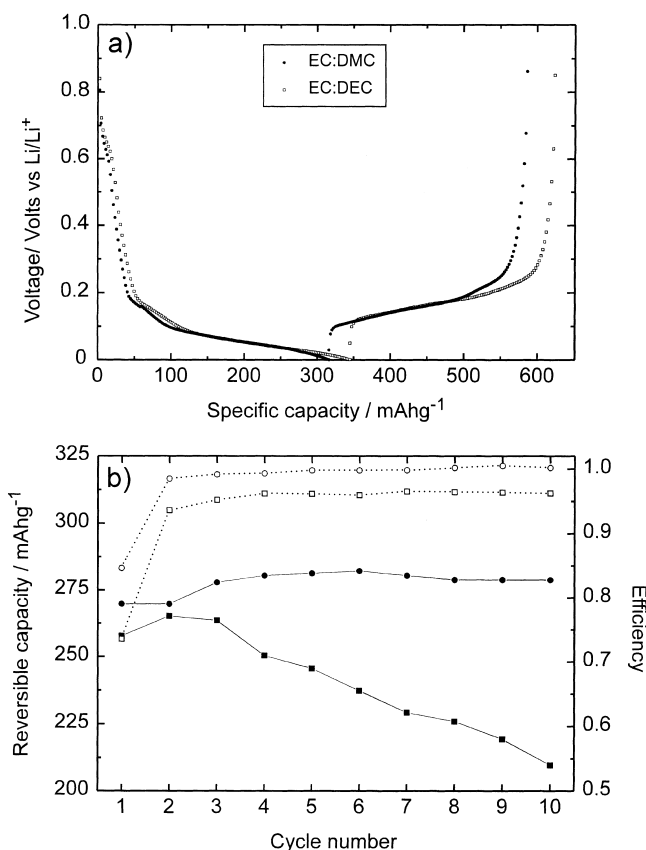

Fig. 7. Influence of electrolyte composition on performance of PA. In all cases, (a) circles correspond to the EC:DMC = 1:1 electrolyte, while squares represent the EC:DEC = 1:1. (b) Solid symbols correspond to reversible capacity and open symbols correspond to efficiency.

are obtained at lower gelatine concentrations. By contrast, stability after prolonged cycling is better at higher gelatine concentrations, probably due to stronger adhesion forces between carbon particles. A technology that would yield optimal results in both respects should probably include a combination of gelatine pretreatment using small gelatine concentrations and addition of an appropriate quantity of classical binder.

Acknowledgements

References

[1] M. Winter, J.O. Besenhard, in: M. Wakihara, O. Yamamoto (Eds.), Lithium Ion Batteries, Fundamentals and Performance, Kodansha/Wiley/VCH, Tokyo/New York, 1998, p. 136.
[2] Z. Liu, A. Yu, J.L. Lee, J. Power Sources 81/82 (1999) 187–191.
[3] J.R. Dahn, A.K. Sleigh, H. Shi, B.M. Way, W.J. Weydanz, J.N. Reimers, Q. Zhong, U.V. Sacken, in: G. Pistoia (Ed.), Lithium Batteries — New Materials, Developments and Perspectives, Elsevier, Amsterdam, 1994 (Chapter 1).
[4] S. Megahed, B. Scrosati, J. Power Sources 51 (1994) 79–104.
[5] A.N. Dey, B.P. Sullivan, J. Electrochem. Soc. 117 (1970) 222–226.
[6] T.D. Tran, J.H. Feikert, X. Song, K. Kinoshita, J. Electrochem. Soc. 142 (1995) 3297–3302.
[7] J.O. Besenhard, P. Castella, M.W. Wagner, Mater. Sci. Forum 91–93 (1992) 647.
[8] J.O. Besenhard, M.W. Wagner, M. Winter, A.D. Jannakoudakis, P.D. Jannakoudakis, E. Theodoridou, J. Power Sources 43/44 (1993) 413–420.
[9] E. Peled, C. Menachem, D. Bar-Tow, A. Melman, J. Electrochem. Soc. 143 (1996) L4.
[10] N. Imanishi, Y. Takeda, O. Yamamoto, in: M. Wakihara, O. Yamamoto (Eds.), Lithium Ion Batteries, Fundamentals and Performance, Kodansha/Wiley/VCH, Tokyo/New York, 1998 (Chapter 5).

4. Conclusions

Gelatine pretreatment of carbon particles used as anode material may lead to improvement of several electrochemical parameters, such as the irreversible loss in the first cycle, Coulombic efficiency and reversible capacity. Better results

[11] M. Winter, H. Buqa, B. Evers, T. Hodal, K.-C. Moeller, C. Reisinger, M.V. Santis Alvarez, I. Schneider, G.W. Wrodnigg, F.P. Netzer, R.I.R. Blyth, M.G. Ramsey, P. Golob, F. Hofer, C. Grogger, W. Kern, R. Saf, J.O. Besenhard, ITE Battery Lett. 1 (1999) 129–139.

[12] M. Gaberšcek, M. Bele, J. Drofenik, R. Dominko, S. Pejovnik, Electrochem. Solid State Lett. 3 (2000) 171–173.

[13] M. Gaberšcek, M. Bele, S. Pejovnik, J. Drofenik, R. Dominko, Patent application No. P-9900238, Bureau for Intelectual Property of the Republic of Slovenia, Ljubljana, Slovenia, October 1999.

[14] M. Bele, S. Pejovnik, J.O. Besenhard, V. Ribitsch, Coll. Surf. A: Physicochem. Eng. Asp. 143 (1) (1998) 17–26.