

USE OF MATERIALS SCIENCE PRINCIPLES IN BATTERY DESIGN:
GELATIN IN LITHIUM BATTERIES[†]

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[†]This paper is dedicated to the late Professor Dr. Drago Kolar

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Abstract

Gelatin-pretreated graphite particles were used to prepare anodes for use in lithium ion rechargeable batteries. The amount of adsorbed gelatin at various conditions is estimated using gravimetry and thermogravimetry. Electrochemical properties, such as irreversible loss of charge, reversible capacity and efficiency of gelatin-pretreated graphite anodes are compared to the properties of conventional graphitic anodes prepared using polymeric binders. A model explaining the different behaviour is presented. At the end, a preliminary testing of a full lithium ion battery prepared without use of conventional binders is shown.

Introduction

Although gelatin has been known and used for hundreds of years, its application has importantly increased only in recent decades. Today, it is extensively used in the food, photographic, and pharmaceutical industries.¹ Gelatin is produced by the acid or alkali denaturation of collagen. Originally, collagen has a form of triple helix, consisting of three associated left-handed helices.² In water solution, gelatin can form structures such as random coils or random coils with collagen-folded structure. The structure depends mainly on the amino acid composition; the concentration of the gelatin solution and on temperature and pH of the solution.¹⁻⁴ Gelatin is an amphoteric polyelectrolyte, which contains both acidic and basic amino groups. In solution, these groups become negatively or positively charged. Sometimes gelatin is used as stabilizer in both colloidal dispersions and emulsions.

Due to its structure and composition, gelatin has a strong tendency to adsorb on various kinds of surfaces. One of the important parameters, which have a direct influence on adsorption mechanism, is its shape. At given temperature and

concentration, the shape is mainly determined by the pH value of gelatin solution during adsorption. For example, Israelachvili *et al.* [ref. 4, see Fig. 1 therein] have shown that near isoelectric point (IEP), gelatin is not expanded due to the electrostatic attraction between the positively and negatively charged groups of adjacent segments. The situation is opposite at pH values much higher or lower than IEP. Based on this model, one might speculate that near IEP a larger amount of gelatin will be adsorbed on the substrate (or particle) surface than at other pH values. For this reason, pH of gelatin solution has been one of the most important parameters to control the properties of gelatin-pretreated battery materials.

Originally, the idea to use gelatin in preparation of electrodes in rechargeable batteries relied mostly on its “sticky” nature. For example, we wanted to use gelatin as a binder to glue together the particles of active anode material (coke or graphite particles of typical dimensions of 10 μm) and, at the same time, to glue the whole composite anode material onto a copper foil which usually serves as a current collector.⁵ It was assumed that gelatin could be a more effective binder as the polymeric equivalents, such as teflon (Poly(tetrafluoroethylene), PTFE, or Poly(vinylidene difluoride), PVDF). Already preliminary electrochemical experiments confirmed our assumption and, beyond that, revealed that gelatin had also other beneficial roles in anode performance.⁵ The present paper tries to explain the impact of gelatin on the electrochemical performance of gelatin-treated anode materials through the inherent properties of gelatin, especially its structure.

Results and discussion

Gelatin properties that are relevant for its use in batteries

The isoelectric point of gelatin type A lies at a pH of about 9.5 (Fig. 1). Using thermogravimetry and gravimetry we have been able to monitor the amount of gelatin adsorbed on the surface of graphite particles as a function of pH of the gelatin solution (Fig.2). The results confirm the prediction based on the model of Israelachvili *et al.*,⁴

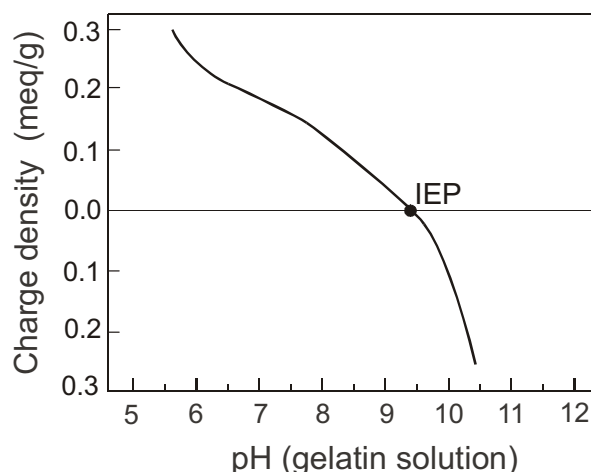


Figure 1. Charge density as a function of pH of gelatin type A. IEP = isoelectric point.

i.e., that the maximum amount of gelatin is adsorbed at a pH value near the isoelectric point (gelatin has a stable but not expanded structure). In the particular case of adsorption on graphite particles, the maximum content of gelatin in graphite-gelatin composites is about 1.7 wt. %, which corresponds to 4 mg of gelatin per 1 m² graphite if the BET surface is used for the calculation. This value is within the range of 1-6 mg/m², *i.e.*, the range found in studies of adsorption of different kinds of gelatin onto different substrates.⁶

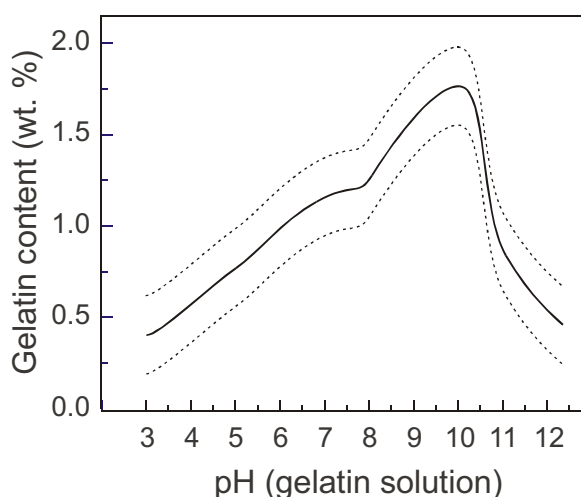


Figure 2. Gelatin content in graphitic anode material as a function of pH. The solid curve represents average values of a series of thermogravimetric and gravimetric determinations. The dashed lines represent the estimated error due to experimental procedure (the error due to procedure is much larger than the error due to both methods used).

The relationship between the adsorbed amount of gelatin and pH of the corresponding solution is very important for anode technology because the amount of gelatin present on the anode surface significantly affects both the mechanical and electrochemical properties of graphite anode (*c.f.* Fig. 5).

In our previous works⁷⁻⁹ using Atomic Force Microscopy it was found that once adsorbed on a substrate, gelatin adopts a “hairy” structure, *i.e.*, many loops and tails are sticking from the surface into the solution. It has been assumed that such a structure might serve as a steric stabilizer of colloidal dispersion. Furthermore, the gelatin-modified surface of a substrate can attract many kinds of particles because gelatin contains many kinds of active groups: cationic, anionic and, also, nonionic. On a macroscopic scale, these properties are observed as the “sticky” nature of gelatin. As already mentioned, the original idea to use gelatin in anode material for lithium batteries was to use it as a glue to bind the anode particles and to fasten them onto a copper current collector. Recently, in a new set of AFM studies,¹⁰ we have directly measured the force between gelatin and the graphite particles SFG44 that are usually used in anode preparation. It has been found that the work needed to break all the “bonds” between gelatin and graphite surface is several thousands kT and that the force is detected to a distance of about 0.5 μm . Both results justify the use of gelatin as a binding material in graphite-based composites.

Impact of gelatin on carbon anode properties

Figure 3 shows the first charge-discharge cycle of three differently prepared anodes. The dashed and the dotted curves correspond to anodes prepared according to the conventional procedure using PTFE and PVDF as binders. The solid curve belongs to an anode prepared with gelatin. The difference in capacity at the last point of deintercalation curve and the capacity at the first point of intercalation curve is defined as the absolute irreversible loss of charge. The ratio between the absolute irreversible loss of charge and the total intercalation charge is known as the relative irreversible loss of charge or simply “irreversible loss”. The irreversible loss of charge is due to non-Faradaic consumption of charge. In the case of graphitic electrodes, the irreversible loss

is mostly due to formation of a passive film on the graphite surface immediately before and during first intercalation of lithium into the graphite structure.

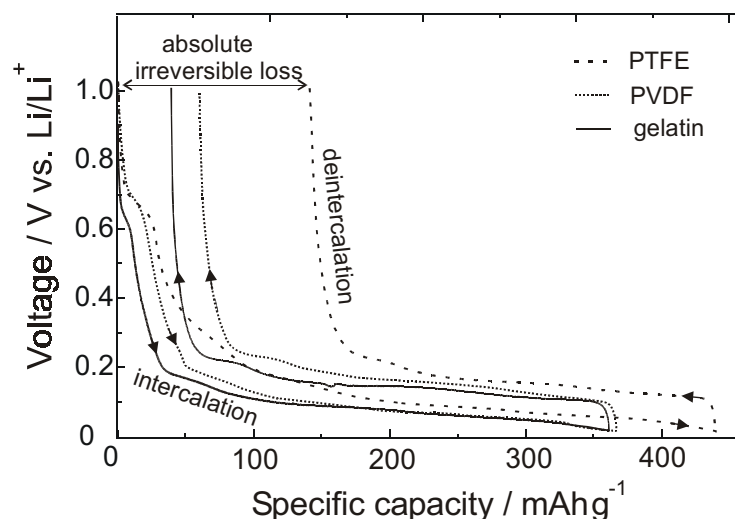


Figure 3. First intercalation and deintercalation curves for anodes prepared with different binding materials, PTFE, PVDF and gelatin (see Experimental). The curves were recorded at a constant current of 50 μA .

The irreversible loss is the highest in anodes made from PTFE, and the lowest in the case of gelatin-treated anodes. Table 1 shows that the irreversible loss is also present in the second, third and fourth cycle, *i.e.*, several cycles are needed before the anode has been fully passivated.

Table 1. Irreversible loss (%) in first 4 intercalation/deintercalation cycles for anodes prepared using 3 different types of binders.

| Binder | Cycle No. 1 | Cycle No. 2 | Cycle No. 3 | Cycle No. 4 |
|---------|-------------|-------------|-------------|-------------|
| PTFE | 32.3 | 24.7 | 1.6 | 1.8 |
| PVDF | 17.2 | 2.7 | 1.7 | 1.0 |
| Gelatin | 15.3 | 1.5 | 0.8 | 0.6 |

The data in Table 1 reveal that gelatin improves the passivation process so that less charge is spent for film formation in every cycle measured. These results together with the results of impedance spectroscopy measurements⁵ indicate that in the presence

of gelatin the passivation proceeds more uniformly and results in a thinner passive film (Fig. 4).

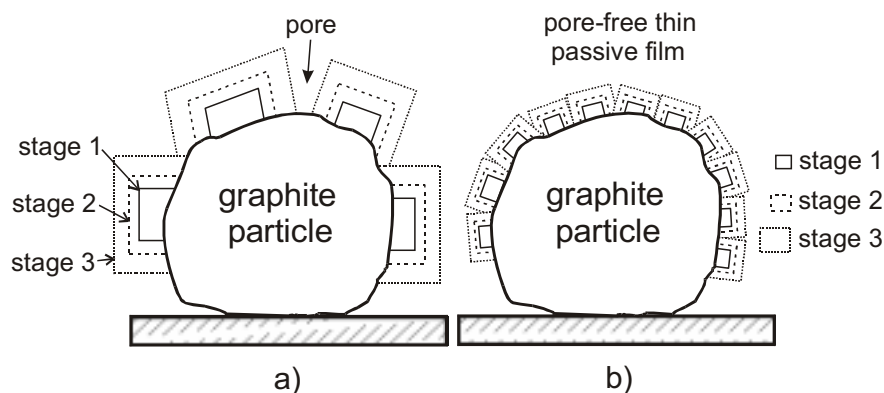


Figure 4. A model explaining the different passivation of a) untreated and b) gelatin-treated graphite particle. The stages shown are arbitrary. The size of film crystallites with respect to the size of graphite particle is exaggerated for the sake of clarity.

The more uniform film growth is most likely due to a more uniform distribution of nucleation sites. Namely, in absence of gelatin the only appropriate nucleation sites for film growth are the prismatic surfaces on graphite¹² which are not very abundant. Conversely, the presence of gelatin with the many tails and loops involving various specific groups significantly increases the density of surface sites appropriate for nucleation and growth of passive film.

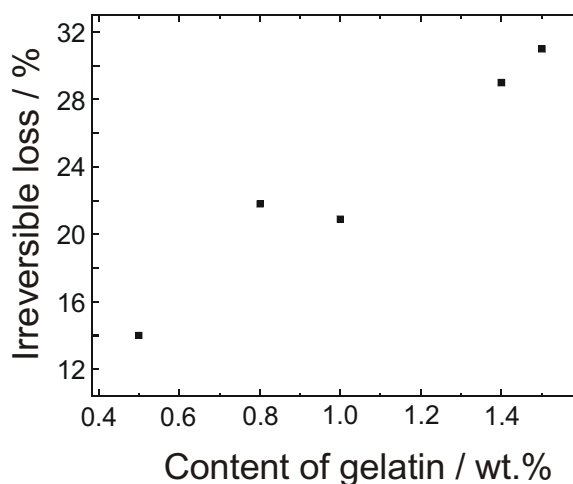


Figure 5. Dependence of irreversible loss on the gelatin content in anode material. Please note that anodes with a gelatin content lower than 0.5 wt. % cannot be prepared due to mechanical instability.

It is interesting to observe the irreversible loss as a function of the content of gelatin in the anode composite (Fig.5). Obviously, smaller contents lead to smaller

irreversible loss, at least until the content of 0.5 wt. % is reached. Below that the anodes become mechanically unstable and tend to disintegrate before or immediately after beginning of the electrochemical testings.

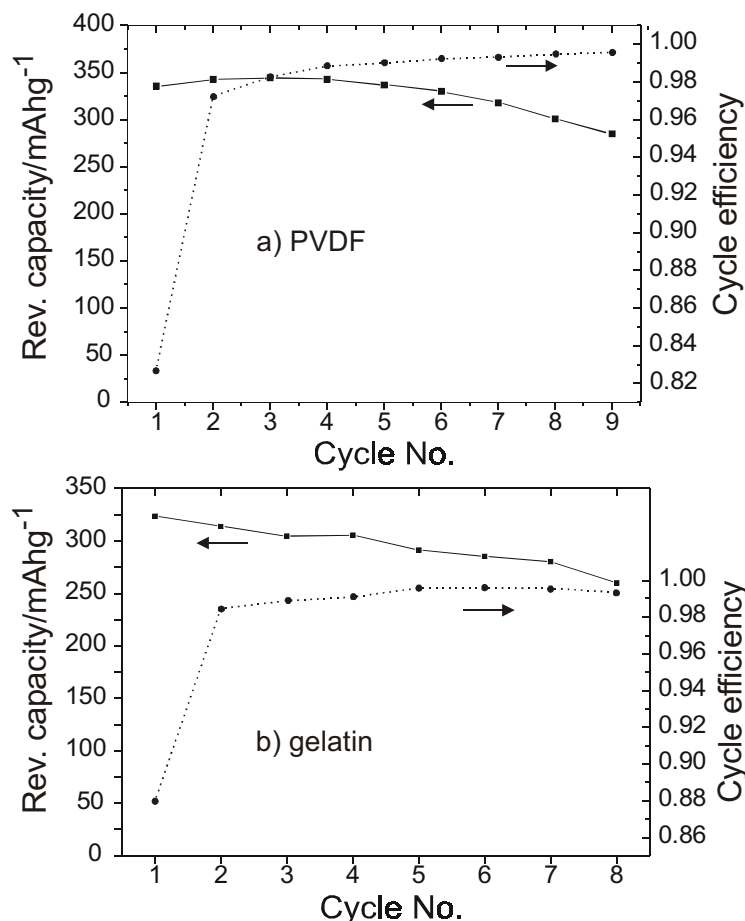


Figure 6. Reversible capacity as a function of cycle number for a) conventional anode with 5% of PVDF and b) new anode prepared by gelatin pretreatment of graphite. On the right axis cycle efficiency for the same anode materials is displayed (cycle efficiency is defined as the ratio between the total capacity achieved during intercalation and the total capacity achieved during deintercalation in the given battery cycle).

The next important electrochemical parameter relevant to estimation of anode efficiency is the reversible capacity - the portion of charge that can be deintercalated after prior full intercalation. The presence of gelatin does not change the reversible charge of the graphitic anode (Fig. 6). The very slow decrease of reversible capacity with cycle number is an indirect evidence that gelatin binds graphitic particles effectively. Namely, in cases when binding is ineffective, the anode rapidly disintegrates

from cycle to cycle and the reversible capacity drops significantly in only a few cycles. The reason for the disintegration is relatively large dimensional changes of graphite particles (15–50 %) ¹² during intercalation and deintercalation. We have shown ¹³ that the stability of anodes is better at higher gelatin contents. As this opposes the requirement for low irreversible losses (*c.f.* Fig. 5), a compromise as regards the gelatin content is needed. The alternative seems to be a combination of gelatin pretreatment and application of PVDF. Optimization in this respect is taking place.

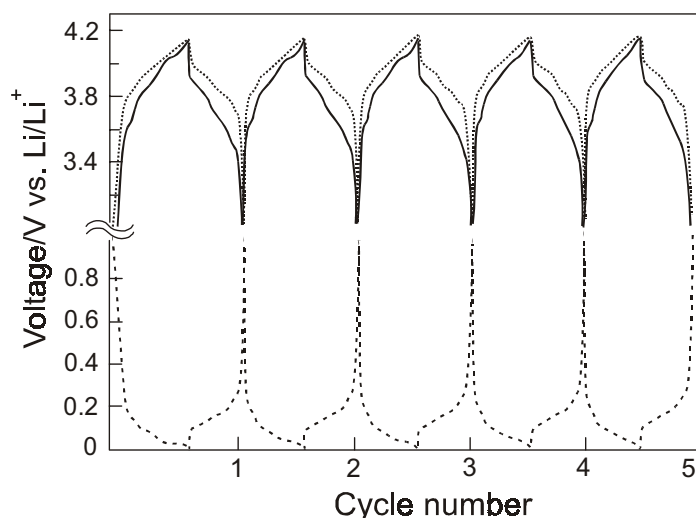


Figure 7. Voltage profiles during 5 consecutive cycles of a full lithium ion rechargeable battery prepared without use of classical binders. Instead polyelectrolytes were used as binders and/or surface modifiers. The dashed line represents the potential profile of anode and the dotted line is due to the potential of cathode, both measured against the potential of a Li/Li⁺ couple. The solid line shows the total voltage of the battery. The curves were obtained at a constant current of 50 μ A. At the end of each cycle both the anode and the cathode were almost fully charged/discharged.

Recently, polyelectrolytes such as gelatin *etc.*, have also been successfully applied in the technology of cathode preparation to improve the electronic conductivity of the oxides used as active materials – in our case LiMn₂O₄ and LiCoO₂ have been tested. A full report of this research will follow after completion of the patent procedure. The main message is that also in the cathode technology, polyelectrolytes can effectively replace the conventional polymeric binders and decrease the content of electrochemically inactive mass in the electrode composite. Hence a complete polymer

binder-free lithium accumulator can be manufactured. A few cycles of a prototype of such an accumulator are shown in Fig. 7.

Conclusions

Anodes prepared from gelatin-pretreated graphite particles have lower irreversible losses and comparable reversible capacity and cycling stability as anodes prepared using conventional binders. Furthermore, the content of gelatin in anodes with good properties can be lower than 1 wt%. By contrast, the typical content of conventional binders in classical anode technology is about 5 wt. %, which reduces the content of electrochemically active mass and, hence, the energy density of anodes. It is assumed that the presence of gelatin increases the density of nucleation sites for passive film formation on the surface of graphite particles. The resulting film is denser and thinner than in the case of conventional anodes.

It is also possible to prepare cathodes without use of conventional binders. Similarly as in anodes, application of polyelectrolytes akin to gelatin increases the content of active cathode mass to 98 wt. % or even higher.

Experimental

TIMREX SFG44 special-graphite obtained from TIMCAL Ltd. (Sins, Swiss) was used for preparation of anode composite materials. The Brunauer, Emmett, Teller (BET) surface of this material is 4.2 m²/g and average particle size is 44 μm (data supplied by TIMCAL Ltd.). Gelatin was used as the surface modifier and binder of carbon particles in anode preparation. Medium gel power gelatin, 180 g Bloom, type A, derived from pigskin was obtained from Fluka Nr.48722 (Fluka Chemie AG, Buchs, Swiss). Two types of surfactants were used; cationic surfactant: cetyltrimethylammonium bromide (CTAB), Aldrich Nr.85,582-0 (Aldrich, Milwaukee, WI, U.S.A); and anionic surfactant: sodium di(iso-octyl) succinyl-sulfonate, Aerosol OT (AOT), (Cytec Industries Inc., West Paterson, NJ, U.S.A.). Metallic lithium foil (0.75mm thick) was obtained from Alfa Aesar (Johnson Matthey GmbH, Karlsruhe, Germany). For comparison, classical graphitic anodes with 5 wt. % of PTFE or 5 wt. % of PVDF as a binder were prepared according to a procedure described elsewhere.⁵

Gelatin content in graphite-gelatin composites was determined from the difference in the mass of graphite particles before and after the treatment with gelatin and by thermogravimetric analysis. Thermogravimetric analysis (TG) was performed in the temperature range from 30°C to 700°C in airflow of 18 l/min and at a heating rate of 10 °C/min using a Mettler TA 3000 apparatus (Mettler, Swiss).

Charge-compensating polyelectrolyte titration was performed using a KOLB (Chem. Fabrik, AG CH-8908, Hedingen) charge detector and a 665 Dosimat (Metrohm, Swiss) titrator.

The electrochemical tests were performed using a laboratory-made three-electrode testing cell as described elsewhere.⁵ The working electrode was a graphitic electrode prepared as described above while the counter and the reference electrodes were made of metallic lithium. The electrolyte used was 1 M solution of LiPF₆ in EC:DMC (1:1 ratio) as received from Merck KGaA (Darmstadt, Germany).

The electrochemical measurements were carried out using a Solartron 1286 Electrochemical Interface (Solartron Mobrey Ltd, Berks, U. K.). The constant current during cell cycling was 50 µA (corresponding to C/7), while the geometrical surface area of the working electrode was always 0.5 cm².

Acknowledgements

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Povzetek

Anode za litijeve ionske akumulatorje smo pripravili iz grafitnih delcev, ki smo jih predhodno obdelali v raztopini želatine. Količino adsorbirane želatine smo ocenili s tehtanjem vzorcev pred in po adsorpciji in s termogravimetrično analizo anodnega materiala. V članku primerjamo elektrokemijske lastnosti (ireverzibilna izguba naboja, reverzibilna kapaciteta, učinkovitost cikliranja) anod, pripravljenih po klasičnem postopku in anod, pripravljenih z uporabo želatine kot veziva. Razliko v elektrokemijskih lastnostih razlagamo na osnovi preprostega modela, ki pojasnjuje vlogo želatine pri nukleaciji in rasti pasivnega filma. Pripravili in testirali smo tudi katode, v katerih namesto polimernih veziv uporabimo polielektrolite. Sestavili smo celoten delujoč litijev akumulator, ki ne vsebuje klasičnih polimernih veziv.