



## Short communication

## Electrochemical binding and wiring in battery materials

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## ABSTRACT

Binders in battery electrodes not only provide mechanical cohesiveness during battery operation but can also affect the electrode properties via the surface modification. Using atomic force microscopy (AFM), we study the surface structuring of three binders: polyvinylidene fluoride (PVDF), carboxymethyl cellulose (CMC) and gelatin. We try to find correlation between the observed structures and the measured electrochemical charge–discharge characteristics. We further measure the binding ability of gelatin adsorbed from solutions of different pHs. While the best binding ability of gelatin is obtained at pH about 9, the least polarization is observed at pH 12. Both properties are explained based on the observed gelatin structuring as a function of pH. In the second part of this study, gelatin is used as a surface agent that dictates the organization of nanometre-sized carbon black particles around micrometre-sized cathodic active particles. Using microcontact impedance measurements on polished pellets we show that using gelatin-forced carbon black deposition the average electronic resistance around  $\text{LiMn}_2\text{O}_4$  particles is decreased by more than two orders of magnitude. We believe that it is this decrease in resistance that improves significantly the rate performance of various cathode materials, such as  $\text{LiMn}_2\text{O}_4$  and  $\text{LiCoO}_2$ .

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## 1. Introduction

Binders in battery anode and cathode composites are electrochemically inactive materials which, however, can have important influence on the electrode performance. The primary role of binders is, of course, to bind various battery components into a compact composite electrode and thus prevent its disintegration due to chemical and mechanical forces occurring during typical charge–discharge. We have already indicated in range of previous papers [1–5] that the binding function of binders could be achieved in two essentially different ways: via direct binding (adsorption) of binder's molecules to adjacent particles forming the so-called interparticle bridges (an example is gelatin, see Fig. 1a) or via indirect binding, that is, formation of chemically inert networks into which the particles are then mechanically captured (a classical example is PTFE forming interconnected web of wires) (see Fig. 1b). Based on practical testings [1–5], it seems that both principles are equally successful in providing electrode cohesiveness; perhaps the main known difference is that the direct binding principle requires a smaller amount of binder (typically less than 1 wt.%) to achieve the same binding function. In the present paper we show some new data to further elucidate the differences between both binding mechanisms.

Besides providing electrode cohesiveness, the binders, however, also importantly affect the surface properties of active particles. For this purpose, the binders possessing direct binding ability are much more interesting than the inert binders. For example, we have demonstrated that finely dispersed gelatin molecules on graphite particles surface can serve as nucleation sites for more effective passive film formation [1]. Similarly, we have shown that gelatin dispersed on the surface of certain cathode materials can force carbon black to uniformly distribute around the cathode particles [6–8]—this way electrons can reach the whole materials surface which decreases polarization at high charge–discharge rates. In the present paper we show some further evidence for this effect which works well regardless of the type of cathode material used. The only condition is that the carbon black particles are considerably smaller than the active particles so as to allow their uniform deposition around the surface of the latter.

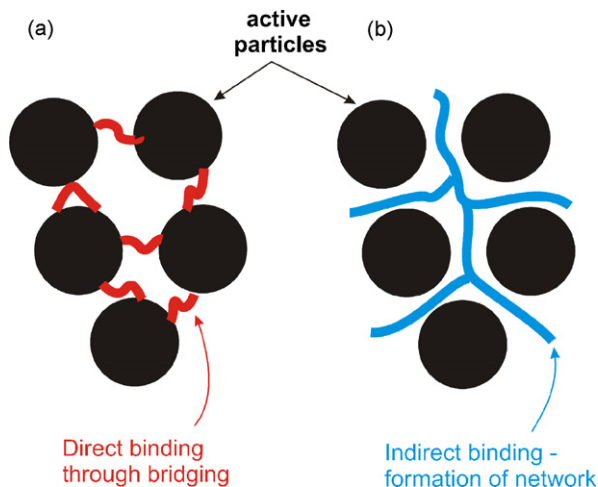
## 2. Experimental

## 2.1. Preparation of anodes

TIMREX SFG44 special-graphite obtained from TIMCAL Ltd. (Sins, Switzerland) was used for the preparation of anode composite materials. Gelatin was used as the surface modifier and binder of graphite 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, Switzerland). The anodes were

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**Fig. 1.** Two different binding principles that can be used for preparation of composite electrodes consisting of powders: (a) direct binding by adsorption of macromolecules on neighbouring particles and forming interparticle bridges; (b) Indirect binding by forming a 3D network into which particles are mechanically entrapped.

prepared by pressing gelatin-pretreated carbon particles onto a copper substrate. The gelatin solution (0.2%) used in the pretreatment procedure was prepared by dissolving gelatin in water at 60 °C. The solution was stored at 4–10 °C and then used after 12 h. The pH value was adjusted with 0.1 M potassium hydroxide or hydrochloric acid solution. The adsorption on carbon particles was carried out in gelatin solution by stirring at a selected pH value for about 30 min at room temperature. The slurry obtained after filtering and rinsing with water was air-dried. The pretreated graphite particles were then pressed onto a copper substrate to obtain a layer of a thickness of ca. 50 μm.

PVdF-based graphite electrodes were prepared by mixing 1 wt.% of PVdF (Aldrich) solution in NMP with SFG 44 graphite. The obtained slurry was spread over the copper substrate, dried and finally electrodes with a diameter of 8 mm were cut out. Similar procedure was used for CMC-based electrodes, unless that 1 wt.% of CMC water solution was used. Before use, the graphite anodes were dried in vacuum at 100 °C for 10–12 h.

## 2.2. Preparation of cathodes

The cathode active materials were Merck SP30  $\text{LiMn}_2\text{O}_4$  (average particle size 30 μm), and Merck SC20  $\text{LiCoO}_2$  (average particle size 7 μm). For preparation of conventional cathodes, each active material was mixed with a PTFE dispersion and carbon black (Degussa, Printex XE2). The slurry was then deposited on an aluminium substrate to obtain an electrode of a thickness of 80 μm (5–7 mg of active material).

Alternatively, a gelatin-based procedure was used for preparation of cathodes. Gelatin (Fluka) was dissolved in water and the solution was modified using LiOH to set pH to a preselected value. The active particles were immersed into the modified gelatin solution. Then, a dispersion of carbon black particles (Degussa, Printex XE2) was added to the gelatin-pretreated active particles. To the obtained mixture, an additional amount of gelatin solution was added to bind the carbon black-covered active particles. The amount of gelatin in the final composite material did not exceed 2 wt.%.

## 2.3. Characterization of prepared materials

Formation of gelatin, cellulose and PVdF networks on highly oriented pyrolytic graphite (HOPG) was observed using an AFM

device: Nanoscope III, Digital Instruments, Santa Barbara, CA. The contact mode using a  $\text{Si}_3\text{N}_4$  tip (Park Scientific) was applied.

The forces between a gelatin-coated glass particle and a graphitic surface were measured in solution using the same device except that the AFM was operated in the force plot mode, as described elsewhere [9–11]. Briefly, the surface of the sample and the cantilever were periodically approached to each other and the deflection of the cantilever was measured. The deflection is proportional to the force exerted on the cantilever. A 15-μm glass sphere was attached to the standard AFM cantilever with a spring constant of  $0.05 \text{ Nm}^{-1}$ . The gelatin film was deposited onto the glass sphere by dipping the entire cantilever holder with the mounted sphere into 0.2 wt.% gelatin–water solution at different pH values for at least 2 min. All measurements were performed in a liquid cell.

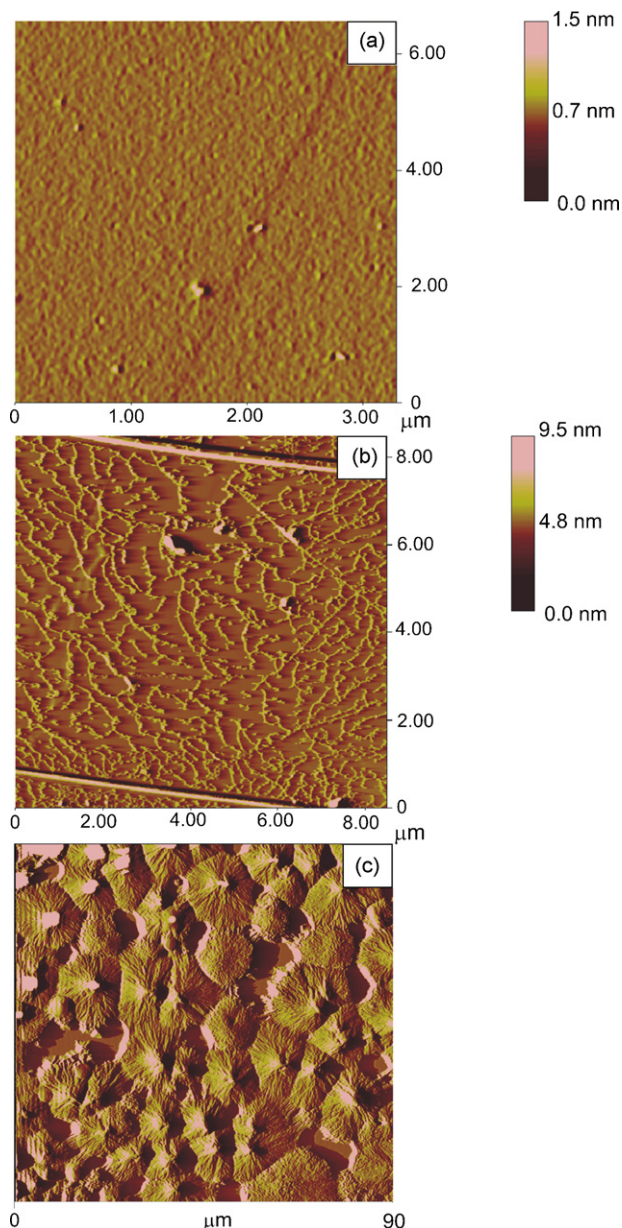
The electrochemical tests were performed using a laboratory-made three-electrode testing cell as described elsewhere [1,6]. The working electrode was a cathode or a graphitic anode as described above while the counter and the reference electrodes were made of metallic lithium. Metallic lithium foil (0.75 mm thick) was obtained from Alfa Aesar (Johnson Matthey GmbH, Karlsruhe, Germany). The working and the 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. The electrolyte used was 1 M solution of  $\text{LiPF}_6$  in EC:DMC (1:1 ratio) as received from Merck KGaA (Darmstadt, Germany).

Charge–discharge curves were recorded using a Solartron 1286 Electrochemical Interface or EG&G Model 283. The constant current (charge and discharge current) during cell cycling was set to a value corresponding from C/20 to 2C cycling rate, and the geometric surface area of the working electrode was always  $0.5 \text{ cm}^2$ .

The microelectrode impedance spectra were measured using a custom-designed apparatus [12]. A Karl Suiss PM5 probe was equipped with two micromanipulators and a Lincam TMS 93 heating table. The samples were observed with a Mitutoyo optical microscope and a Hitachi CCD camera linked to a PC. In the case of high impedance values (typically above  $10^7 \Omega$ ), a Transimpedance amplifier I, H.I.M.S. 96, which allows measurements of impedances up to  $10^{12} \Omega$ , was combined with a 1250 Frequency Response Analyser from Solartron. In the case of lower impedance values, the latter was combined with a 1286 Electrochemical Interface from Solartron.

## 3. Results and discussion

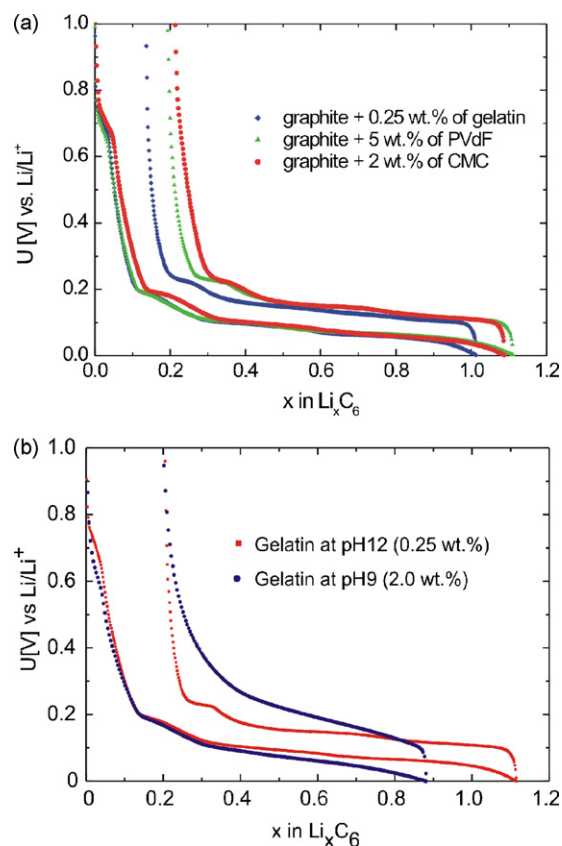
Fig. 2 shows surface distribution of three different binders: gelatin (a), carboxymethylcellulose (CMC) (b), and PVdF (c) on the surface of highly oriented pyrolytic graphite (HOPG). HOPG was chosen because its surface is smooth enough to allow for precise AFM-based imaging. We believe, however, that the basic patterns of binders are preserved also on other surfaces, as long as the attractive forces between the binder molecules themselves are stronger than those between the binder and the substrate. We can see that gelatin covers entirely the substrate surface in a form of nanometre-thick homogeneous film. By contrast, CMC forms thread-like patterns rather than homogeneous film. A large portion of surface remains uncovered. The threads themselves have a thickness of ca. 10–20 nm; they seem to be interconnected, but the structure contains many defects and the whole network seems rather fragile. The structure of PVdF is also partly open; however, large portions are covered by tens of micrometres thick, dense patches. The patches are interconnected, the whole network seems much stronger than that of CMC. The openness of binder surface structure is directly reflected in surface passivation process (Fig. 3a). The most open structure of CMC has basically no impact on passive film growth so irreversible losses in the first cycle are the biggest



**Fig. 2.** AFM images of different binders on the surface of a highly oriented pyrolytic graphite (HOPG): (a) HOPG was dipped into gelatin solution at pH 12 for 1 h; (b) HOPG was dipped into 1 wt.% of CMC solution and (c) HOPG was dipped into 1 wt.% of PVdF solution in NMP.

(Fig. 3a, red circles). PVdF (green triangles) exhibits slightly smaller irreversible losses due to passivation while gelatin (blue diamonds) has the most beneficial impact on the passive film formation. These results confirm our previous model [1–5] in which we supposed that gelatin induces homogeneous (low-defect) growth of passive film due to its homogeneous coverage of surface (namely, gelatin molecules with their many specific groups serve as dense nucleation points leading to homogeneous passivation).

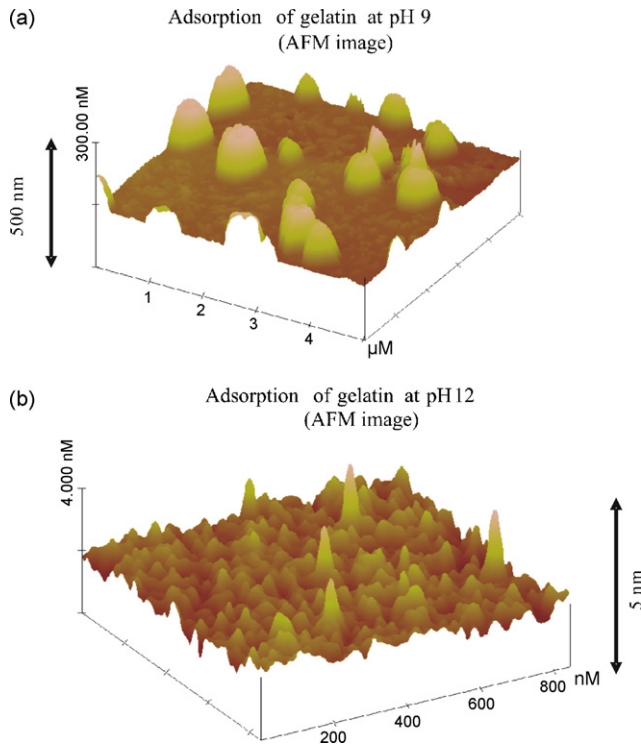
To estimate the “binding strength” of a binder, one can refer to the retention of reversible capacity during cycling. We showed in previous papers [1–5] that the reversible capacity of all three systems is comparable if sufficient (supercritical) amount of binder is used. The critical amount for the three systems is again consistent with observations in Fig. 2: to form a 3D network from the relatively thin threads of CMC one needs about 2.5 wt.% of CMC in the elec-



**Fig. 3.** (a) First charge–discharge of three SFG 44 graphite-based anodes prepared with three different type of additives (binders): gelatin (blue diamonds), CMC (green triangles) and PVdF (red circles); (b) First charge–discharge of two SFG 44 graphite-based anodes with different contents of gelatin: 2 wt.% (red squares) and 0.25 wt.% (blue circles) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

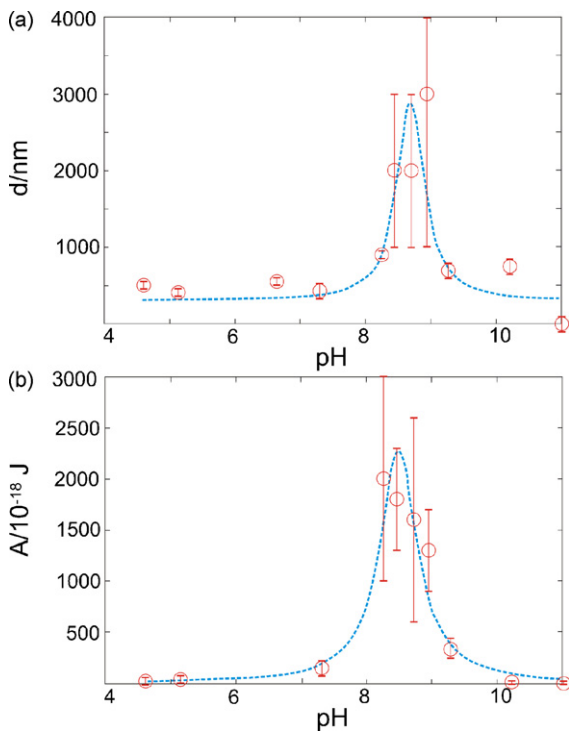
trode composite. By contrast, the thick interconnected structure of PVdF consumes up to 5 wt.% of binder in the composite anode. For the formation of very thin (1 nm) homogeneous film of gelatin one merely needs about 0.25 wt.% of gelatin in the electrode composite.

In an attempt to optimize the gelatin properties as a binding agent and, at the same time, as a surface modifier, we measured gelatin properties as a function of pH. The gelatin structure on HOPG surface at two representative pH values is shown in Fig. 4. At pH 9 thick globular structures with a diameter of up to 200 nm are observed (Fig. 4a). At pH 12, however, very fine, grass-like structures with a typical height of several nm are visible (Fig. 4b). This fine structure is consistent with the smooth top view shown in Fig. 2a where also gelatin at pH 12 was displayed. The present structural dependence on pH is consistent with earlier observations and explanations of general protein behaviour by Israelachvili et al. [13]. We were interested in how these structural differences affect the gelatin binding ability. The basic AFM force experiment was explained in a previous publication [3]. Here we extend this earlier study to a range of pH values (Fig. 5). By approaching and subsequent retracting a gelatin-covered glass sphere to flat HOPG surface we have determined the typical distances to which gelatin retained attractive forces (Fig. 5a). We can see from Fig. 5a that at pH values below 8 and above ca. 9.5 the typical distance of gelatin attractive forces upon retraction is about 500 nm. Inside this interval, however, the attraction forces can extend almost 3  $\mu\text{m}$  from the surface. This can be explained by the much more extended basic structure at pH 9, as shown in Fig. 4a. Consistently, the work needed to break the gelatin bridging forces is also the biggest



**Fig. 4.** AFM images of gelatin on the surface of an HOPG at different pHs: (a) at pH 9 and (b) at pH 12.

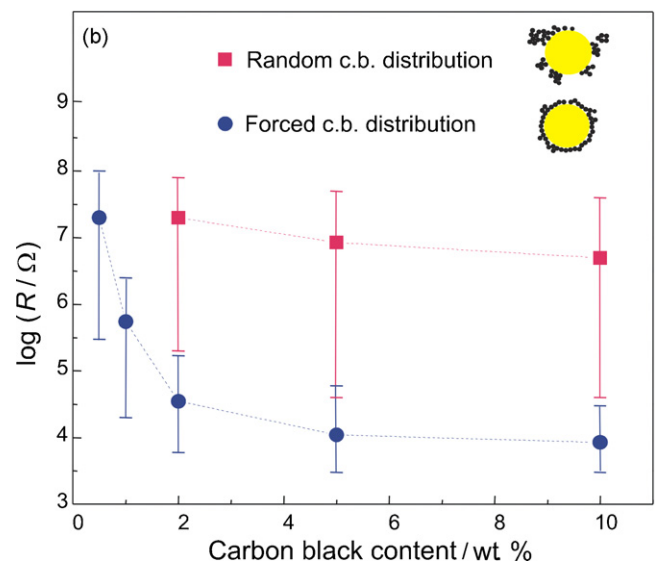
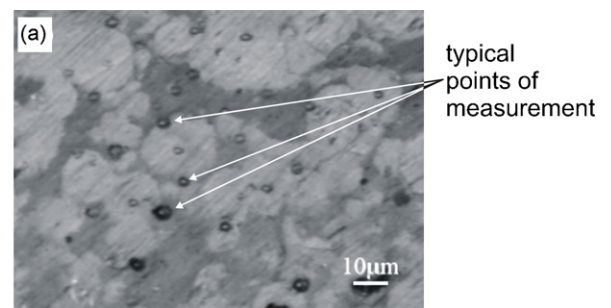
around pH 9 (Fig. 5b). Based on these results, one may conclude that gelatin at pH 9 is more appropriate for use as a binder because it simply has much stronger binding ability at these conditions. While this is certainly a plausible reasoning, one must be careful



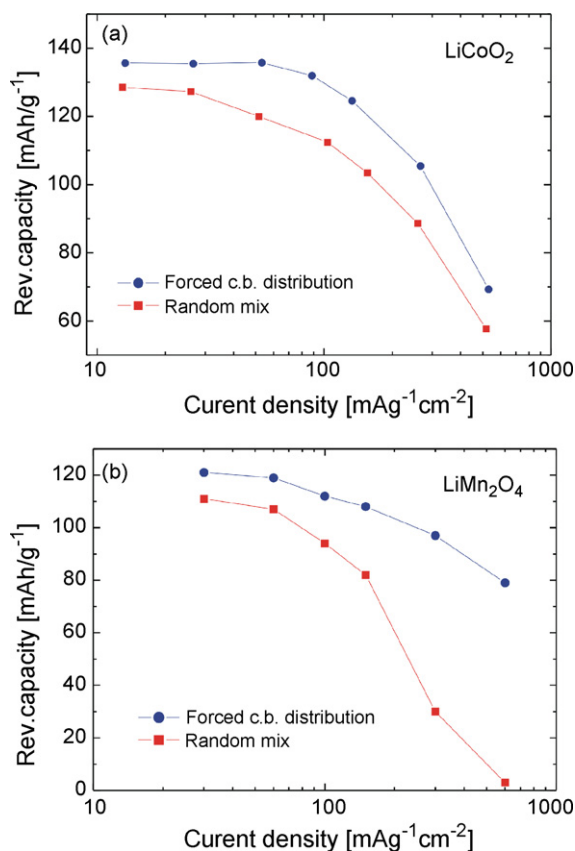
**Fig. 5.** Dependence of two AFM-derived parameters on pH of gelatin solution: (a) distance at which the last gelatin bonds were broken after retraction of gelatin-covered sphere from HOPG surface and (b) work needed to break all the gelatin bonds upon retraction of gelatin-covered sphere from HOPG surface.

because, as mentioned several times, gelatin is not only a binder but also a surface modifier affecting the irreversible losses. Indeed, the electrochemical testing (Fig. 3b) is showing that despite better binding ability at pH 9, the surface modifying properties of gelatin are better at pH 12. We believe that at pH 9 the globular gelatin structure is so thick (200 nm) that it starts to prevent access of charge to the electrode surface. This blockage of surface causes excessive electrode polarization, as can be deduced from Fig. 3b: we see that at pH 9 the gap between charge and discharge curve is bigger than at pH 12. These results once again demonstrate that the binding ability of a binder is only one parameter to be considered when selecting a binder; equally important is how the binder affects the surface properties of active particles.

In several previous works we exploited the surface modification ability of gelatin also in preparation of cathodes. We have shown that in cases where active particles are exposed to gelatin solution, the gelatin first adsorbs on the active particles surface (similarly as shown in Fig. 2a and Fig. 4b of the present work). When such a system is treated with carbon black dispersion, this thin gelatin layer serves as glue that binds the carbon black particles on the surface of active particles. The result is a uniform distribution of carbon black particles around each active particle. The purpose of this carbon black surface layer is to provide uniform electronic conductivity



**Fig. 6.** (a) SEM micrograph of a polished surface of a  $\text{LiMn}_2\text{O}_4$ -carbon black pellet used for microimpedance measurements. Positioning of microelectrode is seen as small circles around brighter bigger circles ( $\text{LiMn}_2\text{O}_4$ ). Carbon black is not seen. (b) Resistances determined by measuring pellets with different amounts of carbon black. Each pellet was measured at least at 30 points (the full ranges and the average values are indicated for each pellet). Red: conventionally prepared cathodes, blue: gelatin assisted forced deposition of carbon black (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).



**Fig. 7.** Electrochemical rate performance for (a) LiCoO<sub>2</sub> cathodes; the conventional random mix electrode contained 5 wt.% of carbon black, the gelatin-based cathode with forced carbon black deposition contained merely 2 wt.% of carbon black and (b) LiMn<sub>2</sub>O<sub>4</sub> cathodes; both cathode types contained 2 wt.% of carbon black (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).

around each particle which should facilitate charge–discharge process. In the present work we check this assumption by measuring the electronic conductivity around selected LiMn<sub>2</sub>O<sub>4</sub> active particles treated by gelatin and exposed to carbon black dispersion. Such a gelatin-and-carbon black treated samples were pressed into a pellet and polished. The typical polished surface is shown in Fig. 6a. LiMn<sub>2</sub>O<sub>4</sub> particles are seen as bright circles. Carbon black is not visible under these conditions. We pressed tungsten microelectrodes with a diameter of 2 μm at many points around each LiMn<sub>2</sub>O<sub>4</sub> particle (see some examples in Fig. 6a) and measured at those points the resistance using impedance spectroscopy; the counter electrode was a macroscopic electrode at the other side of pellet. Using this approach, we measured different pellets with different amounts of carbon black. The results are gathered in Fig. 6b. For comparison, the same type of measurements were also performed on simple mixtures of carbon black and LiMn<sub>2</sub>O<sub>4</sub> (e.g. without the use of gelatin). We can see from Fig. 6b that in the cases where carbon black is forced to surround the active particles covered by gelatin, the average resistance around the active particles is decreased by more than two orders of magnitude. This holds true for all contents of carbon black. It can also be seen from Fig. 6b that the typical microelectrode resistance around LiMn<sub>2</sub>O<sub>4</sub> in conventional cathode (prepared by simple mixing) is ca. 10<sup>6</sup>–10<sup>7</sup> Ω. Note, however, that the same average resistance (10<sup>6</sup>–10<sup>7</sup> Ω) is achieved by forced carbon black deposition by merely using about 0.5–1 wt.% of carbon

black. In view of these important conductivity results, one can also explain the better electrochemical performance of the cathodes prepared by forced carbon black deposition if compared to the conventionally prepared cathodes (Fig. 7). For example, Fig. 7a displays two LiCoO<sub>2</sub> electrodes—one prepared conventionally with 5 wt.% of carbon black (red curve) and the other prepared with the use of gelatin-based forced deposition and 2 wt.% of carbon black (blue curve). Although the latter electrode contains much less carbon black, it exhibits a better reversible capacity at all rates tested. The same phenomenon was observed in the case of LiMn<sub>2</sub>O<sub>4</sub> (Fig. 7b, in this case the electrodes contained equal amounts of carbon black: 2 wt.%).

#### 4. Conclusions

The binding ability of electrode binders can have different origins: it can be based on formation of polymeric networks into which the powder is mechanically entrapped (PVdF, cellulose) or on formation of molecular bridges by directly adsorbing to neighbouring particles (gelatin). Gelatin exhibits very strong and far-reaching bonds at pH 9; there the bonding distance can reach several micrometres. However, despite this strong bonding, gelatin at pH 9 is not necessarily the most appropriate binder because its open structure causes excessive polarization. A good compromise is the gelatin adsorbed at pH 12 (the bonding forces still extend about 500 nm from the given surface, but the polarization is minimized by formation of a fine grass-like structure of a typical thickness in the nanometre range).

The binding ability of gelatin can also be successfully used for creation of ordered carbon black structures around cathodic particles. Such ordered carbon black layers decrease the average electronic resistance around the active particles by more than two orders of magnitude. We have demonstrated that the decreased electronic resistance has a beneficial effect on the rate performance of two cathode types (LiCoO<sub>2</sub> and LiMn<sub>2</sub>O<sub>4</sub>).

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