

Electrodeposition of Lithium in Polystyrene Sphere Opal Structures on Copper from an Ionic Liquid

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In this paper we report on the electrodeposition of lithium on a polystyrene sphere modified electrode from an ionic liquid. By a simple dipping process, polystyrene (PS) spheres with an average diameter of 600 nm arrange in a hexagonal close packed structure onto an electrode surface. Surprisingly, lithium does not grow uniformly from the electrode surface to the electrolyte within the voids of the PS structure. Depending on the experimental conditions a more or less good inverse opal structure made of lithium, lithium spheres or hollow lithium half-spheres can be obtained showing that the growth of lithium in the employed ionic liquid is more complicated than expected. Somehow lithium tends to push away the PS spheres during growth. Applying a slight mechanical pressure on the PS spheres during deposition improves the growth within the voids of the opal structure. Despite this complicated behaviour the PS opal structure seems to suppress a vertical dendritic growth, thus, a lithium/PS composite electrode or other lithium/polymer composite electrodes might be of some interest in rechargeable lithium metal microbatteries where a dendritic vertical growth has to be avoided.

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Introduction

In the recent years there has been extensive research in the field of batteries. The driving force for this research is the development of full electric vehicles that need batteries with higher capacity, longer cycle life and which are safer than those ones currently available. Although great improvements have already been achieved, serious efforts are still needed to develop new electrode materials and electrolytes in order to ensure a better performance. Furthermore, fabrication of novel electrode architectures could overcome the problems associated with the volume change during cycling and the subsequent capacity fading.^[1–7] Recently we showed that electrochemically made 3D-macroporous aluminium films can be regarded as promising electrodes for Li ion batteries.^[8] There was within 10 cycles of lithium deposition/stripping no dendritic growth of lithium. In a recent paper^[9] we could also show that with the help of polystyrene (PS) opal structures, macroporous Li can be made, in principle. Such a composite electrode might allow the dendrite free deposition/stripping of lithium. As known, metallic lithium is a very attractive anode material for rechargeable Li-ion or Li-air batteries as it has a very high energy density of 3.86 Ah g⁻¹.^[10] However, the dendritic growth of Li upon cycling can either lead to a short circuit or poor cycleability. Therefore, employing of Li/PS composite electrodes in Li batteries offers a reasonable solution of this problem. In this work we present a detailed study on the electrochemical synthesis of mechanically stable Li/PS

composite electrodes in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]TFSA containing 0.5 mol L⁻¹ lithium bis(trifluoromethylsulfonyl)amide (Li TFSA). The PS template was applied on a copper sheet by a simple dipping process. The PS spheres were self-assembled in an ordered hexagonal structure and the electrodeposition of lithium occurred in the interstitial voids of the sphere arrays.

It should be mentioned that the aim of the present paper is not to deliver a recipe for a dendrite-free lithium metal anode for large-scale rechargeable batteries. We rather aim to show, on quite a fundamental basis, that lithium can grow within the voids of a PS sphere matrix, but the experimental parameters such as concentration and mechanical pressure seem to have an influence on the growth. Furthermore the ionic liquid and the lithium salt concentration play a role in the deposition process.

Experimental

For the deposition of lithium, a polished copper sheet with a 1 cm × 2 cm surface area was used. Prior to use, the copper sheet was successively polished with silicon carbide emery paper of increasing fineness up to 1200, then degreased with acetone in an ultrasonic bath for ~5 min. This sheet was then covered by a simple dipping process with polystyrene spheres (PS) having an average diameter of 600 nm (Duke Scientific). For this purpose the copper sheet was immersed at 40°C in an ethanol/PS

suspension and pulled out manually. While the ethanol evaporates the spheres self-assemble on the sheet, mainly in a hexagonal ordered structure. The better the electrode is polished, the better the spheres self-assemble. Before depositing lithium the PS-covered sheet was tempered at 65 or 100°C for one to two hours, respectively, to improve the adhesion of the spheres with each other. The Plasma treatment was done under atmospheric conditions with a mobile plasma apparatus (by courtesy of Prof. W. Viöl; HAWK Göttingen). This home-made source consists of an alternating high voltage pulse generator (10–30 kV) and a dielectric isolated high voltage electrode. The copper sheet with the PS spheres acts as the grounded counter electrode. The distance between the high voltage electrode and the counter electrode was around 2 mm. The plasma apparatus delivers a power smaller than 10 W.

The electrochemical cell was prepared by pressing a PTFE cylinder onto the substrate, which leaves a surface area of 0.3 cm². In the deposition process the substrate is the working electrode. As reference and counter electrode a Pt-wire and a Pt-ring (99.99 %) were used, respectively. Fig. 1 shows a sketch of the experimental procedure.

For the experiments presented in this paper the Pt quasi-reference electrode potential is sufficiently stable and varies only a little with time. All electrochemical experiments were carried out in a glove box (OMNI-LAB from Vacuum-Atmospheres) with oxygen and water contents of ~2 ppm. For the deposition of lithium a solution of 0.5 mol L⁻¹ lithium bis(trifluoromethylsulfonyl)amide (Li TFSA) in the ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}][TFSA], custom synthesis from Merck/EMD, all impurities under

10 ppm) was used. Furthermore, the deposition from a saturated solution of Li TFSA (~2 mol L⁻¹) in [Py_{1,4}][TFSA] was also investigated. The electrochemical cell was filled with the solution and an electrode potential between -3 and -3.7 V was applied using a VersaStat II potentiostat/galvanostat (Princeton Applied Research, Power Suite software). In order to test the deposition of lithium in a pseudo-battery design, the PS/Cu electrode was covered with a borosilicate glass microfibre separator (Whatman GF/D) soaked with the Li TFSA/[Py_{1,4}][TFSA] solution. A lithium foil served as counter electrode, which was pressed via the separator onto the PS/Cu electrode. After the lithium deposition the separator and the supernatant ionic liquid were removed and the PS/Cu electrode was rinsed in pure [Py_{1,4}][TFSA]. Subsequently the PS spheres were removed by dry tetrahydrofuran (THF) inside the glove box. Removal of the PS spheres is necessary to gain an analytical insight into the grown structures by scanning electron microscopy (SEM) (Carl Zeiss DSM 982 Gemini). The transport of the samples to the SEM was completed under an inert gas atmosphere. However, a certain contact with oxygen of the atmosphere could not be completely avoided while transferring the sample into the SEM chamber. The structure of the separator was analyzed with a laser microscope (Keyence VK-X200).

Results and Discussion

In the following we summarize – step by step – the results that we obtained when lithium was deposited on the PS sphere modified copper electrode. Fig. 2a shows a typical PS sphere-modified Cu electrode with a regular hexagonal ordering of the spheres on top. The individual domains can have a width of up to 20 μm, which is

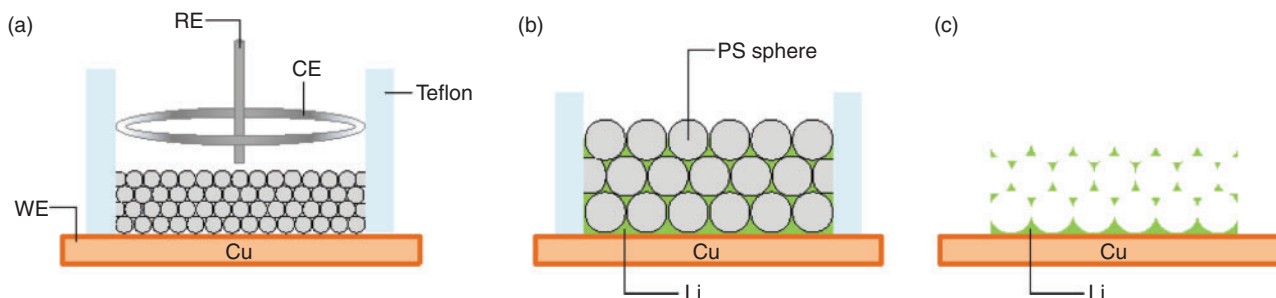


Fig. 1. Schematic illustration of macroporous lithium electrodeposition. (a) Electrochemical cell. (b) Electrodeposition of lithium in the voids of the opal structure. (c) Macroporous structure of lithium after dissolution of PS with THF.

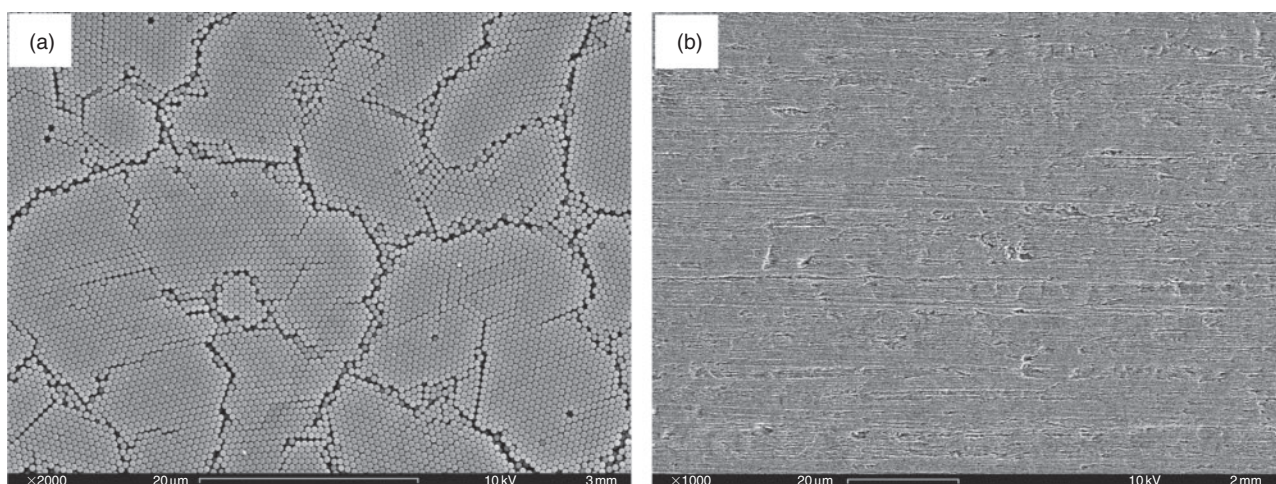


Fig. 2. (a) SEM image of self-assembled PS spheres with a diameter of 600 nm on polished copper electrode. (b) SEM image of the polished copper electrode.

usual if a polished metal surface is coated. In this case roughly ten PS sphere layers were deposited. The SEM image of Fig. 2b shows the bare surface of a polished copper substrate.

Fig. 3a shows a half-cycle for the deposition of Li from 0.5 mol L^{-1} LiTFSA in $[\text{Py}_{1,4}]\text{TFSA}$. The copper electrode with the PS spheres on top was annealed for 90 min at 100°C under air. Subsequently the electrolyte was filled in and was allowed to wet the electrode for 45 min before the potentiostat was switched on. Beginning at the open circuit potential the electrode potential was decreased with a scan rate of 10 mV s^{-1} until -3.3 V v. the quasi reference electrode, where the scan was stopped. There are two reduction peaks, one at -1.8 V and one at -2.75 V , with comparable magnitude that are associated with the formation of Cu/Li alloy and a thin film of Li, respectively. Cu can dissolve up to 18% of Li at room temperature.^[11] Furthermore Cu/Li surface alloys are known.^[12] At electrode potentials of below -3 V the bulk deposition sets in. After removal of the PS spheres, we obtained quite an interesting Li deposit. Instead of a macroporous structure which we would have expected, we observed rather randomly distributed hollow Lithium spheres, Fig. 3b.

Although this is not the result we expected, Fig. 3b gives some interesting insight into the growth of lithium as obviously

the Li growth has first occurred at the Cu/PS sphere/electrolyte interface and then grown over the PS spheres instead of filling the interstices of the PS opal structure. We should mention here that a fundamental in situ STM study^[13] of Li deposition on Au(111) gave some hints that a less defined layer forms on Au(111) before the deposition of lithium starts in this liquid. As was shown by Byrne et al.,^[14] a partial decomposition of the TFSA anion has to be expected when reactive metals are deposited in this liquid. The low order of the hollow spheres is in contrast to the well-ordered PS spheres before the deposition. At a minimum this shows that the PS opal structure can be disturbed during the growth of lithium. In order to exclude that the roughness of the Cu plate is responsible for this surprising effect in the next set of experiments the Cu plate was polished with a diamond polishing paste (METADI II, 3 micron, Buehler), which leads to a mirror like Cu surface. The PS spheres were applied in the same manner as described above and annealed at 65°C for 60 min under air. Subsequently the electrolyte (0.5 mol L^{-1} LiTFSA in $[\text{Py}_{1,4}]\text{TFSA}$) was filled in and allowed for 30 min to wet the electrode. The potentiostat was switched on and three cyclic voltammograms were run with 10 mV s^{-1} between $+0.5$ and -3.5 V v. the quasi reference electrode, as shown in Fig. 4a.

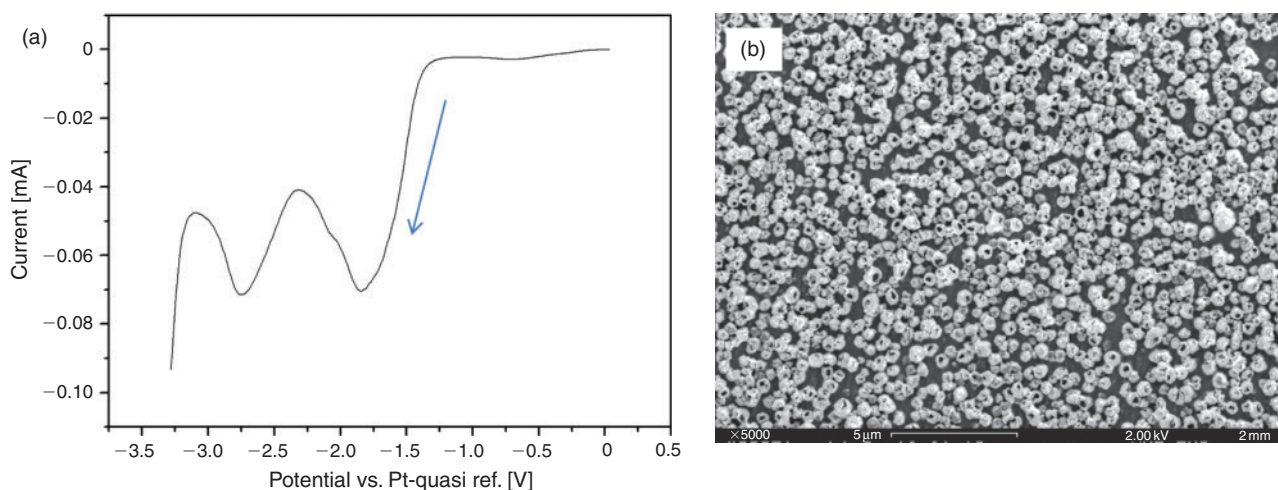


Fig. 3. (a) Half cycle of Li deposition from 0.5 mol L^{-1} LiTFSA in $[\text{Py}_{1,4}]\text{TFSA}$ (details: see text). (b) SEM image of the obtained hardly ordered lithium hollow spheres.

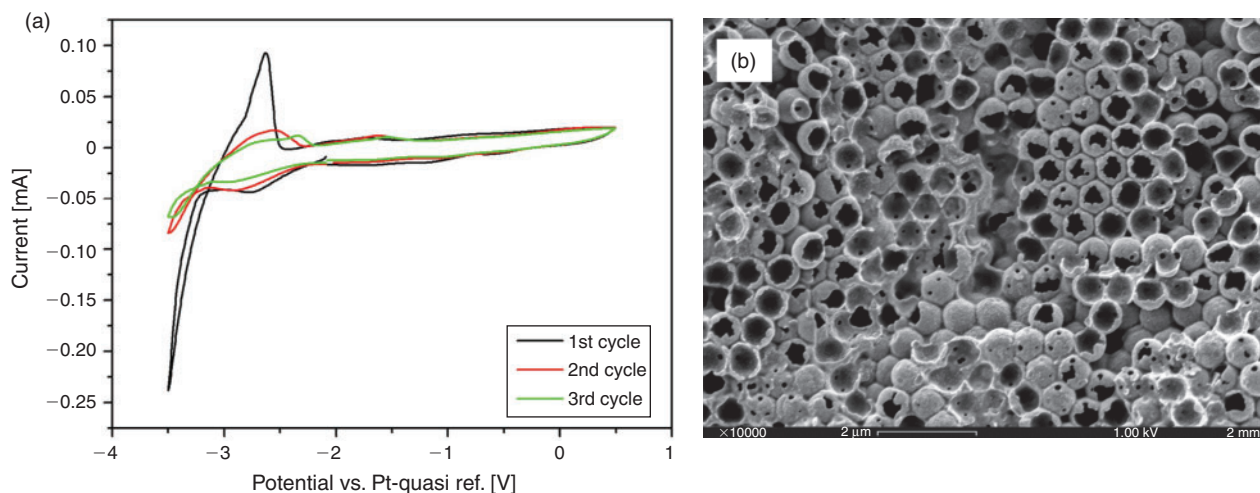


Fig. 4. (a) 3 CV cycles of Li deposition from 0.5 mol L^{-1} LiTFSA in $[\text{Py}_{1,4}]\text{TFSA}$ (details: see text). (b) SEM image of the obtained lithium.

In contrast to Fig. 3a the reduction process at -1.8 V is no more visible as a peak in the first cycle, rather a constant base current is observed and the peak at -2.75 V is less sharp as in the case before. At potentials of below -3 V there is a steeply rising current, which we can attribute to the bulk deposition of Li, followed in the back scan by a stripping peak due to the oxidation of Lithium. In the 2nd and the 3rd CV cycle the electrochemical behaviour becomes less defined and less reversible, showing that some irreversible processes have occurred. Fig. 4b shows a part of the surface after the 3rd CV cycle. The deposited lithium has better filled the interstices of the PS opal structure, but again it is obvious that the lithium rather seems to grow on the surface of the individual PS spheres than to fill the interstices completely. We might speculate that this somewhat hindered growth is due to the partial decomposition of the electrolyte during deposition of lithium. This interpretation is supported by the fact that on the same Cu electrode we found areas where apparently no Li has grown at all. For this purpose we increased for the following experiments the concentration of LiTFSa until saturation, which gave a slightly more viscous electrolyte.^[15] The parameters were only slightly changed.

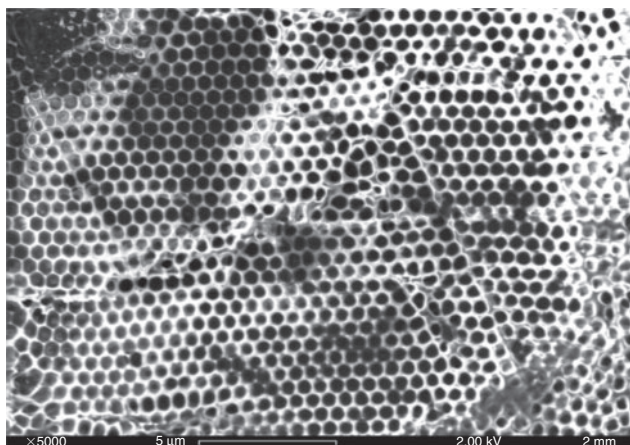


Fig. 5. SEM image of the obtained lithium.

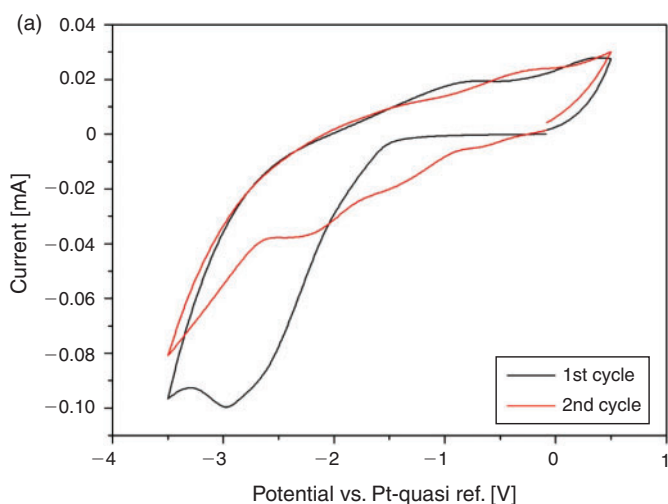
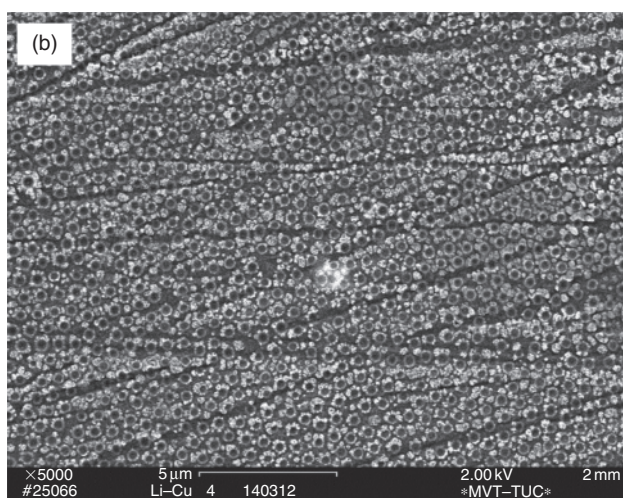


Fig. 6. (a) 2 CV cycles of Li deposition from saturated LiTFSa in $[\text{Py}_{1,4}]\text{TFSa}$. The PS spheres were treated with an air plasma for 10 s before the cell was filled (details: see text). (b) SEM image of lithium obtained from saturated LiTFSa in $[\text{Py}_{1,4}]\text{TFSa}$. The PS spheres were treated with an air plasma for 25 s before filling of the cell with the electrolyte.

Instead of a polishing paste with $3\text{-}\mu\text{m}$ grains, the Cu electrode was polished with emery paper having in the average $5\text{-}\mu\text{m}$ grains. After deposition of the PS spheres the electrolyte was also allowed to wet the electrode for 30 min, but instead of cyclic voltammograms the deposition was directly completed at -3.7 V for 2 min. At the first glance one might wonder why the deposition was completed in a potential regime where the electrolyte decomposition has to be expected. Unfortunately the growth was not uniform and slow if less negative electrode potentials were applied, which might be a consequence of the higher viscosity, therefore we had to apply quite negative electrode potentials. Fig. 5 shows the surface after removal of the PS spheres.

In contrast to Fig. 4 we observe now a more or less regular growth over the whole of the surface, but again the topmost layer consists of hollow half-spheres. The former hexagonal order of the PS spheres is still recognizable but in any case the interstices have not been filled uniformly by lithium. Again, surprisingly, lithium seems to grow preferentially on the surface of the spheres. In order to test if the surface of the polystyrene spheres plays a role, we changed one more parameter. As in the experiments before, the Cu electrode was polished and coated with PS spheres. The electrode was annealed for 2 h at 100°C and then treated for 10 s with a dielectric barrier discharge (DBD) plasma under atmospheric conditions. X-ray photoelectron spectroscopy (XPS) measurements indicate (not shown here), that this treatment leads to a partial oxidation of the PS spheres by introducing oxide groups ($\text{C}-\text{O}$; $\text{C}=\text{O}$) on the surface. These results are in good agreement with XPS results achieved for the interaction of O_2 -Plasma with PS foils.^[16] The electrolyte (saturated LiTFSa in $[\text{Py}_{1,4}]\text{TFSa}$) was allowed to wet the electrode for 45 min before the electrochemical experiment was started. Fig. 6a shows two subsequent CV scans between $+0.5$ and -3.5 Volt with a scan rate of 10 mV s^{-1} .

We observe a main reduction process at around -3 V in the first scan, in the second scan the cathodic current is reduced. In both cases there is no stripping peak, rather a continuously rising anodic current is observed. For Li deposition a 3rd scan was started at the open circuit potential and stopped at -3.5 V. The SEM image of the obtained deposit as seen in Fig. 6b, shows



over quite a large area of the surface an imperfect macroporous structure. There are no longer hollow spheres or half spheres and the lithium has at a minimum much better filled the interstices of the PS opal structures than in the previous cases. From this result we can conclude that the surface oxidation of the PS spheres by an air plasma has a beneficial effect on the regular growth of Li within the voids of the PS opal structure. We cannot yet comment on the surface chemistry of the oxidized PS spheres in the presence of the ionic liquid but we plan to do a fundamental XPS study of plasma-treated PS spheres without and with a thin evaporated ionic liquid layer on top.

We can summarize the results we have obtained so far as follows:

- There is an alloying of lithium with copper
- The electrolyte can be decomposed and the deposition of lithium in the employed electrolyte seems to occur in parallel to a partial electrolyte decomposition
- Lithium grows preferentially on the surface of unmodified PS spheres
- Treatment of the PS spheres for a short time with an air plasma improves the deposition within the interstices of the PS sphere opal structure

In the last set of experiments for this paper we decided to do the deposition in a quasi-battery electrochemical cell, which is sketched in Fig. 7a.

The Cu electrode is covered with the PS spheres as described above, but we did not perform a thermal annealing this time. We applied a glass microfibre separator on the PS spheres (see Fig. 7b) and filled in the electrolyte (saturated LiTFSa in $[\text{Py}_{1,4}]\text{TFSa}$), which was allowed for 30 min to wet the electrode. Subsequently a lithium foil was put on the separator and pressed with a stainless steel cylinder (between 1800 and 8300 Pa), on top of this electrode assembly. We did not perform cyclic voltammograms and completed the lithium deposition during 20 min at -3.1 V. Fig. 7c shows the result we obtained when the cell was disassembled and the PS spheres removed with THF.

We mainly obtain a wizen macroporous structure of lithium. We can conclude that the mechanical pressure applied to the PS opal structure has stabilized it and consequently the lithium grew more uniformly within the voids of the PS structure. Although not yet perfect, this result shows that the dendrite-free deposition of lithium within the voids of a PS sphere opal structure should be possible. In future we will determine whether these results can be improved if the PS spheres are subject to a surface modification, e.g. by a silanization. Furthermore the pressure applied on the electrode will be varied. We also plan to do these experiments with LiFSA/ $[\text{Py}_{1,4}]\text{FSA}$ (FSA = bis(fluorosulfonyl)amide) as the FSA seems to be less sensitive to cathodic breakdown than the TFSa. We should clearly say that the aim of this work is NOT to make lithium

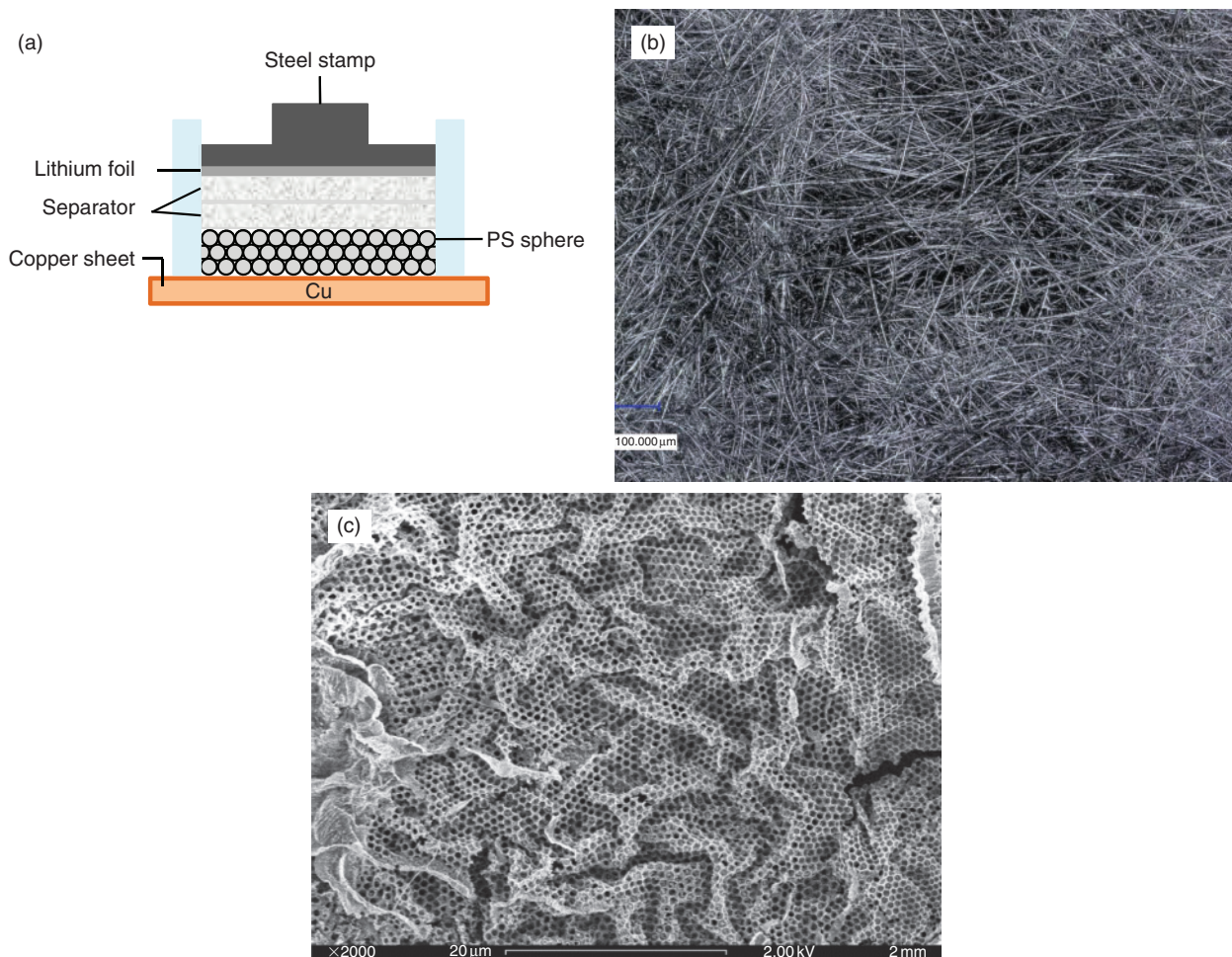


Fig. 7. (a) Experimental set-up (sketch) for lithium deposition on the PS sphere covered Cu in a battery-like cell. (b) LASER microscope image of the separator material. (c) SEM image of the obtained lithium.

anodes for large scale batteries, for example to drive cars. We are interested in a fundamental understanding of lithium deposition from ionic liquids in templates. Such a lithium/polymer composite material would rather be interesting for microbatteries or, as macroporous material, for primary batteries due to the high internal surface. One can expect that such a macroporous lithium structure would deliver – in comparison to a flat lithium foil – higher currents.

Conclusion

In this paper we have shown that lithium can be electrodeposited from LiTFSA in the ionic liquid [Py_{1,4}]TFSA onto a PS sphere-modified copper electrode. In principle Li grows through the voids of the opal structure. Depending on the pretreatment of the electrode, either Li hollow spheres or a macroporous structure can be obtained after removal of the PS spheres. A surface oxidation of the PS spheres by an air plasma seems to improve the growth of lithium through the opal structure. In a quasi-battery setup where the PS sphere covered electrode is pressurized mechanically via a separator a wizen macroporous structure is obtained. This result shows that a mechanical pressure on the PS opal structure seems to be beneficial for a uniform lithium growth. We have so far not obtained dendritic growth in any of our experiments. A final answer on that requires, of course, a detailed analysis with multiple charging/discharging cycling which, however, was not the scope of the present paper.

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