

Electrochemical synthesis of conformal, thin and dense ionomer separators for energy storage and conversion devices

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Abstract

Electrochemical synthesis is a powerful tool for the preparation of conformal, thin solid electrolytes directly on the electrodes, particularly with complex shapes, such as nanostructured electrodes. Such separators should present the highest possible single ion conductivity, negligible electronic conductivity combined with high chemical and mechanical stability. These requirements drive our development work: we synthesize polymers with excellent mechanical properties, which are decisive for a high durability of the separators. The single-ion conductivity is assured by anchoring the counter-ions on the polymer backbone. The solid polymer electrolytes contain no flammable solvent guaranteeing high safety. For cation-conducting membranes, we synthesized polymers with sulfonate groups grafted on the macromolecular chain. These ionomers, including poly(styrene sulfonate) (PSS) can be used for proton exchange membrane fuel cells and Li batteries. Anion-conducting membranes contain quaternary ammonium as fixed cationic groups; they can be applied for example in hydroxide exchange membrane fuel cells. The paper presents the electrochemical synthesis procedures and the relevant structural, microstructural and electrical properties of cation- and anion-conducting polymers, including relevant data of applications, such as Li microbattery cycling. Copyright © 2018 VBRI Press.

Keywords: Polymer electrolytes, cation exchange membranes, anion exchange membranes, Li microbatteries, fuel cells.

Introduction

All solid-state devices are a major topic of research for sustainable and safe energy storage and conversion [1-5]. The synthesis of advanced materials is especially needed in the field of solid electrolytes for electrochemical energy technologies, including fuel cells [6-8], water electrolyzers [9-11] and solid-state batteries [12-14].

High performance separators must present a series of properties, which are difficult to reconcile in a single material [15]. The main requirement is the highest possible ionic conductivity by the electrochemically active ions, if possible single ion conductivity, because the counter-ions do not participate in the electrode reaction but can provoke polarization phenomena on cycling, for instance in lithium batteries [16-19]. At the same time, a high chemical and mechanical stability is mandatory for solid electrolytes in order to guarantee a long life and safe operation. It is evident that the presence of mobile ions in a solid is related to relatively weak ionic-covalent bonds between the constituents, which does not favor the mechanical and chemical stability of the solid.

One possible way to escape from this dilemma is to develop materials with phase-separated structures, such

as ionomers, where the polymer phase is responsible for the mechanical and chemical stability of the material, while the ionic transport takes place in nanochannels, where the ionic motion is solvent-assisted [20-21]. In this way, the antinomic properties of stability and ion mobility can be reconciled to a certain point.

The most popular example of such ionic conducting polymers with microphase separation is Nafion, a perfluorinated polymer with grafted sulfonic acid groups on side chains. The protons are mobile in hydrated nanochannels, where they can be exchanged with other cations. The superacidity and hydrophilicity of the sulfonic groups associated with the highly hydrophobic perfluorinated backbone give an excellent nanophase separation, related to a low tortuosity of the nanochannels and a high proton conductivity [22-25].

We have reported many papers on sulfonated aromatic polymers (SAP), where the sulfonic acid groups are grafted on phenyl groups inside the main chains [26-28]. Such polymers present slightly lower performances in terms of ion conductivity, but are superior in thermal and mechanical stability, especially if tailor-made cross-linking treatments are developed [29].

Anion-conducting membranes were also developed by us and others [30-36]. In this case, the main chain contains generally grafted quaternary ammonium groups and the mobile anions move in hydrated channels. Given the lower mobility of the hydroxide anion vs. protons and the lower degree of dissociation of ion pairs, anion-conducting membranes present generally a lower ionic conductivity [37-39]. Therefore, a high degree of functionalization is mandatory.

A very important point for the improvement of solid-state devices is also the quality of the interface between the solid electrolyte and the electrodes [5]. This point is particularly crucial for ceramic separators, but can also play an important role for stiff polymers. In this case, the direct deposition of the ion-conducting solid polymer can be a method of choice to improve the interface properties. Although polymer casting on top of electrodes can be a way, it is often difficult to realize a very thin and conformal deposit, especially if the electrode presents a complicated microstructure, such as nanotubes, nanowires etc.

Although ceramic and glassy separators have been obtained by PVD techniques, especially by radiofrequency sputtering [40-42], this route is not applicable for electronically insulating polymers with few exceptions. Electrochemical synthesis can be a suitable process for the preparation of polymer electrolyte separators, especially in miniaturized or nanostructured devices, because the deposits are conformal and thin, due to the self-limited growth process (the resistance increases during the deposition). The electrochemical route opens thus wide perspectives for the realization of 3D microdevices [43], such as Li microbatteries [44-45].

In this review, we will report some of our recent work on the electrochemical synthesis of polymer electrolytes, together with some relevant literature reports.

Ionomer membranes for microfuel cells

There are currently two types of fuel cells using polymer membrane separators. In *proton exchange membrane fuel cells* (PEMFC) [46-48], the PEM contains generally superacidic sulfonic groups grafted on the polymer chain. These fuel cells operate thus in acidic conditions; the protons formed at the anode are transported by a water-assisted mechanism through the membrane. PEMFC have been developed since the 1960's; the most prominent membrane is Nafion [25, 49], but SAP have also been used successfully [26, 50-53]. A major drawback of PEMFC is the necessary presence of expensive noble metal catalysts, such as Pt, especially for the ORR. The preparation of thin films of polymer electrolytes is complicated: only few polymers can be deposited by plasma deposition [54], because in most cases irreversible degradation is observed.

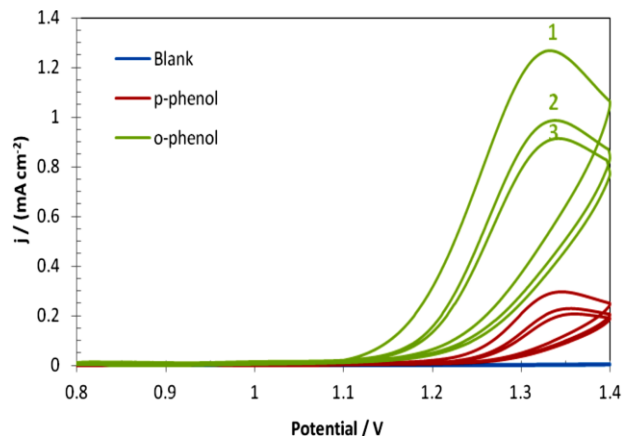


Fig. 1. Cyclic voltammograms of the electropolymerization of o-hydroxybenzene sulfonic acid (green), p-hydroxybenzene sulfonic acid (red) and blank experiment (blue).

To apply electrochemical deposition for the innovative synthesis of thin and conformal PEM, precursor isomers such as o- and p-hydroxybenzenesulfonic acid (sulfonated phenol) can be used [55-56]. The electrochemical synthesis in anodic conditions (**Fig. 1**) gives sulfonated poly(phenyl ether) (SPPE) and allows obtaining a degree of sulfonation of 100%. All potentials are referred to Ag/AgCl reference electrode. An advantage of SPPE is the low molecular mass of the repeat unit, giving a high IEC.

One can observe that the o-isomer is deposited with much larger currents, due to an important steric hindrance of the macromolecule when p-isomer is used [57].

Impedance spectra (**Fig. 2**, frequency: 1 Hz to 6 MHz, oscillating voltage amplitude: 20 mV) allow calculation of the proton conductivity of this ionomer in fully humidified conditions.

Using the membrane thickness, an ionic conductivity of (6 ± 2) mS/cm was calculated [57], which is sufficiently high to allow use in microfuel cells; the experiments are currently in progress.

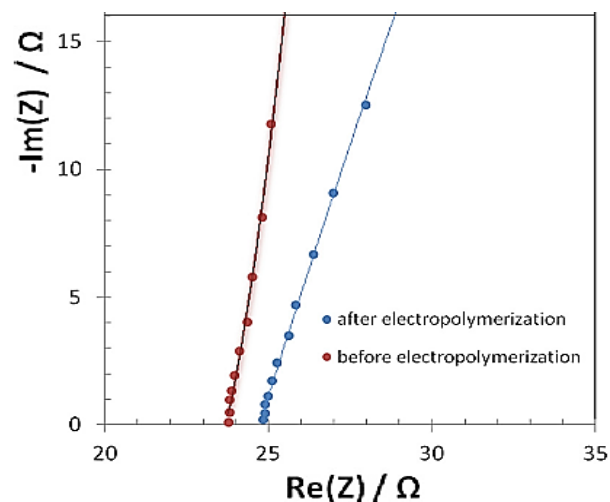


Fig. 2. Typical impedance spectra before and after the electrodeposition of SPPE.

In *anion exchange membrane fuel cells* (AEMFC) [32], a hydroxide-conducting polymer, containing typically anchored quaternary ammonium groups [58], is the separator. These fuel cells operate thus in alkaline conditions; the hydroxide ions formed at the cathode are transported by a water- or solvent-assisted mechanism. However, the formation of ion pairs between ammonium and hydroxide reduces the conductivity especially at low hydration. Other critical points are the possible reaction of hydroxide ions with atmospheric CO₂ and the stability in alkaline conditions. The major advantage of AEMFC is the possibility to operate without noble metal catalysts for the ORR. Recently it was shown that all carbon-based polymers not bearing aryl ether bonds, like polystyrene backbone, can have long-term alkaline stability [34, 39, 59]. Very thin and flexible AEM with low area specific resistance are desirable to optimize the performances, which is one incentive of our work [60].

The electrodeposition of the precursor N-vinylbenzyl-N,N,N-trimethylammonium chloride (VBTMA) allows to obtain carbon-based polymers with low thickness. The synthesis can be performed both in anodic and cathodic conditions (Fig. 3) [61].

The NMR spectra (Fig. 4) show clearly the disappearance of the vinyl double bond after the electropolymerization.

The electropolymerization mechanism in anodic conditions can be written as follows, adapted from Birke and coworkers [62] (Scheme 1).

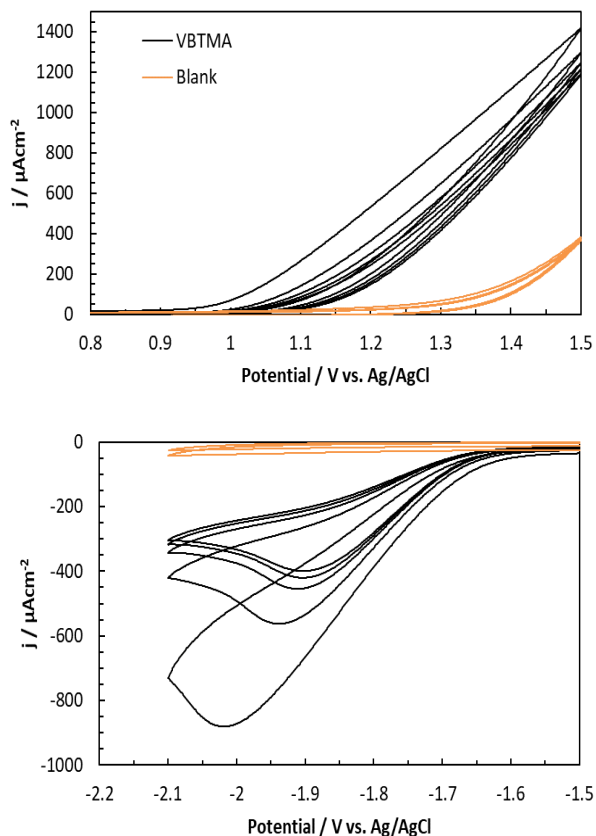


Fig. 3. Electrodeposition of VBTMA in anodic and cathodic conditions (blank: red curve).

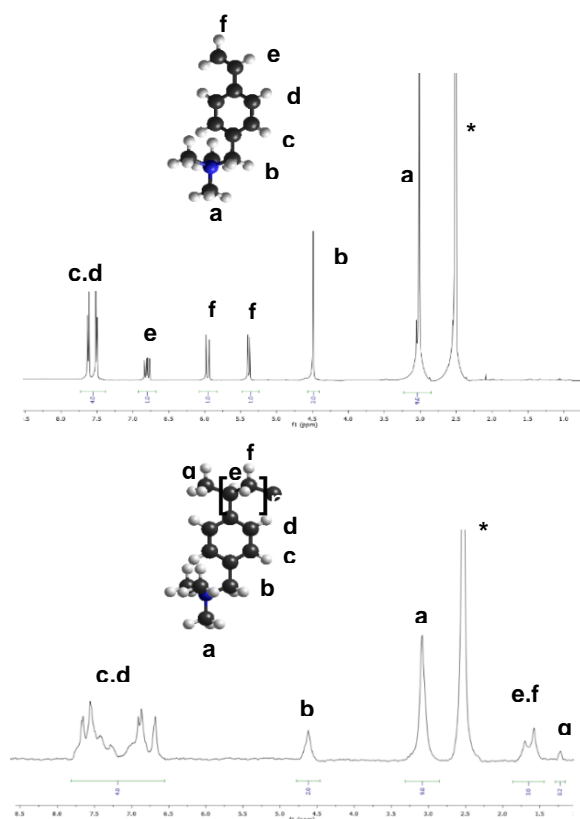
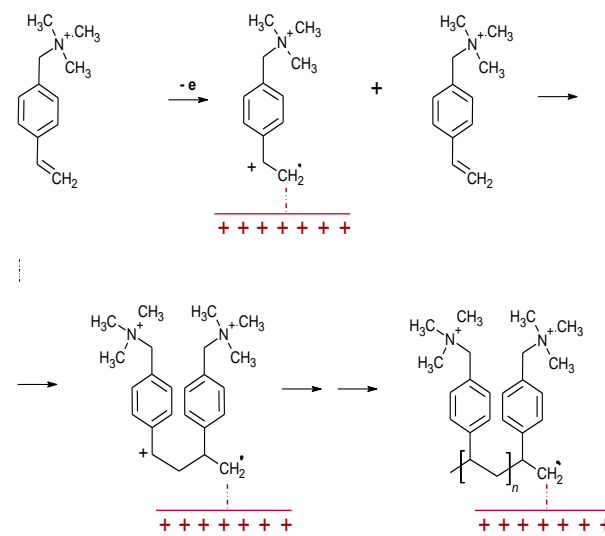


Fig. 4. NMR spectra of VBTMA precursor and electrodeposited polymer. The asterisk indicates the solvent DMSO-d₆.



Scheme 1. Electropolymerization mechanism of VBTMA in anodic conditions, including radical cation adsorption on the anode surface adapted from Birke and coworkers [62].

The hydroxide ion conductivity at 25°C of the membrane synthesized using VBTMA reaches 3 mS/cm, half the value of SPPE in agreement with the lower mobility of the hydroxide anion vs protons. The activation energy is 0.2 eV, slightly higher than typical values for protons, as expected for more voluminous and heavy hydroxide ions.

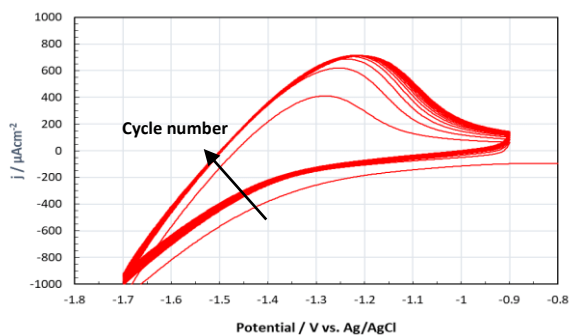


Fig. 5. Cyclic voltammograms of the electrochemical deposition of poly(styrene sulfonate) (PSS) directly on TiO₂ nanotubes.

Ionomer membranes for Li microbatteries

Currently, most microbatteries are conceived with a planar (2D) design with layers of positive and negative electrode materials separated by a thin ion-conducting and electron-insulating membrane. Most often, this separator is inorganic [63], made by PVD techniques, especially sputtering for economic reasons [4, 40]. However, this technique is unable to cover non-planar or complicated electrode designs conformally. We have therefore developed electrochemical deposition as an innovative technique for the synthesis of thin Li ion-conducting polymer films.

Important advantages include the absence of any flammable solvent in the battery and the anchoring of the anions on the polymer chain so that single Li ion conductivity can be realized. Low lithium ion transference numbers cause polarization phenomena, due to the formation of a concentration gradient that limits the maximum power delivery during the charge-discharge process of the battery. Furthermore, SAP membranes present a high mechanical stability so that dendritic growth, which might lead to catastrophic battery failure, can be avoided.

Fig. 5 shows the cyclic voltammograms of the electrochemical deposition of poly(styrene sulfonate) (PSS) directly on TiO₂ nanotubes in cathodic conditions [64]. In fact, styrene derivatives can also be electropolymerized anodically [65]. We can observe in **Fig. 5** the current decrease in successive deposition cycles, due to the formation of the ionomer layer on the nanotubular electrode.

The corresponding NMR spectra of precursor molecules and electrodeposited polymer show, like in Figure 4, clearly the absence of the double bond in the latter [66].

The battery tests were performed using Swagelok cells with TiO₂ nanotubes assembled against a circular Li foil with a diameter of 9 mm. The microbattery cycling (**Fig. 6**) shows an excellent Coulombic efficiency around 100% after the first 3 cycles. The loss of capacity observed during the first cycles is due to irreversible lithiation reactions, for example with OH groups present on the titania surface [44]. The microbattery performances in terms of power and energy density are among the best in literature, as shown in the Ragone plot below [67-69]. The rate capacity up to 10 C is also excellent.

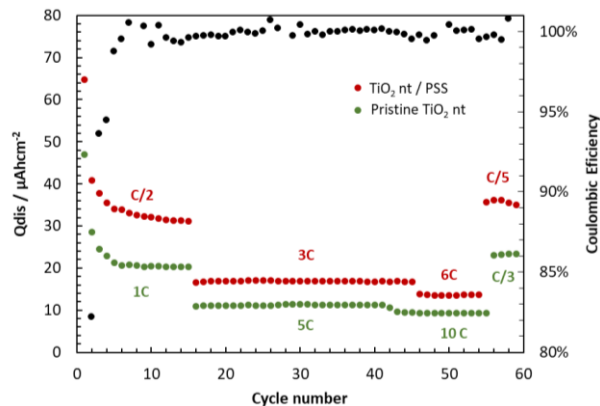
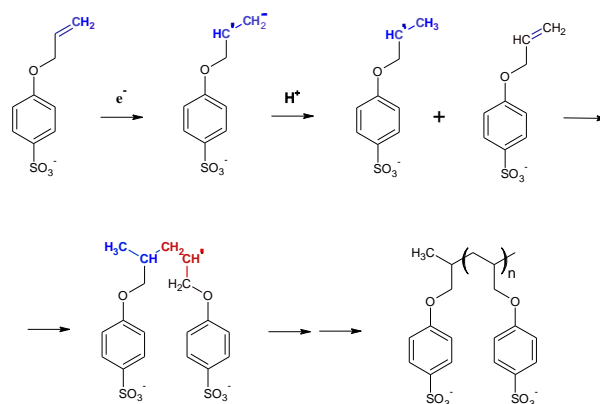


Fig. 6. Areal capacity values for various C-rates at 25 °C for PSS and Coulombic efficiency. The TiO₂nt length is ~1.5 μm.

Another interesting precursor for Li-ion conducting polymers is sulfonated allyl-phenyl-ether. The double bond can be opened in cathodic conditions with formation of a radical anion, which can attack further precursor molecules according to **Scheme 2**. XPS data of the ionomer sulfonated poly(allylphenylether) (SPAPE) are in good agreement with the wanted composition [70].

The electropolymerization mechanism is presented in **Scheme 2**.



Scheme 2. Electropolymerization mechanism of SPAPE in cathodic conditions.

Electron micrographs (**Fig. 7**) show the microstructure of the samples with a ~300 nm thin polymer layer on top of ~2 μm thick layer of TiO₂ nanotubes.

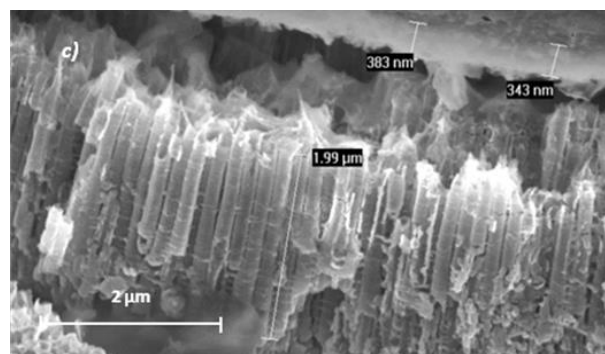


Fig. 7. SEM micrographs of TiO₂nt with a SPAPE layer on top.

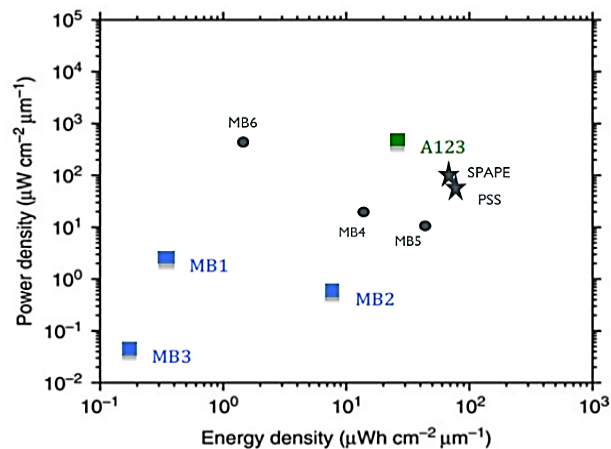


Fig. 8. Ragone plot for various microbatteries (MB) from literature and our data (Li / SPAPE or PSS / TiO₂nt). A123 is a commercial microbattery. Adapted from references [67, 69].

The cycling tests of microbatteries with Li / SPAPE / TiO₂nt configuration show also an excellent rate capability, up to high C values, explored until 12 C. A comparison of the energy and power density with microbatteries from literature is shown in the Ragone plot (**Fig. 8**). Our data are among the best in the literature, particularly from the point of view of the energy density. The excellent performances of our microbatteries are currently further improved.

Conclusion and future perspectives

The outlined electrochemical synthesis is an excellent route for the preparation of thin and conformal anion and cation-conducting ionomer membranes. Major advantages of these solid separators are the absence of flammable solvent, improving safety, the single ion conductivity, due to the anchoring of counter-ions directly on the polymer chain, removing polarization phenomena at the electrodes, and the good mechanical properties of SAP (high stiffness and strength), eliminating the risks due to lithium dendrite formation.

The membranes were characterized by a large spectrum of techniques, including various spectroscopies (NMR, FTIR, XPS, EIS) and electron microscopy. The cycling performances of Li-ion microbatteries were evaluated and especially the rate capability is excellent. Future work on this topic will focus on more complex systems, including precursors for the realization of random and block co-polymers in order to study the impact of mixed vs alternate layers on relevant properties. Mixtures of precursors containing ammonium and sulfonic groups will be electrodeposited in order to prepare amphoteric polymers, with random or alternate layer (block copolymer) structures.

Furthermore, we will explore the co-polymerization of aromatic and aliphatic precursors in order to optimize the mechanical and electrical properties. A larger amount of less rigid aliphatic polymer should reduce the strength and stiffness of the membrane, but might increase the conductivity, due to a better nanophase separation. Evidently, the particular composition of the precursors

can also modulate the hydrophilic/hydrophobic character of the blocks and improve the nanophase separation.

This emerging electrochemical synthesis approach is offering great opportunities to design and generate functional materials for future nano-technological applications in energy storage and conversion.

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