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INVITED ARTICLE

Sol-gel-modified membranes for all-organic battery based on bis-(*tert*-butylphenyl)nitroxide

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Abstract
It has been shown that sol-gel modification of Nafion membrane with amino-containing silica nanoparticles followed by neutralization converting the membrane in the salt form prevents decomposition of the model redox-active compound, bis(*tert*-butylphenyl)nitroxide, and suppresses its crossover yet maintaining sufficient permeability of a supporting electrolyte in acetonitrile solution. Bis(*tert*-butylphenyl)nitroxide is stable under the operation conditions of the redox flow battery assembled with Celgard membrane.

Keywords Nanocomposites · Polymer membranes · Modification · Diaryl nitroxide · Sol-gel

Introduction

The field of all-organic batteries is an emerging part of energy-related research [1]. The attempts to make a battery "greener" have stimulated an interest to organic materials which can be prepared from renewable sources and easily recycled using low-temperature procedure, with low energy consumption and low greenhouse gases release. In addition to sustainability, organic redox-materials exhibit structural diversity and tunability of the properties via modification of carbon skeleton providing high cell voltage in non-aqueous solutions and reversible cycling [2].

To separate the catholyte and anolyte solutions in electrochemical cells, membranes permeable to redox-inactive charge carriers (thus completing the electrical circuit) are necessary. High reactivity of the involved species seriously restricts the range of chemistry used for the preparation of the membranes for organic batteries; this has been limited to porous polyolefins (Celgard, Daramic, etc.), perfluorinated cation-exchange membranes (Nafion), or fluorinated porous (co)polymers (polyvinylidene fluoride) [2, 3]. Generally speaking, the ion-exchange membranes (i.e., Nafion) are used in aqueous media (with, for example, polyphenols, anthraquinone sulfonic acids, or quinoxaline derivatives as redox-active species), whereas porous separators are preferred for non-aqueous systems (with phthalimide, quinoxaline, TEMPO, polythiophene, etc. as redox-active species) [2]. Ionic conductivity of conventional ion-exchange membranes such as Nafion in organic media is much lower than in water, which imparts high area resistance of the electrochemical cell and limits the practical current density [2]. On the other hand, porous separators exhibit lower area resistance but may suffer from pronounced crossover of the redox-active species. Their use in combination with polymeric redox couples has been demonstrated [4], yet the applicability with low molecular species is questionable. Moreover, to the best of our knowledge, the use of Nafion membrane in non-aqueous nitroxyl-based battery systems has not yet been explored. It should be noted that certain dialkyl nitroxyls have been applied as ESR probes to investigate the state of Nafion membrane under varied conditions [5–7]. At the same time, side reactions involving TEMPO-type compounds in aqueous acidic and alkaline media under conditions of redox battery operation have been reported [8], and therefore the stability of redox-active nitroxyl species in contact with Nafion membrane containing residual acidic groups and moisture is a critical issue.

In view of this, we performed primary screening of the behavior of Nafion and Celgard membranes for the possible

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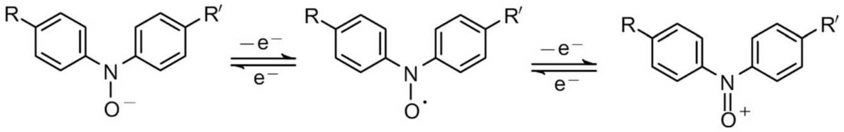
application in all-organic battery utilizing a stable *N*,*N*-disubstituted NO radical, diaryl nitroxide, as redox-active component. Recently, a series of stable diaryl nitroxides containing *tert*-butyl and trifluoromethyl substituents in the phenyl rings has been synthesized [9]. The compounds exhibit fast electron transfer kinetics, sufficient stability of the oxidized and reduced forms, and high solubility in organic solvents making nitroxides possible candidates for testing as ambipolar redox-active materials [10]. In the present paper, bis(*tert*-butylphenyl)nitroxide was chosen as a model compound for screening of the modified membranes for the possibility to be applied in the electrochemical cells. Scheme of redox transformation of bis(*tert*-butylphenyl)nitroxide is shown below (the starting diaryl nitroxide is in the middle).



Tetrabutylammonium hexafluorophosphate (TBA) was used as the redox-inactive charge carrier, and acetonitrile was used as the solvent.

Materials and methods

Prior to the use, Nafion 112 membrane was conditioned via a conventional procedure [11] to remove any impurities which could appear during the shelf storage. The conditioning consisted in sequential boiling in distilled water (1 h), aqueous H_2O_2 (3 wt%, 1.5 h), distilled water (1 h), aqueous H_2SO_4 (0.5 M, 1.5 h), and distilled water (1 h). The so conditioned membrane will be further referred to as the pristine one.

In certain experiments, the membrane was neutralized with NaOH prior to use via refluxing in 0.01 M aqueous solution of NaOH during 1 h.

The final step of the samples preparation involved incubation in a large volume of distilled water (at least 3 days, the water was exchanged with fresh portion each 12 h) in order to wash out the excess of low molecular species.

To tune the permeability the ion-exchange membrane to low molecular species, we took advantage of the approach elaborated by us earlier [12]. It has been found [12] that the modification of Nafion with [*N*-(2-aminoethyl)-3-aminopropyl]trimethoxysilane (AATMS) results in the progressive decrease in the membrane swelling in water as well as permeation of protons and vanadyl ions through the membrane, due to partial blocking of sulfonic groups of Nafion with amino-containing silica nanoparticles. To test the applicability of such modification for organic solvents, dry Nafion 112 specimens were soaked with AATMS in isopropanol, and then AATMS was turned into amino-containing silica nanoparticles via the sol-gel method. Concentration of the AATMS precursor in the external solution was chosen so that the total amount of the amino groups equaled to 2.5–50% (the nominal modification degree) of the sulfonate groups content in the Nafion specimen. The true modification degree (the decrease in the ion-exchange capacity of Nafion upon the modification) was determined from the data on ion-exchange capacity of the samples.

Prior to determination of the Nafion membranes ion-exchange capacity (related to the apparent equivalent weight of the polymer), the specimens were dried in air at 60 °C overnight and weighed; the dried specimens were incubated in 30 mL of 2 M aqueous NaCl solution during 48 h which facilitated the substitution of sulfuric groups protons contained in the membrane with sodium ions. The membrane was then removed from the solution and washed with water. The external solution was combined with the washings, and the resulting mixture was titrated with 0.050 M NaOH. Using the dry specimen mass and the amount of NaOH consumed in the titration, we calculated the Nafion apparent equivalent weight (i.e., the mass of dry polymer containing 1 mol of the ionizable sulfonate groups).

The determined equivalent weight for the pristine membrane was of 1100 ± 40 g mol^{-1}, fully coinciding with the data from the manufacturer.

Swelling degree (equilibrium solvent uptake) of the membranes was tested by weighing the specimens after equilibrium swelling in water or acetonitrile and after drying at 60 °C to constant mass. The swelling degree was expressed as the ratio of the masses of equilibrium swollen piece of the membrane and the same specimen dried to constant mass.

Transport parameters of the membranes in an aqueous medium (through-plane ion conductivity measured by impedance spectroscopy and permeability coefficient for vanadyl ions measured via stationary diffusion) were extracted from ref. [12].

The membranes permeability towards TBA in acetonitrile was determined using a two-compartment glass diffusion cell (Adams & Chittenden Scientific Glass, USA) with the tested membrane as the separator. The cell compartments were filled with 5.0 mL of (i) 1 M solution of TBA in acetonitrile and (ii) pure acetonitrile. The initially TBA-free solution was periodically sampled, and TBA content was determined by conductometry using the earlier obtained calibration curve. Permeability of TBA through the membrane was expressed by the fraction of TBA passed in the second compartment during 4 h.

For the sake of comparison, the permeation parameters were normalized to those of the pristine membrane.

Permeability of the membrane towards the selected model redox-active compound bis(*tert*-butylphenyl)nitroxide in terms of permeability coefficient *P* was determined similarly to that towards vanadyl ion in ref. [12], using standard two-compartment Teflon diffusion cell and processing the kinetic data of accumulation of the redox-active compound in the second compartment using conventional equations for stationary diffusion. A customized feature of the setup was that in order to monitor low concentrations of the redox-active species and to simultaneously confirm their stability, we equipped the standard diffusion cell with three electrodes: reference RE, working WE, and counter CE ones (Fig. 1). The Teflon cell compartments volume was 1.5 mL each; the working electrode with 3-mm diameter was made of glassy carbon; the Ag/Ag^+ electrode (0.01 M $AgNO_3$ and 0.1 M TBA) was used as the quasi reference electrode calibrated with respect to the ferrocene–ferricinium (Fc/Fc^+) pair; the counter electrode was glassy-carbon 3-mm-diameter rod. The surface of the working electrode was on the diameter of the cell cross-section, and the distance between the working electrode and membrane was 5 mm. The initial concertation of the redox-active compounds was $c_0 = 0.01$ M, the supporting electrolyte (TBA) concentration was 0.01 M as well. Cyclic voltammetry (CVA) curves were recorded periodically for the initially blank (free of the redox-active specie) solution of the supporting electrolyte during the diffusion experiment. The growth of the peak current marked the increase in the concentration of the redox-active due to its diffusion. To avoid the determination of the diffusion coefficient required for recalculation of the peak current into the concentration using the Randles–Sevcik equation, we calibrated the peak current response using a series of the solutions of bis(*tert*-butylphenyl)nitroxide in the supporting electrolyte. The peak current in the CVA experiment was found linear up to the nitroxide concentration of at least 0.015 M. Since the initial concentration of it in the loaded half-cell equaled was $c_0 = 0.01$ M, the measured concentration during the diffusion experiment was expected to be below 0.005 M, well within the linear peak current range.

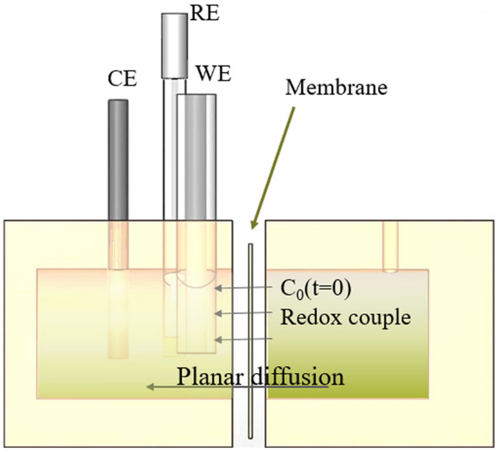


Fig. 1 Schematic view of the diffusion cell modified for electrochemical detection of permeating redox-active species

Celgard 2075 (thickness 20 μm, porosity 48%, average pore diameter 35 nm) and 2400 (thickness 25 μm, porosity 41%, average pore diameter 43 nm) membranes were used for testing as examples of porous inert separators. In detail, we determined its permeability to the supporting electrolyte TBA and to the redox-active specie bis(*tert*-butylphenyl)nitroxide as described above.

Results and discussion

Selected properties of the modified Nafion membranes are collected in Table 1. First, we focused on permeability to TBA (in acetonitrile MeCN), in comparison with that for H^+ and VO^{2+} (in aqueous sulfuric acid). To be able to compare the permeability data expressed in different units, the values were normalized to those for pristine Nafion.

The efficiency of the sulfonic groups modification with the amino groups of silica nanoparticles (estimated as the ratio of the true modification degree to the nominal one) was around 100% at the degree of modification up to 10%, remaining reasonably high (around 80%) for deeper modification, despite steric hindrance of the surrounding species during the sol-gel process. It should be noted that the modification effects are noticeable starting from the nominal degree of modification 15–30% (depending on the considered property).

The results obtained in this study showed that Nafion membranes swelled in acetonitrile much less than in water, and the degree of modification did not affect the swelling degree in acetonitrile (Table 1). Both trends were explained by suppressed dissociation of the sulfonic groups of Nafion in the organic medium; likely, the measured swelling degree reflected physical inclusion of acetonitrile in the nanopores of the membrane without pronounced interaction with the functional groups of the latter.

The rate of TBA permeation through the membranes in acetonitrile was constant over the 0–20% modification degree, being somewhat reduced for deeper modified membranes. Interestingly, even for the membrane with 50% nominal modification degree, the permeation of TBA was comparable to that of pristine Nafion membrane. In contrast, the water-swollen membranes [12] exhibited the proton and vanadyl permeation decreased by 2–3 orders of magnitude at the same degree of modification. The possible explanation might be as follows. In acidic aqueous medium (the conditions of proton and vanadyl transport measurements), ammonium-containing silica nanoparticles are highly swollen and almost completely block the

Table 1 Characteristics of the modified Nafion membranes

Degree of modification, %		Swelling ratio		Relative permeability		
Nominal	True	In H_2O (± 0.01)[a]	In MeCN (± 0.03)	To VO^{2+} in water[a]	To H^+ in water[a]	To TBA in MeCN
0	0	1.34	1.08	1.00 ± 0.05	1.00 ± 0.09	1.00 ± 0.05
2.5	3.0 ± 0.2	1.33	1.11	–[b]	–	1.1 ± 0.1
5	4.6 ± 0.5	1.35	1.07	–	–	0.9 ± 0.1
10	10 ± 1	1.35	1.08	0.75 ± 0.2	1.07 ± 0.11	1.0 ± 0.1
15	13 ± 1	1.30	1.12	–	–	1.1 ± 0.1
20	17 ± 1	1.30	1.05	0.20 ± 0.05	0.95 ± 0.11	1.1 ± 0.1
25	22 ± 1	1.29	1.09	–	–	0.75 ± 0.10
30	25 ± 1	1.26	1.06	0.08 ± 0.05	0.74 ± 0.06	0.5 ± 0.1
50	39 ± 2	1.16	1.06	$< 10^{-3}$	0.004 ± 0.001	0.4 ± 0.1

[a] Data from Ref. 12

[b] "–" stands for "not measured"

channel cross-section, thus preventing the ion transport at certain degree of the membrane modification (50%). In acetonitrile medium (conditions of TBA permeation measurement), silica nanoparticles are less swollen and cannot completely span the channel cross-section, leaving the pathways for TBA transfer across the membrane. The practical outcome of the TBA permeation measurement is that the Nafion membranes modified with AATMS at any nominal modification degree in the studied range can be potentially used in electrochemical cell in acetonitrile with TBA as the supporting electrolyte.

Besides being permeable to TBA, a membrane to be used in electrochemical cell should not pass the redox-active species. Therefore, the permeation of bis(*tert*-butylphenyl)nitroxide through the modified Nafion membranes was studied. The experiment was performed using a standard diffusion cell consisting of two compartments separated by the tested membrane. The compartments were charged with 5 mL of 0.1 M. TBA solution in acetonitrile ("blank" half-cell) and 5 mL of the same solution containing the nitroxide ("loaded" half-cell). During the diffusion experiment, the solutions from both half cells were periodically sampled, and the content of the species was determined by measuring the electronic absorption spectra.

Preliminary tests revealed that bis(*tert*-butylphenyl)nitroxide was stable in acetonitrile solution in air during at least 10 days, as marked by no changes in the electronic absorption spectrum. However, immersion of a dry Nafion film (pristine as well as the silica-modified) resulted in partial decomposition of bis(*tert*-butylphenyl)nitroxide reflected in the change in the solution color from yellowish to red. This is exemplified in Fig. 2 by the absorbance spectra recorded during the diffusion experiment using the membrane with nominal degree of modification 50% (the data for the pristine Nafion were similar). It is to be seen that no absorbing species appeared in the blank cell after 5 h of the experiment, whereas the spectrum of the starting bis(*tert*-butylphenyl)nitroxide solution was significantly changed.

The decomposition of bis(*tert*-butylphenyl)nitroxide can be possibly caused by the presence of residual moisture and sulfonic groups in Nafion membrane. Indeed, acid-catalyzed disproportionation of nitroxyl radicals R2NO$^\bullet$ into oxoammonium cations R_2NO^+ and hydroxylamines R_2NOH has been previously observed [13]. The kinetic stability of $R_2NO^\bullet$ species in acidic medium depends on the basicity of the nitroxyl group and its redox properties [14].

Attempting to minimize that disadvantageous effect of the SO_3H groups, we treated the Nafion membranes with excess of aqueous solution of sodium hydroxide and then removed water as completely as possible by repeated swelling of the membranes in acetonitrile and drying. The results of the diffusion experiment for the so treated Nafion membranes

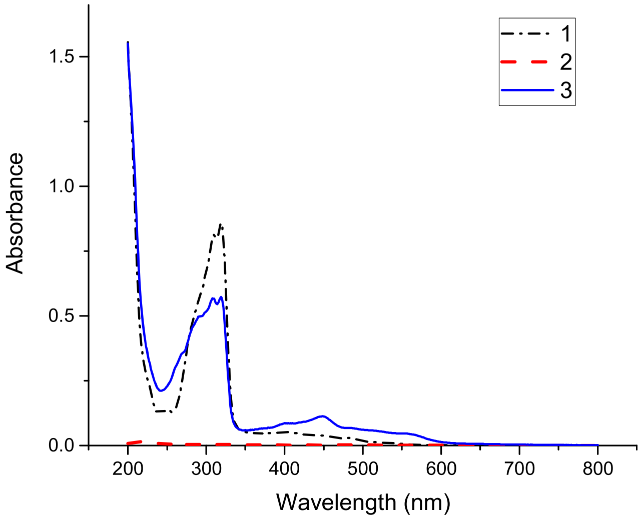


Fig. 2 Electronic absorption spectra recorded during diffusion of bis(*tert*-butylphenyl)nitroxide through Nafion membrane modified with AATMS to nominal degree of modification 50%. *1*—"loaded" cell at the start of experiment; *2*—"blank" cell after 5-h diffusion; *3*—"loaded" cell after 5-h diffusion

(pristine and with 50% nominal modification degree) are shown in Fig. 3.

The plot in Fig. 3 in comparison with Fig. 2 clearly demonstrates that neutralization of the membranes significantly suppressed the decomposition of bis(*tert*-butylphenyl)nitroxide: the spectrum of its solution was only slightly changed, and no absorbing species were detected in the blank solution. The comparison of the data for pristine and silica-modified Nafion membranes revealed that the incorporation of the amino-containing silica particles in the membrane did not accelerate the process of nitroxide decomposition.

Due to limited accuracy of electronic absorption spectroscopy measurement, the data in Fig. 3 did not allow any solid conclusion on the possibility of suppression of bis(*tert*-butylphenyl)nitroxide diffusion through the Nafion membrane due to the modification with silica. Therefore, we performed additional accurate measurement of the permeation coefficient of the model redox-active specie through the same membranes using a diffusion cell equipped with a setup to record the CVA response in the course of the diffusion. The experimental data (peak current versus the diffusion duration) are shown in Fig. 4. It is to be seen that the difference in the recorded signal (slope of the curve 8.2 ± 0.1 nA/s for pristine Nafion 112 and 2.1 ± 0.1 nA/s for Nafion membrane modified with AATMS to nominal degree of modification 50%) was sufficient for accurate determination of the permeability coefficient ($1.3\cdot10^{-4}$ and $3.1\cdot10^{-5}$ $\mathrm{cm^2/min}$ for pristine and AATMS-modified Nafion 112, respectively). Hence, it can be reliably concluded that the modification of Nafion membrane with silica nanoparticles suppressed the diffusion of bis(*tert*-butylphenyl)nitroxide through the membrane more than fourfold. Moreover, comparison of the CVA curves recorded for the species in both compartments of the diffusion cell confirmed chemical stability of the model specie in contact with Nafion membrane in an acetonitrile solution.

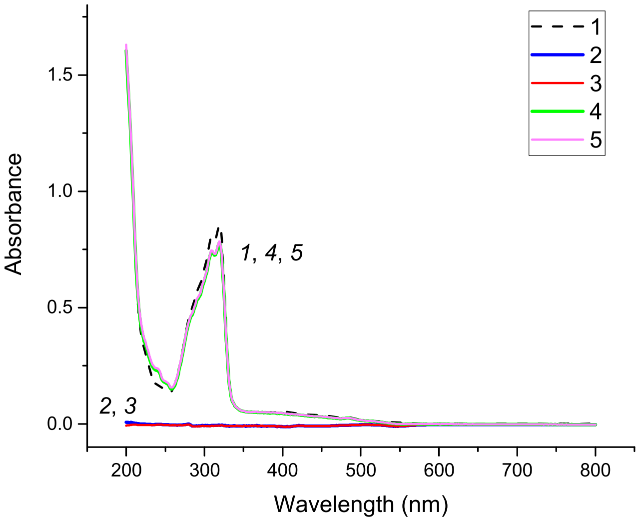


Fig. 3 Electronic absorption spectra recorded during diffusion of bis(*tert*-butylphenyl)nitroxide through pristine Nafion membrane (*1*, *2*, *4*) and Nafion membrane modified with AATMS to nominal degree of modification 50% (*1*, *3*, *5*). Both membranes were neutralized as described in the text. *1*—“loaded” cell at the start of the experiment; *2*, *3*—“blank” cell after 4-h diffusion; *4*, *5*—“loaded” cell after 4-h diffusion

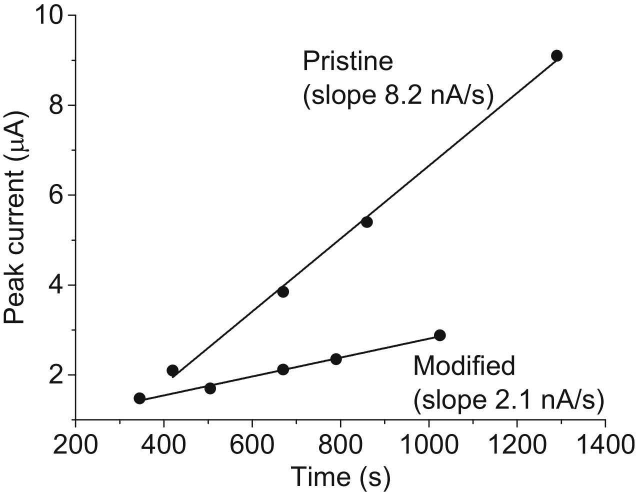


Fig. 4 Kinetics of the peak current (CVA measurement) growth during diffusion of bis(*tert*-butylphenyl)nitroxide through pristine Nafion membrane and Nafion membrane modified with AATMS to nominal degree of modification 50%

For comparison, we estimated the rate of bis(*tert*-butylphenyl)nitroxide diffusion using Celgard 2075 separator (Fig. 5). Since the average pore diameter in Celgard 2075 (35 nm according to the manufacturer data) was about an order of magnitude larger than the channels diameter in Nafion, it is no surprise that the diffusion of bis(*tert*-butylphenyl)nitroxide through the membrane was much faster in the Celgard case. Importantly, the Celgard membrane contains no acidic groups and could be dried more efficiently than Nafion; therefore, no decomposition of the organic molecule

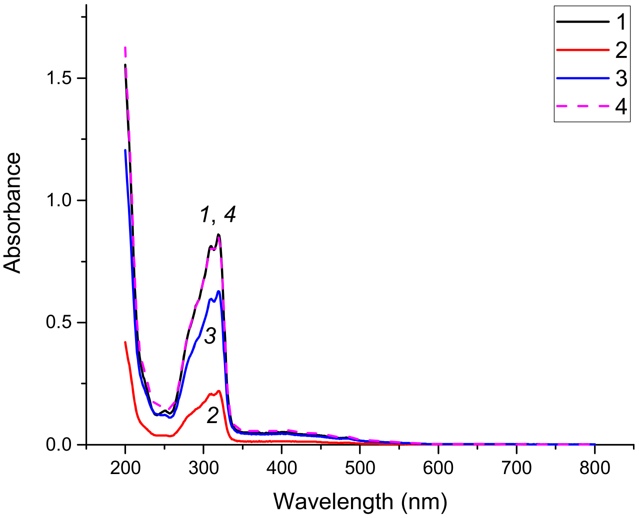


Fig. 5 Electronic absorption spectra recorded during diffusion of bis(*tert*-butylphenyl)nitroxide through Celgard 2075 separator. *1*—“loaded” cell at the start of the experiment; *2*—“blank” cell after 5-h diffusion; *3*—“loaded” cell after 5-h diffusion; *4*—sum of spectra *2* and *3*

was observed (the sum of the spectra in the half cells was identical to the starting spectrum).

Conclusion

In summary, we performed initial screening of the membranes for the further application in all-organic battery with bis(*tert*-butylphenyl)nitroxide as the redox-active component in acetonitrile solution. Nafion membranes (pristine as well as silica-modified) were found highly permeable to the supporting electrolyte (TBA), whereas efficiently preventing crossover of bis(*tert*-butylphenyl)nitroxide. However, the nitroxide turned out to be unstable in the presence of the Nafion in the acidic form. We demonstrated that the problem could be overcome by the membranes transformation in the salt form using NaOH. The nitroxide was stable in the contact with thus prepared membrane and its crossover was precluded, whereas the ionic transport of the supporting electrolyte remained highly efficient.

Celgard separator, as a more inert and available alternative, might be a feasible option if its effective pore size is reduced by at least 5 times. This can be also achieved via the sol-gel modification of Celgard separator with silica particles, as the latter were found inert to bis(*tert*-butylphenyl)nitroxide; this study is currently in progress as well as testing the modified Nafion membrane in charge/discharge processes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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