Full communication

Investigating the factors that influence resistance rise of PIM-1 membranes in nonaqueous electrolytes

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1. Introduction

Redox flow batteries (RFBs) are a promising technology option for energy-intensive grid storage applications, but cost reductions are needed for broad deployment [1,2]. Considered the archetypal system, the all-vanadium RFB leverages four different oxidation states of vanadium salts dissolved in an acidic aqueous electrolyte with the negative (V^{2+}/3+) and positive (V^{4+}/5+) redox couples separated by an ion-exchange membrane (e.g., perfluorosulfonic acid or hydrocarbon-based) [3–6]. Vanadium is an attractive redox species because crossover does not lead to irreversible performance losses as capacity can be recovered through periodic rebalancing. However, as the high cost of electrochemical grade vanadium salts may ultimately limit economic viability, considerable efforts have been dedicated to the discovery and development of new charge-storage materials [7,8], separation strategies [9,10], and reactor formats which offer new pathways to lower-cost flow battery technologies [11]. As many of the newly-proposed redox chemistries are asymmetric (different redox couples on the positive and negative sides of the cell), active species crossover is a significant concern, inspiring new coordinated approaches to membrane and redox couple development that enable size-selective separation [10,12]. A recently reported strategy is the application of polymers of intrinsic microporosity (PIMs), which are typically used for gas separations [13], as size-exclusion membranes within electrochemical systems [10,12,14]. While PIMs (specifically PIM-1) have proven effective in nonaqueous RFBs and lithium-sulfur (Li-S) batteries, their operational properties when contacted with flowing liquid electrolytes (e.g., swelling, stability, resistance) are not yet well-documented [15,16]. Indeed, in most prior work, tests were performed under conditions where performance decay can be due to confluence of confounding factors (e.g., unstable active species for RFBs, solid-electrolyte-interphase formation for Li-S batteries), which can mask changes in the PIM properties. Continued advancement of this molecular platform requires an understanding of performance-determining factors within device embodiments that mirror intended applications. To this end, we evaluate the impact of electrolyte flow rate, membrane thickness, and pretreatment conditions on the ohmic resistance of a PIM-1 membrane in a single electrolyte flow cell.

2. Experimental

PIM-1 was synthesized and characterized as described in the Supplementary Data, according to the previously reported procedure [17]. Free-standing PIM-1 membranes (17–80 μm thick, Fig. S1a) were...
prepared by solvent casting (20 mg mL\(^{-1}\) in CHCl\(_3\)) as reported in the Supplementary Data.

For the swelling tests (run in triplicate), PIM-1 membranes (80 \(\mu\)m thick, 16 mm diameter) were soaked in deionized water (18.2 M\(\Omega\), Millipore), acetonitrile (ACN, anhydrous, 99.7%, Sigma-Aldrich), and propylene carbonate (PC, anhydrous, 99.7%, Sigma-Aldrich) for 48 h at 25 °C. ACN and PC have been selected among other solvents as they are the most widely used for nonaqueous RFBs owing to their wide electrochemical stability window and their relatively high conductivities. Further, ACN and PC (especially ACN) have already been employed in combination with PIM-based membranes for RFB applications [10,14]. The in- and through-plane swelling along with associated weight increases were measured after gently wiping the membrane surfaces with a Kimwipe to remove excess solvent. Wetting dynamics were measured with a Contact Angle Goniometer (Ramé-Hart Instrument Co.). A solvent drop (2 \(\mu\)L) was deposited on the dry PIM-1 membrane surface, and images were captured at fixed time intervals (1 s for water and PC and 0.002 s for ACN). The height (h) and diameter (2r) of each drop were then obtained by image analysis (ImageJ software) and the volume (V) was calculated according to Eq. (1) and normalized by the initial droplet volume. All measurements were performed in triplicate.

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V = \frac{\pi h (3r^2 + h^2)}{6}
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A field emission scanning electron microscope (FE-SEM, SUPRA™ 35, Carl Zeiss SMT) was used to evaluate the morphology of the PIM-1 membranes. Prior to imaging, the samples were sputtered with a thin layer of gold using an Emitech K550X coater (Quorum Technologies) to prevent sample charging. To obtain cross-sectional images, dry membranes were cut with a scalpel at RT. FTIR spectra were collected on a Nicolet 550 spectrometer (Thermo Fisher Scientific) in attenuated total reflection (ATR) mode over the range 400–4000 cm\(^{-1}\) to further confirm the PIM-1 structure.

Electrochemical impedance spectroscopy (EIS) was used to quantify membrane resistance in a custom-built small-volume flow cell (Fig. S1b), which has been previously described [18]. A single electrolyte flow cell configuration was used with an electrolyte consisting of 0.5 M tetraethylammonium tetrafluoroborate (TEABF\(_4\), BASF, > 99.9%) dissolved in ACN [19]. During operation, the electrolyte was sealed in a perfluoroalkoxy alkane (PFA) jar (10 mL, Savillex) and delivered to the flow cell using a peristaltic pump (Masterflex L/S series) through PFA tubing (4 mm, McMaster-Carr) over a range of volumetric flow rates (0.1 to 10 mL min\(^{-1}\)). Prior to data collection, cells were conditioned by circulating electrolyte through the apparatus for 30 min to ensure component wetting and bubble removal. EIS was recorded every hour using a Biologic VMP-3 potentiostat at open circuit voltage (OCV), with an amplitude of 10 mV over a frequency range of 200 kHz to 500 mHz. At the end of the experiment, prior to cell disassembly or further tests with fresh electrolyte, two washes with ACN (30 min each at 10 mL min\(^{-1}\)) were run to remove TEABF\(_4\).

3. Results and discussion

A combination of physical, chemical, and electrochemical measurements were performed to better understand both the properties of the PIM-1 membrane as well as its behavior in nonaqueous electrolytes. The chemical structure (Fig. 1a) was confirmed by \(^{1}\)H NMR: \(\delta_{\text{H}}\) (ppm) = 6.84 (2H, s), 6.45 (2H, s), 2.36–2.19 ppm (4H, dd), 1.45–1.26 ppm (12H, br), and GPC indicated that high molecular weight (M\(_{\text{w}}\) = 118 kg mol\(^{-1}\) and PDI = 2.2) was obtained.

Swelling tests (Fig. 1b) evidenced that while water does not readily imibe into the membrane (0.31 mmol g\(_{\text{PIM-1}}\)\(^{-1}\)), soaking in either ACN or PC leads to significant dimensional changes. Although the extent of in-plane and through-plane swelling is different for the two solvents, the average solvent concentration in the membrane is comparable: 12.2 mmol g\(_{\text{PIM-1}}\)\(^{-1}\) and 12.5 mmol g\(_{\text{PIM-1}}\)\(^{-1}\) for ACN and PC, respectively. This suggests that, for the two solvents examined, the PIM-1 structure can accommodate a given number of molecules independent of their chemical structure, which, in turn, causes different degrees of swelling based on the solvent molar mass.

To further investigate the interactions between the PIM-1 membranes and the different solvents, surface wetting analyses were performed on dry membranes (Fig. 1c). Small contact angles were estimated for ACN (33.4°) and PC (37.6°), indicating favorable wetting, whereas a neutral contact angle was observed for water (80.8°), indicating poorer wettability. Measurements of dynamic wetting behavior revealed a fast imbibition rate of ACN (< 1 s), while negligible absorption was observed for PC over the experimental time (40 s) (Fig. 1c). We tentatively attribute the slower wetting kinetics to the higher viscosity of PC (2.5 cP) as compared to ACN (0.37 cP). Based on the swelling and wettability results, electrochemical experiments were only performed in ACN-based electrolytes.

The time-dependent resistance of the PIM-1 membranes was evaluated in a single electrolyte cell setup with a blank electrolyte (i.e., no redox-active species) (Fig. 2a). Periodic EIS measurements were used to monitor time-dependent area-specific ohmic resistance (R\(_{\Omega}\)) estimated by the high frequency intercept of the Nyquist plot. We assume that the PIM-1 membrane resistance contribution is the dominant ohmic resistance in the cell, although, even if this were not the case, the measurement serves a reasonable proxy for membrane resistance as all
other variables were held constant. As expected, initial $R_Ω$ monotonically increased with PIM-1 membrane thicknesses, ranging from 17 to 61 μm (Fig. S2a). However, a significant increase in resistance as a function of time was observed for all PIM-1 membranes (Fig. 2b). The percent change in resistance ($ΔR_Ω$) is inversely proportional to the membrane thickness (Fig. 2c) and consists of two distinct regions with a higher rate of increase for the first 9 h followed by a reduced rate of increase for the remainder of the experiment (15 h), approximately half of the magnitude of the earlier region. After 24 h on stream, $ΔR_Ω$ was 203% for the thicker (61 μm) and 349% for the thinner (17 μm) membrane, representing an increase of the initial $R_Ω$ from 125 to 381 Ω cm² and from 16 to 70 Ω cm², respectively (Fig. S3a). Moreover, the rates of increase range from 18.6 to 10.8% per hour for the first region, and 9.3 to 6.0% per hour for the second region (Table S1).

Additionally, the linear correlation between $R_Ω$ and membrane thickness is maintained over the whole course of the experiment (Fig. S4a), suggesting that the entire membrane evolves uniformly upon electrolyte exposure. The effect can also be visualized in Fig. S4b as a monotonic and mostly linear change in membrane resistivity ($ρ$, slope of $R_Ω$ versus thickness) as a function of time. We note that a negative intercept, located between −30 and −45 Ω cm², is observed in all cases and does not vary with time (Fig. S4a). At this juncture, it is difficult to explain this observation. It is possible that non-linear resistance may arise at thicknesses below 17 μm where the structure of the film has been reported to be compromised [20]. However, this may be a sign of some deeper, as of yet unknown, phenomena associated with this class of materials.

Following these initial observations, we sought to reduce the magnitude and rate of resistance rise by varying other experimental conditions. In particular, electrolyte flow rate appears to impact both the initial resistance (Fig. S2b) as well as its increase over time (Fig. S3b). The initial $R_Ω$ scales directly with the logarithm of the volumetric flow rate (thus, linear electrolyte velocity) such that cells with low flow rates yield a low resistance. Moreover, the rate of resistance increase is slower for low flow rates as shown for a 48 μm thick membrane (Fig. 2d). After 24 h of operation, $ΔR_Ω$ was 56%, 204%, and 253%, at 0.1 mL min⁻¹, 1 mL min⁻¹, and 10 mL min⁻¹, respectively. This observation led us to consider the role of hydrodynamic shear stress as a contributing factor in resistance rise as mechanical stress at the membrane-electrolyte interface may lead to materials deformation and degradation. With this in mind, a PIM-1 membrane (48 μm) was sandwiched between two Daramic® 175 separators to further mitigate the shear stress, and the resistance was measured over 24 h at 10 mL min⁻¹. Although reduced, $ΔR_Ω$ (136%, minus the Daramic separator contributions) was still observed, which was about 2.5× higher than the low flow rate. Taken together, these results suggest that changes in PIM-1 are related to membrane-electrolyte interactions and that the process is not only influenced by the membrane thickness, but also by the electrolyte flow rate. This change in resistance is unexpected as typically, if the membrane is wetted and ionic connection established between the two electrodes, the observed ohmic resistances are constant and independent of flow rate [12,21]. However, the interplay of these various factors warrants further analysis as the exact mechanism cannot be deduced from this data alone (vide infra).

To better understand the influence of the solvent on the $R_Ω$ increase, PIM-1 membranes were prewashed with ACN, which was pumped through the cell for 24 h, prior to the introduction of the electrolyte and subsequent EIS measurements. When comparing untreated and ACN-pretreated membranes of the same thickness (48 μm), the initial $R_Ω$ values are similar (94 Ω cm² and 89 Ω cm², respectively), suggesting that the solvent wash does not induce any changes in the PIM-1 structure that impact ionic conduction. However, the solvent prewash reduces the rate of resistance rise in the PIM-1 membrane: after 24 h of testing, the prewashed membrane displays a $ΔR_Ω$ reduction of 8.8× as compared to the untreated sample (Fig. 2d). This is lower than the rate of increase observed at the lowest electrolyte flow rate (0.1 mL min⁻¹) for an untreated membrane.

Leveraging the results from these initial experiments, extended testing was performed on a PIM-1 membrane under favorable conditions with the aim of achieving stable and low $R_Ω$ over time. Specifically, a 17 μm thick membrane was prewashed with ACN for 48 h (20 mL min⁻¹) and then monitored with an electrolyte flow rate of 0.1 mL min⁻¹. An increase of <35% above the initial value was observed after 7 days of testing (Fig. 3), demonstrating that the combination of low flow rate and solvent pretreatment can hinder resistance rise.

After the 7-day test, post mortem analyses were performed on PIM-1 membrane to determine if the $R_Ω$ increase is correlated to chemical...
evolution and/or degradation of the polymer. GPC tests showed no changes in molecular weight or polydispersity (Fig. 4a). Further, both $^1$H NMR (Fig. 4b) and ATR-IR (Fig. 4c) measurements confirmed that the original chemical structure of PIM-1 was maintained and that the characteristic nitrile stretches (2240 cm $^{-1}$) were preserved (Fig. S5). Finally, membrane morphology did not appear altered as SEM micrographs (Fig. S6) evinced smooth and uniform surfaces on both sides of the membrane as well as a dense and homogenous cross-section.

As the $R_\Omega$ increase did not appear to correlate to changes in the chemical structure of PIM-1, we hypothesized that these processes are reversible and that performance could be recovered via ex-situ and in-situ rejuvenation strategies. To this purpose, the area-specific ohmic resistance was measured over 24 h for the pristine membrane (run I, Fig. 4 left panel) and after rejuvenation (run II, Fig. 4 right panel). The ex-situ rejuvenation comprised the following steps: 1) recovering of the membrane from the cell, 2) soaking in ACN for 24 h, and 3) drying under vacuum until a constant weight was reached. On the other hand, for the in-situ rejuvenation, ACN was recirculated through the flow cell for 24 h prior to electrolyte addition. In both cases, a fresh electrolyte solution was used for the second set of cell tests (run II). Both treatments demonstrated that the structural or chemical modifications underlying the time-dependent $R_\Omega$ increase are not permanent, as the initial resistance value can be recovered by simple solvent washing (Fig. 4d). Dynamic (in-situ) rather than static (ex-situ) methods appear more effective (96% vs. 82% of recovery, respectively). To qualitatively evaluate the robustness of this strategy, in-situ rejuvenation was performed six consecutive times with good repeatability (Fig. S7), opening the possibility of clean-in-place protocols to extend the lifetime of devices that utilize this membrane, similar to procedures already proposed for aged membranes in gas separation technologies [22].

Although strategies to minimize resistance increase and to restore initial performance have been identified, the fundamental processes that govern this phenomena remain shrouded. In gas separation, it is known that PIM-based membranes undergo physical aging due to the relaxation of the polymer chains over time to a more thermodynamically stable state and decreased fractional free volume [23,24]. It is also known that solvent rejuvenation, typically via immersion in alcohols (e.g., methanol) followed by drying, restores the original chain conformation and inefficient packing through polymer swelling [25]. However, the aging process observed here, where the membrane is electrolyte-swollen and in contact with an electrolyte solution, is anticipated to be different from that which would occur in gas separations, where the membrane is dry and in contact with gas streams. Further, exposure to solvent alone does not lead to resistance rise, at least over the present experimental timescales. Thus, we conjecture that the presence of electrolyte is the cause of the increase in $R_\Omega$ over time. In particular, we hypothesize that specific polymer chain relaxation phenomena, induced by the electrolyte chemical composition and shear stress at the membrane-electrolyte interface, most likely lead to resistance rise. However, further work is necessary to unambiguously confirm or refute these assertions.

Fig. 3. Evolution of $R_\Omega$ over one week of continuous operation for a solvent-prewashed 17 μm thick PIM-1 membrane (flow rate: 0.1 mL min$^{-1}$).

Fig. 4. Pristine and post mortem analysis on PIM-1 membranes: (a) GPC elugram, (b) $^1$H NMR, c) ATR-IR patterns (sides A and B); (d) evolution of $R_\Omega$ for ex-situ and in-situ rejuvenated PIM-1 membrane (48 μm thick, electrolyte flow rate: 10 mL min$^{-1}$).
4. Conclusions

In this work, we have explored the time-dependent resistance rise of PIM-1 membranes in nonaqueous electrolytes as a function of membrane thickness, electrolyte flow rate, and solvent prewashing. By combining thin membranes with low electrolyte flow rate and solvent prewash, we have been able to keep the initial area-specific ohmic resistance below 40 Ω cm² and to limit the resistance rise to < 35% after 7 days of measurement. Our results also indicate that the resistance increase does not correlate with irreversible chemical and structural changes, and thus it can be reversed via ex-situ or, perhaps more importantly, in-situ solvent washes. Although strategies for performance stabilization and recovery have been proposed, more comprehensive investigations are needed to uncover the processes that give rise to these macroscopic changes as well as optimize the wash processes for mitigating rise and recovering performance.

Acknowledgments

Research at MIT was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Work at University of Rome Tor Vergata and travel support for M.G. was enabled by the project “Polymeric Materials for Energy Applications”. B.J.N gratefully acknowledges the National Science Foundation Graduate Research Fellowship Program under Grant No. 1122374. Goniometry experiments were performed at the Institute of Soldier Nanotechnologies at the Massachusetts Institute of Technology.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.106530.

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