



Random quaternary ammonium Diels-Alder poly(phenylene) copolymers for improved vanadium redox flow batteries



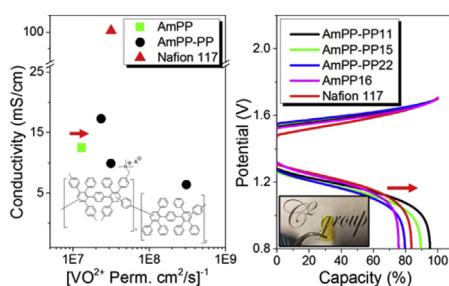
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HIGHLIGHTS

- A quaternary ammonium Diels-Alder poly(phenylene) (AmPP) was studied within a VRB.
- AmPP electrochemical properties at 10 mA/cm² had a 14% increase in CE.
- Ionomer hydroxyl conductivity in the carbonate form was 17 mS/cm at an IEC of 2.2.
- VO²⁺ permeability was reduced by 55.7% as compared to Nafion117 (9.7E-08 cm²/s).

GRAPHICAL ABSTRACT



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ABSTRACT

This study analyzes the effect of quaternary ammonium homopolymer (AmPP) and ionic and non-ionic random unit copolymerization (AmPP-PP) of Diels-Alder poly(phenylene)s on electrochemical and transport properties, vanadium redox flow battery performance, and material stability. AmPP-PP materials were synthesized with IEC's up to 2.2 meq/g, displaying a carbonate form ion conductivity of 17.3 mS/cm and water uptake of 57.3%. Vanadium ion permeability studies revealed that the random copolymers possess superior charge carrier selectivity. For materials of comparable ion content, at 10 mA/cm² the random copolymer displayed a 14% increase in coulombic efficiency (CE) corresponding to a 7% increase in energy efficiency. All quaternary ammonium materials displayed ex situ degradation in a 0.5 M V⁵⁺ + 5 M H₂SO₄ solution, with the rate of degradation appearing to increase with IEC. Preliminary studies reveal that the neutralizing counter-ion has a significant effect on VRB performance, proportional to changes in vanadium ion molecular diffusion.

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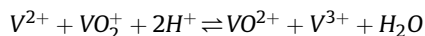
1. Introduction

The United States Energy Information Administration has predicted that energy consumption will increase by 56% by 2040 [1]. To meet this growing demand, renewable energy solutions have received growing attention. Traditional solutions such as lithium ion systems are costly, have limited energy availability, degrade in

capacity, and are typically highly flammable. The all-vanadium redox battery (VRB), patented in 1986 by the University of South Wales [2], is a promising technology that touts a high power density and considerable energy efficiency. VRB's consists of sulfuric acid solutions of V(II)/V(III) and V(IV)/V(V) redox couples at the negative and positive electrodes, respectively. During charge, electrons move from the catholyte through an external circuit to the anolyte, and during discharge, the reverse occurs. The overall redox reaction during charge and discharge is:

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A semi-permeable ion exchange membrane is required to maintain the charge balance during charge and discharge. Obtaining an ideal ionomer for this application has proven challenging, as the ideal membrane requires high ion conductivity, high chemical stability, a low vanadium ion permeability, and low electric area resistivity [3]. Significant effort has been made regarding the optimization of cation exchange membranes [4–9]. The use of anion exchange membranes (AEMs) has been proposed as theory suggests a reduction in vanadium ion permeability due to the Donnan exclusion principle. In addition, AEMs are able to transport multiple charge carriers to balance the redox reaction that includes protons, sulfate, or sulfuric acid based electrolytes. Work regarding AEMs in VRBs include those pertaining to functionalized poly(fluorenyl ether)s [10], poly(phthalazinone ether ketone)s [11,12], and poly(sulfone)s [13].

Recently, a completely phenylated quaternary ammonium Diels-Alder poly(phenylene) was synthesized that revealed good chemical stability under high pH conditions, adequate mechanical strength, conductivities up to 50 mS/cm [14], and competitive VRB performance [15]. In this study, the effect of ionic and non-ionic random unit copolymerization of a quaternary ammonium Diels-Alder poly(phenylene) on electrochemical and transport properties, vanadium redox flow battery performance, and material stability is reported.

2. Experimental

2.1. Materials

Methylated poly(phenylene) (mPP) and block copolymers (mPP-PP) were synthesized via Diels-Alder polymerization, as reported elsewhere [16]. Aqueous trimethylamine (50 wt.%, Acros Organics) and Chloroform (99.8%, Fisher Scientific) were used as received. Dupont's Nafion® 117 (Nafion 117) was purchased from Fuel Cell Store®. Prior to use, Nafion 117 underwent pretreatment in 0.5 M H₂SO₄ (Fisher Sci., 98.0 w/w%) and twice in DI-H₂O each at 80 °C for 2 h.

2.2. Bromination, amination, and membrane formation

Bromination of Diels-Alder poly(phenylene)s was performed by allylic bromination using *N*-bromosuccinimide, with benzoyl peroxide as a radical initiator, as described elsewhere [14]. The degree of bromination was determined by ¹H NMR, and used to calculate a theoretical ion exchange capacity. Brominated polymers were cast in chloroform (5 wt%). Solutions were filtered through 5 μm PTFE syringes onto a glass mold. The solvent evaporation rate was controlled by covering the casting plate. After 24 h, the polymer films were placed in a vacuum oven at room temperature to ensure the membranes were completely dry. The orange brominated films were transparent, robust, and creasable. Aminated polymers were formed by placing the brominated films in an airtight vessel containing a 1 M solution of trimethylamine in water. Quaternary ammonium homopolymers (AmPP) consisted of only ionic units, while quaternary ammonium random copolymers (AmPP-PP) consisted of an equal number of ionic and non-ionic units (Fig. 1). The materials were allowed to soak for 48 h to ensure complete amination. Membranes were then removed, washed with water, and placed into an aqueous 1 M solution of sodium hydroxide for 48 h. Aminated films were soaked in deionized water for 48 h in an open cup, replenishing the soaked water at least twice, to ensure property stability.

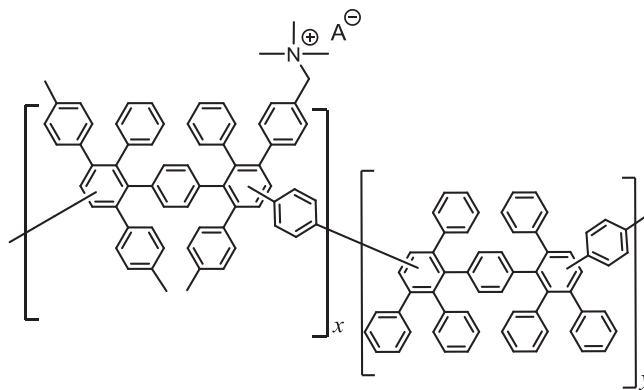


Fig. 1. Chemical structure of a quaternary ammonium Diels-Alder poly(phenylene) copolymer.

2.3. Material characterization

In order to confirm complete polymerization, determine copolymer composition, and the degree of bromination, ¹H-NMR analysis were performed using a Bruker AVANCE III-HD 400 MHz NMR in CDCl₃ solvent. The degree of bromination was used to determine a theoretical ion exchange capacity (IEC_t).

Gravimetric determination of water uptake for the aminated materials was obtained. Thin films were first soaked in deionized water at room temperature for 48 h. The membrane was then removed, quickly blot dried to remove surface water, and weighed to obtain a “wet mass” (*m*_{wet}). The membranes were dried under vacuum at 30 °C for 24 h, and weighed to determine a “dry mass” (*m*_{dry}). Water uptake was determined by the equation

$$\text{Water uptake} = \left[\frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \right] \times 100 \quad (1)$$

Ion conductivity was determined using electrochemical impedance spectroscopy. The experiments were performed by applying a 10 mV signal and scanned with frequencies of 100 kHz to 100 Hz. A Nyquist plot was generated, and the resistance was obtained where the non-real resistance was equal to zero (Fig. 2). The ion conductivity was calculated using the equation $\sigma = L/(R \cdot A)$, where *L* is the length between the two sampling electrodes, *R* is the

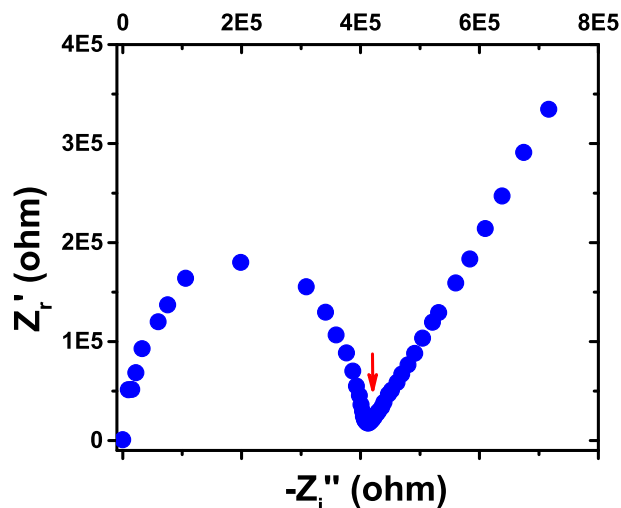


Fig. 2. Typical Nyquist plot obtained via electrochemical impedance spectroscopy.

real resistance, and A is the membrane area available for proton conduction. For this study, experiments were performed at 30 °C in a temperature controlled water bath.

Vanadium ion permeability was measured using a liquid diffusion apparatus. The apparatus included a water jacketed, membrane-separated, 20 ml PermeGear® diffusion cell. Both compartments were temperature controlled, and vigorously stirred using submerged Teflon® magnetic stir bars. A 1 M VOSO₄ + 2.5 M H₂SO₄ solution was placed in one compartment, and, to negate osmotic effects, a 1 M MgSO₄ + 2.5 M H₂SO₄ in the other. Aliquots were taken near the membrane every 2 h and analyzed using UV-VIS spectroscopy to determine vanadium ion concentration as a function of time.

To assess performance in a vanadium redox flow battery (VRB) cell, membranes were sandwiched by copper current collectors, graphite serpentine flow fields, and SIGRACELL® carbon felt (GFD4.5) housed by Teflon® gaskets (22% compression). In this system the hydrated membrane thicknesses of synthesized samples were 70–85 μm, and 200 μm for Nafion 117, with an effective cell area of 5 cm². A solution of 1 M VOSO₄ dissolved in 2.5 M H₂SO₄ was used as the starting electrolyte. 80 ml and 40 ml of the starting electrolyte were placed in the positive and negative electrolyte tanks, respectively. The negative half-cell tank was equipped with a nitrogen purge due to V²⁺ reactivity with air, and the flow rate set to 20 ml/min. A constant current method with a current density of 30 mA cm⁻² was used to charge the cell to 1.7 V. Once achieved, 40 ml of electrolyte was removed from the positive half-cell tank. Charge-discharge tests at 10–40 mA/cm², in 10 mA/cm² increments were then performed with terminal voltages set at 1.7 V and 0.8 V respectively. The coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) was calculated using the equations:

$$CE = \frac{t_d}{t_c} \times 100\% \quad (2)$$

$$VE = \frac{V_d}{V_c} \times 100\% \quad (3)$$

$$EE = CE \times VE \quad (4)$$

where t_d is the discharging time, t_c is the charging time, V_d is the average discharging voltage, and V_c is the average charging voltage. On completion, the cell was charged to a set capacity (~50% SOC), and an open circuit voltage (OCV) test was performed.

3. Results and discussion

3.1. Electrochemical properties and vanadium ion permeability

The ion exchange capacity, water uptake, conductivity and vanadium ion (VO²⁺) permeability is listed in Table 1. It has been discovered that on exposure to CO₂, absorption causes the rapid

Table 1
Theoretical anion exchange capacity (IEC_t), water uptake, ion conductivity (σ), and vanadium ion (VO²⁺) permeability.

	IEC _t (meq/g) ^a	w.u. (wt%)	σ (mS/cm) ^b	P(VO ²⁺) (cm ² /min)
AmPP16	1.6	53.1	14.0	7.7E-08
AmPP-PP11	1.1	31.6	6.4	3.3E-09
AmPP-PP15	1.5	45.2	9.9	3.2E-08
AmPP-PP22	2.2	57.3	17.3	4.3E-08
Nafion117	1.0	33.0	100.4	9.7E-08

^a Determined by NMR.

^b At 100% humidity.

neutralization of hydroxide to the carbonate/bicarbonate counter ion [17,18]. For this reason all films were kept for one week in an open cup before testing to ensure property stability, and then assumed to be fully neutralized into the carbonate/bicarbonate form. The anion exchange membranes (AEMs) display significantly lower conductivities than the cation exchange membrane Nafion 117, as the carbonate/bicarbonate anion has significantly lower dilute solution mobility than the proton. Quaternary ammonium random copolymers (AmPP-PP) were synthesized with high, medium and low ion exchange capacities, controlled by the degree of bromination. With increasing IEC an increasing water uptake, conductivity, and vanadium ion permeability is observed. A quaternary homopolymer, AmPP16, has been synthesized to assess the effect of ion distribution on vanadium redox flow battery performance. AmPP16 and the random block copolymer AmPP-PP15 are similar in ion content, yet AmPP-PP15 displays a water uptake almost 8% lower. The data suggests that the random copolymer chemistry encourages larger hydrophobic domains suppressing water uptake. The drop in water uptake is accompanied by a lower ion conductivity and vanadium ion permeability.

Fig. 3a displays proton conductivity as a function of water uptake. The figure reveals that the relationship between water uptake and conductivity is unchanged for AmPP16 and the AmPP-PP copolymers. The acid form of Nafion 117, the commercial competitor, has a well-defined morphology that ensures a high ion conductivity and low water uptake [19]. This morphology results in a high molecular permeability, a principle concern in redox flow battery systems [20]. Fig. 3b displays conductivity versus the inverse of vanadium ion permeability, used to represent a vanadium ion resistance. In this plot, an ideal ionomer would lie in the upper right hand corner. It is important to note that the vanadium ion permeability experiment is largely affected by membrane thickness, and therefore direct comparisons between Nafion 117 and the synthesized materials can be misleading. Regardless this plot reveals that Nafion 117 lacks adequate ion selectivity for competitive vanadium redox flow battery performance. The AmPP-PP trend lies to the right of the homopolymer, AmPP, indicating that random block copolymerization has a net positive effect on the ion conductivity/vanadium permeability trade-off, potentially translating to improved VRB system performance.

3.2. Vanadium redox flow battery performance

The coulombic efficiency (CE), displayed in Fig. 4a, is a measure of capacity loss within the system. A low CE is primarily the result of energy loss due to vanadium ion crossover. It can be seen that CE increases with increasing charge/discharge current density. This occurs as higher charge and discharge currents allow less time for vanadium ions to diffuse across the membrane. Despite a lower measured vanadium ion permeability observed in the diffusion studies, AmPP16 displays lower coulombic efficiencies than Nafion 117. As mentioned, this is because commercial Nafion 117 is purchased with a hydrated membrane thickness of 200 μm, while, to minimize resistivity, the quaternary ammonium Diel-Alder poly(-phenylene)s were used with thicknesses of 70–85 μm. At all current densities, despite almost twice the water uptake and less than half the membrane thickness, AmPP-PP22 has CE's comparable to that of Nafion 117. AmPP-PP11 and AmPP-PP15 reveal excellent vanadium ion rejection during charge and discharge, as indicated by high CE's. AmPP-PP15 displays a CE increase of 14% versus AmPP16 at 10 mA/cm² demonstrating improved charge-carrier selectivity in the random block copolymers.

Fig. 4b displays the voltage efficiency (VE) as a function of current density. Charge and discharge voltage is influenced by the thermodynamic reduction potential of the redox couples in the half

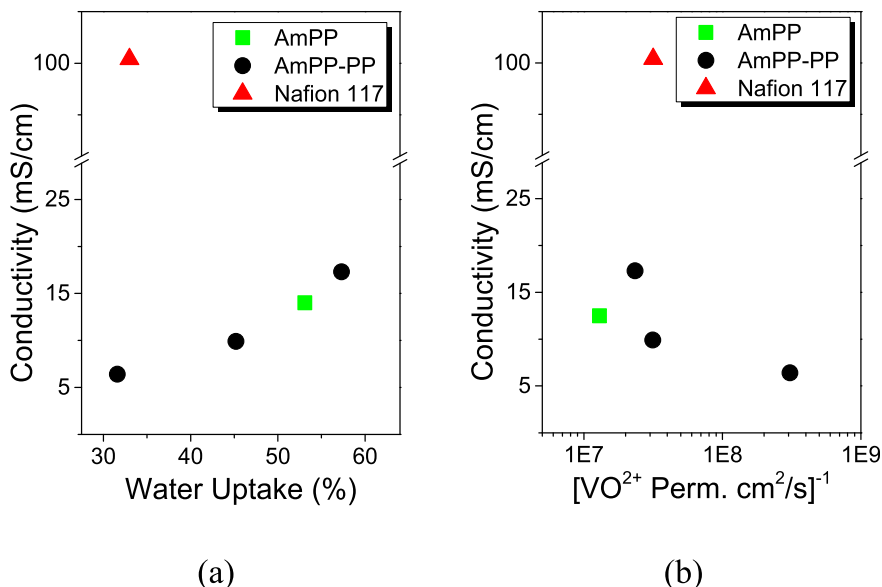


Fig. 3. (a) Ion conductivity versus water uptake and (b) ion conductivity versus vanadium ion resistivity (VO^{2+} permeability $^{-1}$).

cells, and the overpotential of the cell. Membrane resistance contributes to the overpotential, and therefore higher membrane resistances will result in greater charge and lower discharge voltages, lowering the VE. In addition higher currents will increase the ohmic resistance, causing the observed decrease in voltage efficiency with increasing current density. A variation in VE of only roughly 2% is observed for the AmP-PP materials despite large differences in IEC. In addition, despite an incredibly high conductivity, Nafion displays a VE of at most only 8% higher than that of the other materials. This may indicate that in this highly acidic environment there is a lesser difference in ionic conductivity, and therefore area resistivity, a conclusion also reached in similar studies [21–23]. The energy efficiency (EE) is the product of the CE and VE, and can be used to represent the overall efficiency of the system (Fig. 3c). This analysis has proven useful as improvements in the CE or VE is typically an efficiency trade-off. At low current densities the materials with the lowest vanadium permeability display the highest EE, most notably

AmPP-PP11 and AmPP-PP15. This may indicate that these highly selective materials are most useful for low current applications. As discussed, at higher current densities less time is taken to achieve the maximum set voltage which effectively lowers the CE contribution. Therefore AmPP16 and Nafion117, due to high VE's, display superior performance during quick charge/discharge cycles.

Fig. 5a displays the charge and discharge curves at $10 \text{ mA}/\text{cm}^2$, whereby the capacity has been normalized to highlight the differences in charge and discharge time. A self-discharge test was performed which is a measure of capacity loss of the battery when the system is not connected to any electrodes. As discussed, the primary loss of capacity is due to permeation of vanadium ion across the ion exchange membrane. The open circuit voltage plot for all materials is displayed in Fig. 5b. All plots decline slowly to 1.25 V and then drop suddenly. The OCV discharge times correlate well to the CE values at $10 \text{ mA}/\text{cm}^2$. Nafion 117 had an OCV discharge time of roughly 75 h. AmPP16 and AmPP-PP22 display poor selectivity,

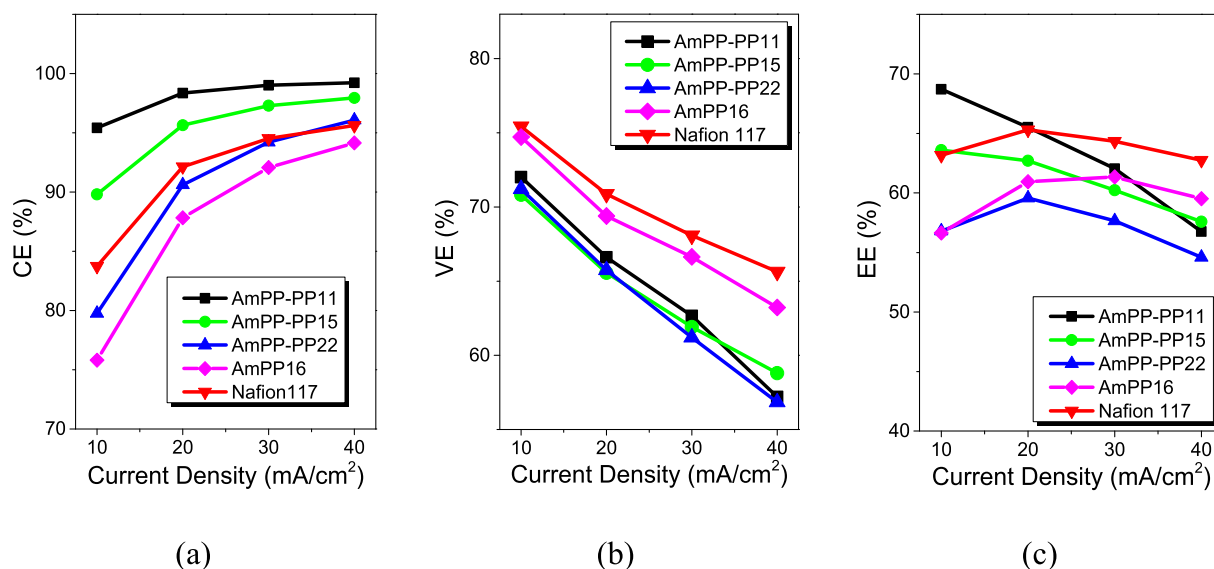


Fig. 4. The (a) coulombic efficiency (CE), (b) voltage efficiency (VE) and energy efficiency (c) as a function of current density.

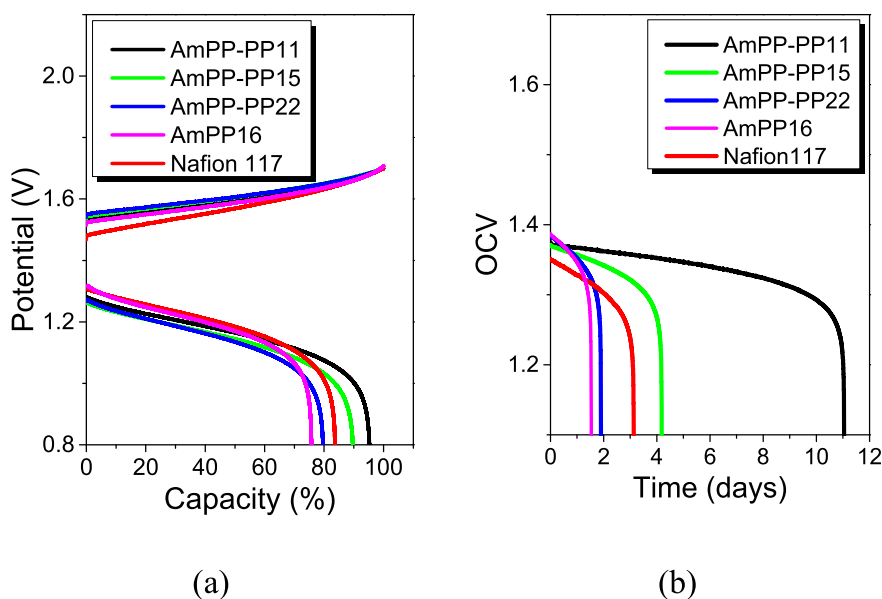


Fig. 5. (a) The charge and discharge curves for AmPP, AmPP-PPs and Nafion 117 at 10 mA/cm². (b) OCV decay of the VRB cell.

with OCV discharge times of 37 and 45 h, respectively. AmPP-PP15 had a discharge time of 100 h, over double that of AmPP16. AmPP-PP11 took 11 days to discharge, highlighting incredible vanadium ion rejection in the random copolymers.

3.3. Degradation studies

In recent work *ex-situ* strategies have been proposed that allow for the observation of changes in material appearance when exposed to reactive vanadium ion species (Fig. 6). In this study a stability test was performed by placing a material in a solution of 0.5 M V⁵⁺ and 5 M H₂SO₄ at 60 °C for a number of days. The V⁵⁺ solution is bright yellow, and changes to blue during polymer degradation, attributed to reduction to the VO²⁺ ion during backbone degradation. This *ex situ* method allows one to qualitatively observe gradual changes in solution and membrane color. It has been hypothesized that AEM's may exhibit slower rates of degradation over CEM's due to electrostatic repulsion. After 48 h, the parent polymer gave no indication of degradation, while the quaternary ammonium random polymer solutions gradually turned

from yellow to green, at a rate increasing with IEC. Such degradation has been observed anion exchange membranes with alternative backbone chemistries [12,21,24]. After 1 week, the materials were removed from the vanadium solutions and rinsed with water (Fig. 6a). As observed in previous studies for AmPP [15], none of the materials broke apart, and despite darkening of the film (Fig. 6c) AmPP-PP11 and AmPP-PP15 retained their flexibility.

3.4. The effect of the counterion

As has been discussed, due to the instability of the hydroxyl counterion, anion exchange membranes are often utilized in alternate ionic forms [25]. Although it is well understood that counterion species has an impact on transport and viscoelastic properties, the effect of the anion exchange membrane counterion on VRB performance has not yet been studied. This brief assessment has been performed to determine if AEM counterion size, mobility, or Lewis Basicity plays a significant role in VRB performance. Table 2 displays properties for AmPP-PP22 materials that have undergone different pretreatment procedures. Initially all

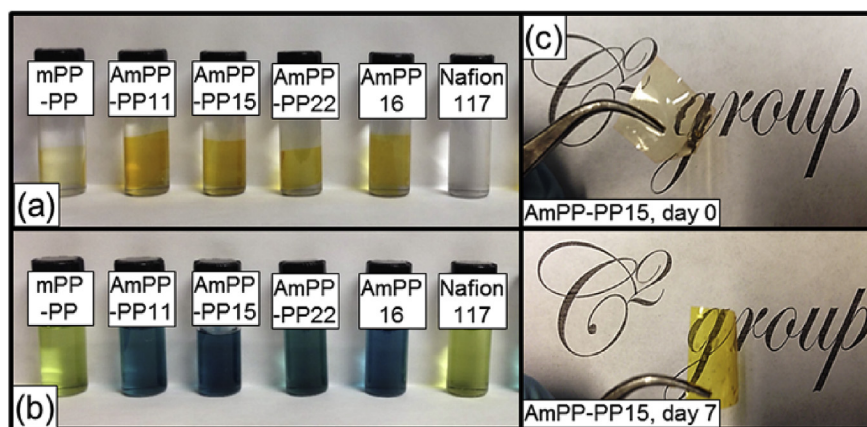


Fig. 6. (a) Polymer films and (b) solution color after one week of degradation. (c) The change in film color from the start (top) and end (bottom) of the degradation study. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
The theoretical anion exchange capacity (IEC_t), water uptake, ion conductivity (σ), and vanadium ion (VO²⁺) permeability for treated AmPP-PP22 materials.

Sample #	Label	IEC _t (meq/g) ^a	w.u. (wt%)	σ (mS/cm) ^b	P(VO ²⁺) (cm ² /min)
–	AmPP-PP22	2.2	57.3	17.3	4.3E-08
1	AmPP-PP22 – CO ₃ ²⁻	2.2	49.5	7.3	2.7E-08
2	AmPP-PP22 – Cl ⁻	2.2	44.6	9.9	2.7E-08
3	AmPP-PP22 – PO ₄ ³⁻	2.2	50.3	6.0	4.2E-08

^a Determined by NMR.

^b At 100% humidity.

samples were converted to the hydroxyl form by soaking the membranes in a 1 M NaOH solution for 48 h, and then removed for individual treatment. Sample 1 underwent a heat treatment in DI-H₂O at 80 °C for 2 h. Samples 2 and 3 were placed in 1 M solutions of NaCl and Na₃PO₄, respectively, and heated at 80 °C for 2 h. The membranes were removed, rinsed, and heated at 80 °C for 2 h in DI-H₂O.

Previously, low ion conductivities in AEM's have been attributed to the “rapid CO₂ neutralization” phenomenon, and some predictions have been made to account for the theoretical hydroxyl ion mobility [18]. Here, we observe large differences in the properties of AmPP-PP22 that underwent the “open cup method”, and sample 1 that received heat pretreatment. Although it was initially suspected that heating the sample would cause additional swelling ultimately increasing both ion conductivity and vanadium ion permeability, AmPP-PP22-CO₃²⁻ displayed a decrease in these properties. This would suggest that the open cup method insufficiently neutralizes the material from the hydroxyl into the carbonate form. For the annealed samples (1–3), an increasing water uptake is observed with ion valence attributed to a larger ionic hydration radius. That is, the ionic group interacts with more water molecules during solvation. Ion conductivity is predominantly dependent on counterion mobility, and vanadium ion permeability proportional to water uptake.

Fig. 7a displays the coulombic and voltage efficiencies for the pretreated AmPP-PP22 materials as a function of current density. The coulombic efficiencies of the materials correlate well to the measured water uptake and vanadium ion permeability. AmPP-PP22-Cl⁻ displays a water uptake 5% lower than that of AmPP-PP22-CO₃²⁻, resulting in a 6.2% increase in CE. Interestingly VE (Fig. 7b) displays no correlation to ion conductivity or water uptake. A

weakened relationship between ion conductivity and VE in materials with large differences in ion content has been attributed to high electrolyte acidity [21–23]. The high voltage efficiency of AmPP-PP22-PO₄³⁻ may therefore be due to increased electrolyte permeability. Since the primary loss of capacity is due to permeation of vanadium ions across the ion exchange membrane, the OCV discharge times shown in Fig. 6c correlate well to CE values. All materials that underwent thermal treatment displayed improved self-discharge times. AmPP-PP22-Cl⁻ revealed a 60% greater discharge time over AmPP-PP22, matching Nafion 117 of roughly 75 h.

4. Conclusions

This study observes quaternary ammonium homopolymer (AmPP) and ionic and non-ionic random unit copolymerization (AmPP-PP) of a Diels-Alder poly(phenylene) on electrochemical and transport properties, vanadium redox flow battery performance, and material stability. AmPP-PP materials were synthesized with IEC's up to 2.2 meq/g, displaying a carbonate form ion conductivity of 17.3 mS/cm and water uptake of 57.3%. The random copolymer displayed lower water uptake than the homopolymer resulting in a marginally lower ion conductivity. Vanadium ion permeability studies revealed that the random copolymers possess superior charge carrier selectivity. Homopolymer and random block copolymer vanadium redox flow battery performance were compared for IEC's of 1.6 and 1.5 meq/g, respectively. At 10 mA/cm² the random copolymer displayed a 14% higher coulombic efficiency (CE) of 89.9%. Despite a lower voltage efficiency (VE), the random copolymer outperformed the homopolymer with a 7% higher energy efficiency. All quaternary ammonium materials displayed ex

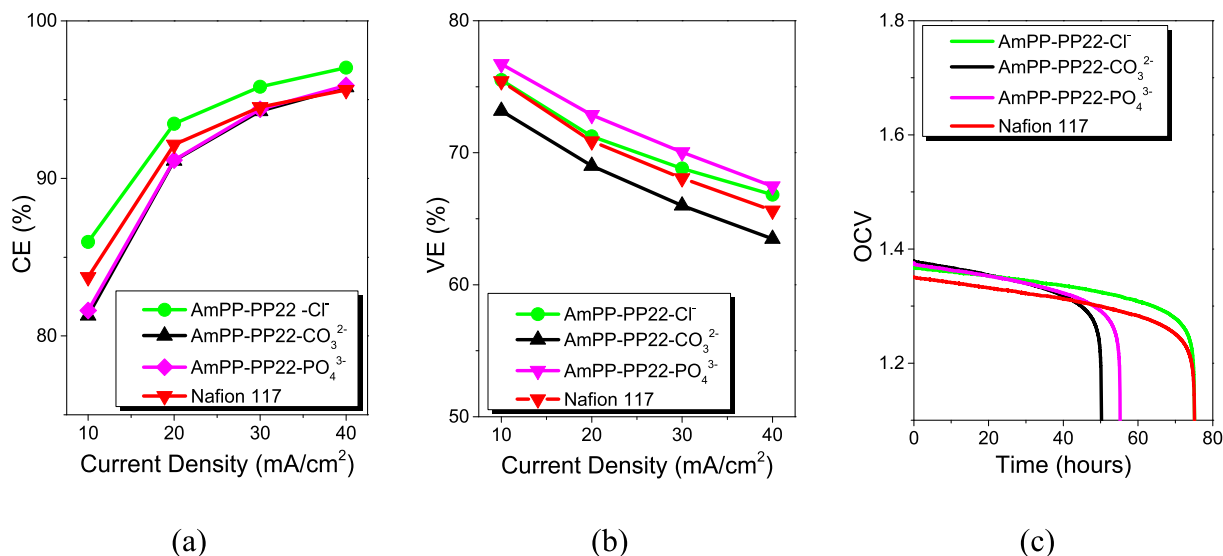


Fig. 7. (a) Coulombic (CE) and (b) voltage (VE) efficiencies for neutralized AmPP-PP22 membranes. (c) OCV decay of the VRB cell for the aforementioned materials.

situ degradation in a 0.5 M V^{5+} + 5 M H_2SO_4 solution, with the rate of degradation appearing to increase with IEC. Preliminary studies reveal that the neutralizing counterion has a significant effect on VRB performance. The typical efficiency trade-off was not observed, with membrane resistance showing little correlation to VE suggesting large contributions from molecular diffusion.

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