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BRIEF COMMUNICATION

High ion selectivity Aquivion-based hybrid membranes for all vanadium redox flow battery

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Abstract
Polymer based on norbornene was synthesized via ring-opening metathesis polymerization with norbornene possessed the advantages of easily modified molecular architectures, simple and controllable polymerization method, and great chemical stability. Novel Aquivion-based hybrid membranes were prepared by introducing polymer based on norbornene to Aquivion ionomers with short side chain. The resistance of Aquivion/PAN-10% hybrid membrane was the lowest among them due to the formation of hydrogen bonds between "acid-base" pairs. At the same time, all Aquivion-based hybrid membranes in this work possess excellent VO^{2+} permeability owing to the ionic crosslinking and Donnan effect. The Aquivion/PAN-2.5% hybrid membranes can still last for 31 h above 0.8 V because of the low VO^{2+} permeability. And Aquivion/PAN-2.5% hybrid membranes also exhibited more excellent Coulombic efficiency than Aquivion/PAN-5% hybrid membranes and Aquivion/PAN-10% hybrid membranes. The voltage efficiency of Aquivion/PAN-10% hybrid membranes was higher than that of Aquivion/PAN-2.5%. Aquivion/PAN-2.5% possesses an energy efficiency of 73.02% at the current density of 160 mA·cm^{-2}.

Keywords Vanadium redox flow battery · Hybrid membranes · Aquivion ionomers · Ionic crosslinking

1 Introduction

The all vanadium redox flow batteries (VRBs), as the most widely used large-scale energy storage system, have the advantages of high energy efficiency, long life, and high flexibility [1–4]. Ion exchange membrane, as a key component of VRBs, directly affects the performances of the VRBs [5, 6]. Among them, the commercialized perfluorinated sulfonic acid polymer has received extensive attention owing to its high ionic conductivity, excellent chemical stability, and mechanical property [7, 8]. Due to the presence of sulfonic acid functional group at the end of the side chain, membrane materials with perfluorinated sulfonic acid structure have hydrophilic and hydrophobic microphase separation structures [9, 10]. The perfluorinated sulfonic acid polymer has been used in various fields due to its excellent property, such as electrodialysis and water treating [11, 12]. Novel composite materials were prepared by cooperating perfluorinated sulfonic acid polymer with various organic and inorganic fillers according to their areas of application.

The membrane materials for VRBs need to possess excellent ionic conductivity, chemical stability, and ion selectivity. Although perfluorinated sulfonic acid membrane material has excellent ionic conductivity, its ion selectivity is poor due to the serious crossover of vanadium ions [13]. To improve the ion selectivity of perfluorinated sulfonic acid polymer membrane materials, lignin with abundant hydroxyl groups is introduced to Nafion, which not only increases the size of the proton transport channels to ensure high proton transport and but also reduce the crossover of vanadium ions. Therefore, Nafion/lignin cooperation achieves the goals that improve the ion selectivity of membrane materials and reducing cost by reducing the consumption of Nafion [14]. Besides, Nf/S-U66 membranes were prepared by introducing U66-SO_3H as a carrier for hindering vanadium ions crossover [15]. And ion conductivity of membranes was improved by forming two kinds of ion transport channel. The pore size of S-U66 is less than vanadium ions, which results in the low vanadium permeability of Nf/S-U66 membranes [16].

Besides, Aquivion resin is also a common perfluorinated sulfonic acid polymer [17]. They have similar chemical

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structures; the only difference is that the length of the side chain connecting the main chain and the sulfonic acid group [18]. Nafion came from the DuPont Company is a copolymer of tetrafluoroethylene and fluorocarbon vinyl ether with a sulfonyl fluoride group. The short chain of Aquivion polymer contains two fluoro-carbon groups, an oxygen atom, and sulfonic acid functional groups [9].

Compared with a long branched perfluorinated sulfonic acid polymer containing long chain (such as Nafion), Aquivion polymer with short side chain has a higher content of sulfonic acid functional groups, the higher the ion exchange capacity, and the higher the ionic conductivity. In addition, Aquivion polymer with short branched chains is conducive to achieving higher mechanical strength [9]. The chemical stability of Aquivion ionomers is better than that of Nafion because the short side chains of Nafion polymer possess ether groups and tertiary carbon atoms [19]. In the aspect of the surface morphology, there are obviously differences of the surface of the Nafion membrane in the dry and wet states [20]. However, Aquivion possesses only slight structural changes and has higher ionic conductivity at low humidity [19].

Hence, we have prepared a series of Aquivion-based hybrid membrane-based Ammoniated polymer synthesized by ring-opening metathesis polymerization. Due to the formation of acid-base interaction ionic crosslinking (as shown in Fig. 1) and hydrophilic-hydrophobic microphase separation structure, the modified Aquivion hybrid membranes materials showed the good mechanical property and ion selectivity. Aquivion/pan-2.5% membrane possessed Coulombic efficiency of 92.47%, which indicated that the addition of ammoniated polymer-based norbornene (PAN) effectively inhibits vanadium ions transport. Aquivion/pan-2.5% hybrid membrane exhibited an energy efficiency of 73.02% at the current density of 160 mA·cm^{-2}.

2 Experimental

2.1 Materials

Aquivion ionomer dispersion (25% polymer) was provided by Solvay company; endic anhydride (98%), norbornene (99%), 1,6-diaminohexane (99%), *N*,*N*-dimethylformamide (99.9%), and acetic acid (99.5%) were purchased by Energy Chemical.

2.2 Preparation of Aquivion-based hybrid membranes

Polymer PAN was synthesized in the previous work ($x/y = 2/1$) [21]. The solvent of Aquivion ionomer dispersion was removed at the temperature of 60 °C, which dissolved in *N*,*N*-dimethylformamide later. The homogeneous casting solution was prepared by mixing Aquivion resin dissolved in *N*,*N*-dimethylformamide with polymer PAN at 60 °C. Finally, the casting solution was cast into clean glasses plate and then lasted for 12 h at 70 °C. Aquivion/PAN-a% membranes were obtained by casting method (referred as the mass ratio of polymer PAN to membrane at the dry state).

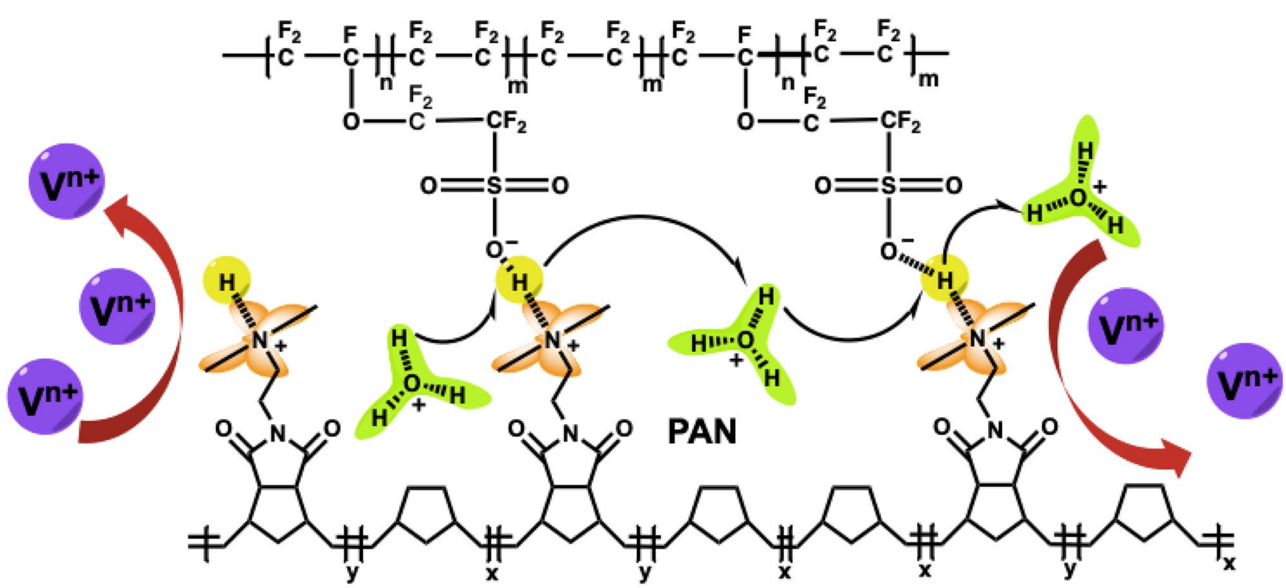

Fig. 1 The ion conduction methesis of Aquivion-based hybrid membranes

2.3 Ion selectivity of Aquivion-based hybrid membranes

2.3.1 Ohim resistance and area resistance

The cell was divided into two cells with 1 M H_2SO_4 solution. And the effective membrane area was 2.5 cm^2. The electrochemical impedance spectrum was obtained by using Bio-Logic potentiostat in the frequency range of 100 to 0.1 Hz. Then, area resistance of Aquivion-based hybrid membranes is measured by cell hardware. The area resistances are obtained as the followed equation [22]:

$$AR = (R1 - R2) \times S \tag{1}$$

where R_1 and R_2 are the battery's high frequency resistances installing and uninstalling a membrane, respectively, and S is the effective area of the membrane.

2.3.2 VO^{2+} permeability

The permeability of vanadium ions was measured by using a lab self-made device. The membrane material was placed between two containers with equal volume. And the mixed solutions of 1.5 M $VOSO_4$/3 M H_2SO_4 and 1.5 M $MgSO_4$ and 3 M H_2SO_4 were added to the left and right sides, respectively. $MgSO_4$ solution with equal concentration mainly plays the role of balancing ion concentration and weakening the effect of osmotic pressure. Then, we measured the concentration of VO^{2+} in the right container at the interval of 12 h by ultraviolet-visible spectrophotometer (UV-2550, Shimadzu) at the wavelength range from 800 to 400 nm. Finally, the vanadium ion permeability of the membrane material was calculated by the following formula [23]:

$$V\frac{dc(t)}{dt} = A\frac{P}{L}\left[c_0 - c(t)\right] \tag{1}$$

where V is the volume of the mixed solution of 1.5 M $MgSO_4$/3 M H_2SO_4, and A and L are the effective area and thickness of the membrane material, respectively. P represents the vanadium permeability of the membrane material, C_0 is the original concentration of VO^{2+} in the mixed solution on the left side, and $C(t)$ represents the VO^{2+} concentration on the left side as a function of time.

2.4 Single cell performances of Aquivion-based hybrid membranes

The vanadium single cell is composed of membrane material, carbon felt electrodes, flow plates, collector plates, and end plates. The active area of the electrode is 5 cm^2, the cutoff voltage of the charge-discharge process is set to 1.6 V and 1.0 V, respectively. Both the initial positive and negative electrolytes are the mixed solution of 1.6 M $V^{3.5+}$/4 M H_2SO_4. We have charged to 50% SOC (state of charge) at the current density of 80 mA·cm^{-2} before starting to test single cell performances. The Coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the flow battery were measured at current densities of 40, 80, 120, and 160 mA·cm^{-2}, respectively, by using the Neware battery tester. Then, the various efficiencies were calculated by the following formula [23]:

$$CE = \frac{Q_{dis}}{Q_{ch}} \times 100\% \tag{2}$$

$$VE = \frac{V_{dis}}{V_{ch}} \times 100\% \tag{3}$$

$$EE = CE \times VE \tag{4}$$

where Q_{dis} and Q_{ch} are discharge capacity and charge capacity, respectively. V_{dis} and V_{ch} represent the average voltage during discharging and charging process, respectively.

3 Results and discuss

3.1 Ohim resistance

The electrochemical impedance spectrums of all Aquivion-based hybrid membranes are shown in Fig. 2. The smaller the ohmic resistance of membranes, the higher the ionic conductivity. The resistance of Aquivion/PAN-10% hybrid membrane was lower than that of Aquivion/PAN-2.5% hybrid membrane and Aquivion/PAN-5% hybrid membrane. This phenomenon is mainly due to the formation of hydrogen bonds between "acid-base" pairs, which could promote ion transport [24]. In addition, the bifunctional side-chain structure of PAN facilitates the formation of highly efficient ordered water channels (facilitating ion cluster aggregation), thus further enhancing the ionic conductivity of all Aquivion-based hybrid membranes [22]. Then, we measure area resistances, which are shown in Fig. 2b. The area resistance of Aquivion/PAN-10% is 0.175 Ω cm^2, indicating that Aquivion/PAN-10% possesses better electrochemistry performance than Aquivion/PAN-2.5% and Aquivion/PAN-5% (Nafion, 0.41 Ω cm^2) [22].

3.2 VO^{2+} permeability

To rapidly and accurately evaluate the vanadium permeability of membrane materials, we firstly measured the UV-Vis spectrum of vanadium (IV) with the four standard concentrations (0.02 M, 0.04 M, 0.05 M, and 0.1 M). As shown in Fig. 3, the UV-Vis spectrum of vanadium (IV) is

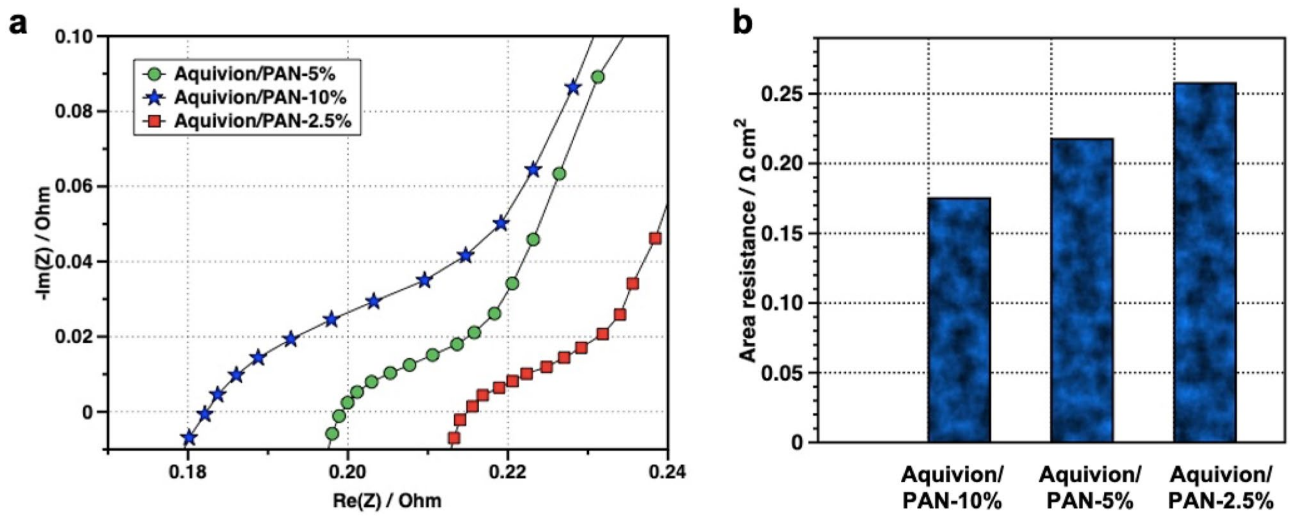

Fig. 2 **a** The EIS test. **b** Area resistance of Aquivion-based hybrid membranes

at the wavelength of 760 nm [25], then the standard curve of absorbance (ABS) and vanadium (IV) concentration according to Lambert-Beer law.

$$ABS = 17.327x - 0.00975 \tag{5}$$

where x is vanadium (IV) concentration.

As the thickness of all Aquivion-based hybrid membranes is about 50 μm, commercial membrane Nafion 212 with the same thickness is selected for comparison. Figure 4 shows the vanadium ion concentration as a function of time. Compared with Nafion 212, Aquivion/PAN hybrid membranes have a low level of vanadium crossover (the vanadium ion permeability of Nafion 212 membrane is 11.6 times that of Aquivion/PAN-2.5% hybrid membrane), which is mainly due to the ion-crosslinking between sulfonic acid functional groups and N-containing groups of PAN, and Donnan effect between N-containing groups of PAN and vanadium ions. However, when the content of PAN is higher than 2.5%, the vanadium ion permeability increases with the increase of PAN content. The high content of APNB polymer will lead to poor compatibility between PAN and Aquivion ionomers, which accelerates vanadium ion transport. When the PAN content reaches 10%, the vanadium ion permeability of Aquivion/PAN-10% membrane material is only about 1/3 of that of Nafion 212.

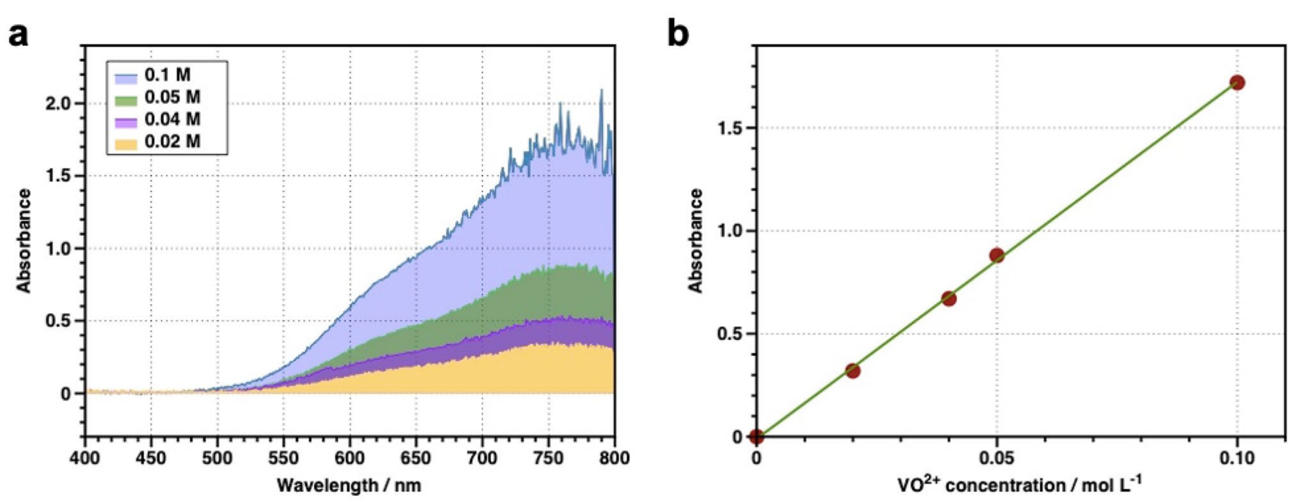

Fig. 3 **a** The UV-Vis spectrum of V(IV) solutions of different concentrations. **b** The standard curve of V(IV) solutions of different concentrations at the wavelength of 760 nm

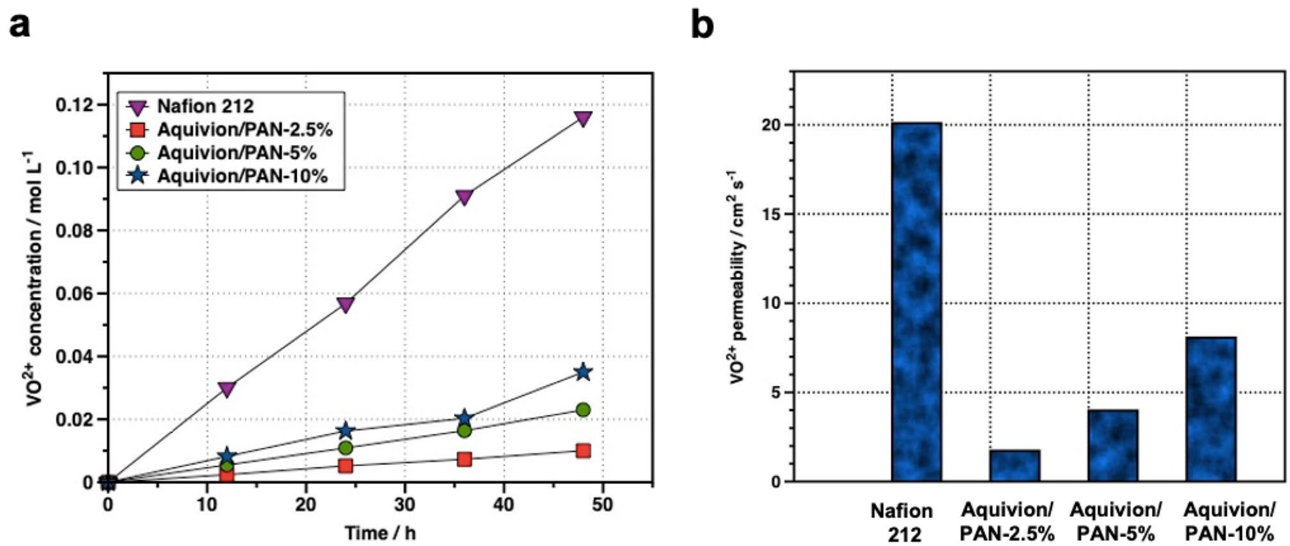

Fig. 4 **a** The concentration change of VO^{2+} in $MgSO_4$ solution. **b** The VO^{2+} permeability of Aquivion-based hybrid membranes

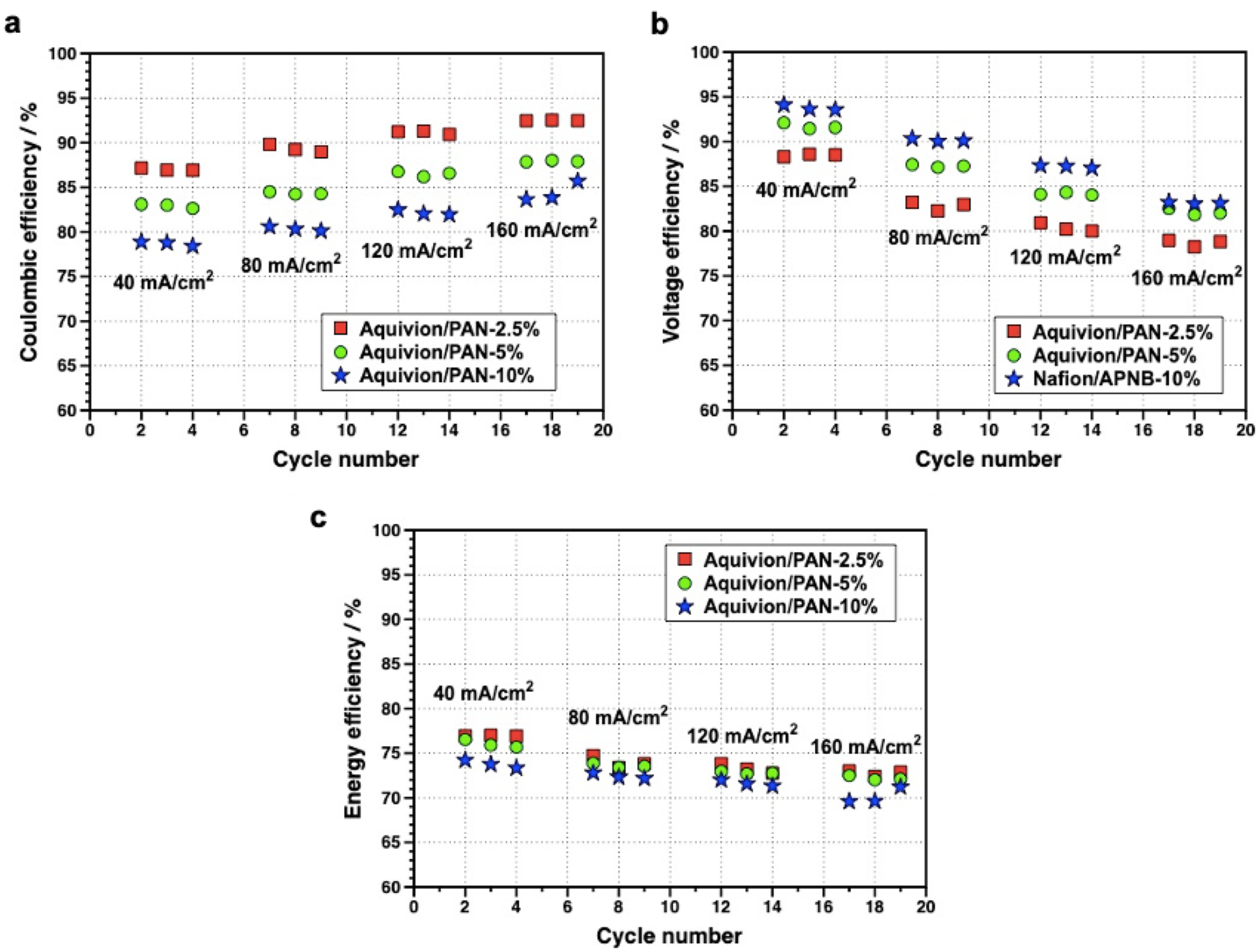

Fig. 5 The single cell efficiency of Aquivion-based hybrid membranes: **a** Coulombic efficiency. **b** Voltage efficiency. **c** Energy efficiency

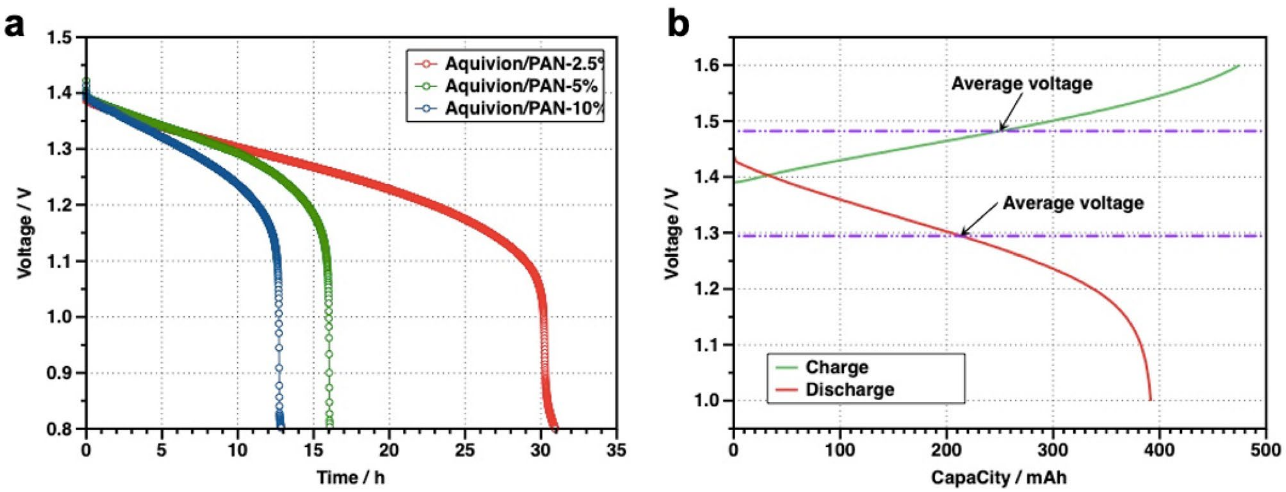

Fig. 6 **a** The self-discharge curves of Aquivion-based hybrid membranes. **b** The charge-discharge curves

3.3 The efficiency of VRB assembled with Aquivion-based hybrid membranes

In order to avoid the corrosion of carbon felt and flow plates, the cutoff voltages are set as 1.0 and 1.6 V. Then, we tested the performance of single cells at different current densities. Figure 5 shows the charge-discharge performances, such as Coulombic efficiency, voltage efficiency, and energy efficiency at the current density of 40, 80, 120, and 160 mA·cm^{-2}. The Coulombic efficiency of all Aquivion-based hybrid membranes can reach more than 78% at the low current density of 40 mA·cm^{-2}. With the increase of current density, the Coulombic efficiency gradually increases, mainly due to the decrease of the time of the charge-discharge process at high current density. However, the differences in Coulombic efficiency of all Aquivion-based hybrid membranes are slight due to the low vanadium ion permeability (less than 10^{-8} cm^2 s^{-1}). The voltage efficiency decreases with the increase of current density owing to the increase of ohmic polarization and over-potential at high current density. At the current density of 40 mA·cm^{-2}, the energy efficiency can reach more than 73%.

The ion-crosslinking between sulfonic acid functional groups and N-containing groups of PAN, which result in the phenomenon that the CE Aquivion/PAN-10% (87.6%), is higher than that of Nafion (75.6%) [22]. Aquivion/PAN-10% possesses better VE than that of at current densities of 40, 80, 120, and 160 mA·cm^{-2}, owing to low area resistance. The EE of Aquivion/PAN-2.5% is higher than that of Nafion 212 at the current density of 40 mA·cm^{-2}.

3.4 The self-discharge curves and charge-discharge curves of VRB assembled with Aquivion-based hybrid membranes

The open circuit voltages (OCV) were measured, which was the direct and simple method to evaluate the degree of self-discharge of Aquivion-based hybrid membranes. Firstly, the single battery was charged to 50% state of charge at the current density of 80 mA·cm^{-2}. Then, the self-discharge test began, and the related results are shown in Fig. 6a. the Aquivion/PAN-2.5% hybrid membranes can still last for 31 h above 0.8 V (Nafion 212 can only maintain about 10 h in the same condition) [26]. The self-discharge degree of the VRB assembled with Aquivion-based hybrid membranes mainly depends on the VO^{2+} permeability of the membranes. As can be seen from Fig. 6a, the self-discharge degree of VRB from high to low is Aquivion/PAN-10% hybrid membranes, Aquivion/PAN-5% hybrid membranes, and Aquivion/PAN-2.5% hybrid membranes. This result is consistent with the vanadium ion osmosis result in Fig. 4b. Figure 6b shows the charge-discharge curve of Aquivion/PAN-10% hybrid membranes at 120 mA·cm^{-2}. Its voltage efficiency can still reach 87.8% due to the ohmic polarization and over-potential.

4 Conclusion

In this work, a series of Aquivion/PAN hybrid membranes were prepared by the solution casting method. Polymer PAN has a flexible side-chain structure, which plays an important role in the performances of Aquivion-based hybrid membranes. The addition of PAN not only improves ion selectivity but also reduces the cost of membranes due to the low consumption of Aquivion ionomers. Aquivion/PAN-2.5% hybrid membrane exhibits a Coulombic efficiency of 92.54% and energy efficiency of 73.02% at the current density of 160 mA·cm^{-2}, which indicated that Aquivion/PAN-2.5% hybrid membranes possess good stability. All measured results show that Aquivion-based hybrid membranes can meet the requirements for VRB applications.

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Declarations

Conflict of interest The authors declare no competing interests.

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