

Short communication

Leveraging sulfonated poly(ether ether ketone) for superior performance in zinc iodine redox flow batteries

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ABSTRACT

Sulfonated poly (ether ether ketone) SPEEK membranes with a degree of sulfonation of approximately 73 % were synthesized and investigated as the cation exchange membrane (CEM) for the zinc iodine (ZI) redox flow battery (RFB). Specifically, SPEEK was used in ZI RFB with 1 mol L⁻¹ electrolyte and its performance was compared to the current benchmark CEM, NafionTM. Notably, columbic and energy efficiencies of 92.9 % and 75.9 %, respectively, were measured for the ZI battery with SPEEK at 17 mA cm⁻², which was a 370 % increase in energy density compared to those with Nafion 212 membranes. RFBs with SPEEK exhibit a peak power density of 122 mW cm⁻² at a current density of 166 mA cm⁻² (98 mW/cm² at 133 mA/cm² with Nafion 212) because of their lower overpotential and higher discharge voltage. These results demonstrate the high cation selectivity of the SPEEK membranes in neutral, salt-based electrolytes, and provide the groundwork to develop a suitable replacement to Nafion for low-cost RFBs.

1. Introduction

With approximately 80 % of today's worldwide energy consumption supplied by fossil fuels, [1] which are the major contributor to greenhouse gas emissions and environmental pollution, many developed countries are rapidly developing and integrating environmentally friendly and sustainable alternatives, such as solar and wind power. [2,3] However, these renewable energy sources are intermittent and unpredictable – they vary significantly with time of day, season, and weather patterns. Thus, for large-scale integration of wind and solar energy generation systems, reliable and inexpensive energy storage technologies must be readily available. [4]

One such electrochemical energy storage device, the redox flow battery (RFB), has emerged as a promising candidate for grid-scale energy storage due to its unique advantage of decoupled energy and power outputs. [5] In these devices, redox-active species dissolved in electrolytes are pumped through porous carbon electrodes and accept or donate charges to facilitate the conversion of electrical to chemical energy. The ability to independently size the energy capacity, which is determined by the electrolyte and tank properties, and the power output, which is based on the size of the cell stack, offers an unprecedented degree of scalability over other storage technologies, e.g., Lead-acid or Li-ion batteries. While there are a number of different RFB chemistries

available, the most common is based on vanadium ions in a sulfuric acid electrolyte. [6] This battery is advantageous because vanadium is extremely stable, highly electrochemically active, and used on both sides of the battery (V⁵⁺/V⁴⁺ in the catholyte and V²⁺/V³⁺ in the anolyte), which is important to avoid electrolyte crossover. [7–9] However, grid-level adaption of the vanadium redox flow battery (VRFB) faces two major obstacles: the cost of vanadium is high and volatile due to its limited access and difficulty in extraction and the corrosive acid electrolyte is difficult to handle and requires expensive materials of construction. [10]

Various aqueous chemistries have been evaluated in search for low cost and less caustic alternatives to vanadium. [11] The zinc iodine (ZI) RFB, in particular, is a promising electrochemical energy storage technology because of its high energy density. [12] This flow battery chemistry has a number of advantageous that make it a viable alternative to the VRFB, including the use of low-cost and naturally abundant materials, benign salts as the supporting electrolytes, and highly electroactive zinc and iodine redox species. [13–15] In their original conception, the ZI RFB was inefficient and slow because Zn²⁺ cations serve as the primary charge carriers; the larger ionic size of the hydrated Zn²⁺ (4.30 Å) resulted in slower transport compared to H⁺ (2.82 Å) and poor electrolyte conductivity, both of which govern the battery rates and efficiency. [16–18] Moreover, the conversion of Zn²⁺ ions to metallic Zn

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during the charging cycle reduces the number of charge carriers in the electrolytes further decreasing ion conductivity. Recently, salts of potassium chloride (KCl) and ammonium chloride (NH_4Cl) have been added to the electrolyte increase the rate of ion transport across the separator, where the smaller ammonium (NH_4^+ ; 3.31 Å) and potassium (K^+ ; 3.31 Å) ions serve as main charge carriers to facilitate faster charge and discharge rates. [14,19–21]

While the ZI RFB addresses several drawbacks of the VRFB, one component that is common between the two batteries is the polymer (ionomer) membrane, which acts as both a physical separator between the catholyte and anolyte and as a medium for cation transport. The properties of the ionomer are critical to the performance and lifetime of the RFB. [22] For example, the ion selectivity of the affects the columbic efficiency of the battery, which is a ratio of the charge to discharge capacity of the battery. [13] That is, the ideal cation exchange membranes (CEMs) are those with high conductivity of charge carriers and low crossover rates of the redox active species, such as triiodide (I_3^-). Further, the thickness and resistance of the ionomer membrane also affects the voltage efficiency of the battery. [15,16] Columbic and voltage efficiency are two key metrics of battery performance that affect the amount of energy that can be stored for later use and the maximum power output. To date, Nafion™ is the benchmark ionomer used in a wide variety of energy storage and delivery technologies. [22,24] due to its high proton conductivity, as well as its robust thermal and mechanic properties. In the presence of water, the hydrophilic sulfonic acid-terminated pendant chains coalesce to form ion channels, within a hydrophobic matrix of the poly(tetrafluoroethylene)-like backbone, through which facile transport of ions occurs. [17,25,26] However, the wide scale adoption of RFBs is markedly restricted by the high cost of Nafion (>\$4500 per kg), as well as limited design flexibility due to its proprietary nature. [27,28]

Recently, sulfonated poly(ether ether ketone) (SPEEK), as well as its derivatives, have garnered significant attention as a replacement CEM to Nafion in applications such as fuel cells. However, the use of this class of ionomers for redox flow batteries is in its infancy. [28] Poly(ether ether ketone) (PEEK) is a semi-crystalline polymer with a rigid, aromatic backbone. The sulfonation of PEEK in sulfuric acid introduces the sulfonic acid groups into the hydroquinone segment of the backbone via electrophilic substitution reaction, which makes the sulfonated PEEK ion conductive. The inherent hydrophobicity of the aromatic backbone and hydrophilicity of the introduced sulfonic acid groups leads to a similar segregated microstructure to that of Nafion where the size of the hydrophilic channels in SPEEK is around 3–5 nm, which fits the transport of water molecules and charge carriers nicely. [29]

These sulfonated ionomers can be easily prepared via sulfonation of PEEK, introducing sulfonic acid groups ($-\text{SO}_3\text{H}$) into the hydroquinone segment of the polymer backbone via an electrophilic substitution reaction. The rigid, aromatic backbone of SPEEK provides mechanical stability, while the hydrophilic domains formed by the aggregated sulfonic acid groups facilitate rapid transport of ions, endowing SPEEK with comparable ion conductivity ($\approx 130 \text{ mS cm}$) to that of the current benchmark material, Nafion ($\approx 100 \text{ mS cm}$). [30] The degree of sulfonation of the ionomer, and thus the spacing of the sulfonic acid groups along the polymer backbone, can then be altered, providing an avenue to directly tune the ionic nature of the CEM. [30] Additionally, electrostatic repulsion between the sulfonic acid groups in the membrane and the iodine may help reduce the undesired crossover of iodine ions (specifically, I^- and I_3^-). [31,32] Moreover, when compared to Nafion, the low cost of SPEEK (<\$300 per kg) makes it an ideal membrane to increase the likelihood of adopting ZI RFBs as a cost-effective, grid-scale energy storage device. [33]

SPEEK based membranes have garnered attention in zinc-based RFBs, where SPEEK and its composites have been primarily utilized in zinc-iron batteries. [34–36] However, to date, there is only one prior investigation on the use of neat SPEEK membranes as the CEM for ZI

RFBs. Specifically, Chola et al. [37] showed performance properties of SPEEK-covalent organic framework (COF) composite membranes in zinc-iodine redox flow batteries. In this study, they found that the SPEEK-COF composites exhibited higher discharge energy capacities as compared to neat SPEEK membrane. However, cycling performance of the neat SPEEK membrane relative to the composite membranes was not discussed. Further, the performance of their composites was not compared to Nafion, making it hard to put the battery performance in the context of the current landscape of materials for CEMs.

In this work, we seek to overcome the material cost-performance of flow batteries by developing a low-cost and highly efficient ZI RFB using more cost-effective sulfonated ionomers – e.g., neat SPEEK – as the CEM. Specifically, sulfonated poly(ether ether ketone) (SPEEK) membranes were fabricated and employed as the CEM in the ZI RFB. To the best of our knowledge, this is the first report of the cycling performance and polarization curve analysis of neat SPEEK membranes as the CEM for the transport of K^+ in a neutral ZI RFB. Specifically, SPEEK ionomer membranes were synthesized with a DS of $\approx 73\%$ and utilized in ZI RFBs with KCl as the supporting electrolyte, and thus, the potassium ions (K^+) serve as the primary charge carriers. For comparison, analogous battery tests were performed using Nafion 212 as the CEM. Polarization curves were developed from galvanostatic charge-discharge cycle tests to compare battery performance, and electrochemical impedance spectroscopy was used to determine the internal resistance of RFBs with each membrane type. Compared to those with Nafion, RFBs with SPEEK exhibited improved electrolyte utilization, lower resistance and overpotential, and therefore, higher power and energy densities. Specifically, the use of a SPEEK membrane with an ion exchange capacity (IEC) about 75 % greater than Nafion 212 resulted in a 25 % increase in power density and 370 % increase in energy density in the ZI RFB.

2. Materials and experimental methods

2.1. Materials

The poly(ether ether ketone) (PEEK) used in this work was “VICTREX PEEK 450PF” and was purchased from Victrex (Lancashire, UK). Hydrogen peroxide (30 wt% in H_2O), sulfuric acid (H_2SO_4 ; 98 %, ACS reagent), *N,N*-dimethylacetamide (DMAc; for HPLC, $\geq 99.5\%$), deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), and sodium chloride were purchased from Sigma Aldrich. Potassium iodide (KI, $>99\%$, Acros Organics), zinc bromide (ZnBr_2 , 98 %, Alfa Aesar), and potassium chloride (KCl, $>99\%$, Alfa Aesar) were purchased from Fisher Scientific. Multiwalled carbon nanotubes containing approximately 5–8 wt % iron catalyst (M-grade, diameter = 70–80 nm, length = 10 μm) were purchased from NanoTechLabs (Yadkinville, NC). Nafion™ 212 ($\approx 50 \mu\text{m}$) membranes were purchased from Beantown Chemical, Inc. (Hudson, NH). Reverse osmosis (RO) water (resistivity $\approx 18 \text{ M}\Omega \text{ cm}$) was used for all experiments and membrane synthesis.

2.2. SPEEK membrane preparation

Prior to the sulfonation reaction, approximately 4 g of PEEK powder was dried at room temperature under dynamic vacuum for 24 h. After drying, the PEEK powder was slowly added to 60 mL of H_2SO_4 and the mixture was stirred at room temperature until a clear, homogenous solution was obtained ($\approx 2 \text{ h}$). Next, the PEEK- H_2SO_4 solution was heated to 50 °C for 3 h (the solution was mixed using a mechanical stirrer at $\approx 350 \text{ RPM}$) to obtain SPEEK. Following sulfonation, the final SPEEK was precipitated by pouring the solution SPEEK- H_2SO_4 into an excess of iced RO water, after which the precipitate was washed $\approx 30\times$ with RO water to remove residual sulfuric acid, then dried at room temperature under dynamic vacuum for $\approx 30 \text{ h}$. To prepare the casting solution, a specified amount of dried SPEEK was dissolved in DMAc at a concentration of 10 wt% ($m_{\text{SPEEK}}/(m_{\text{SPEEK}} + m_{\text{DMAc}})$). Next, the SPEEK-DMAc casting solution was poured onto a polished quartz

substrate that was placed on heating plate set at 80 °C, after which the substrate was covered by a funnel with Kim-wipe flue to allow evaporation of DMAc overnight. Once the solvent was evaporated, the ionomer membranes were annealed at 140 °C for 2 h under dynamic vacuum, after which the oven was turned off and allowed to cool down to room temperature under static vacuum. Prior to beginning measurements, the membranes were hydrated in RO water for 3 days. The thickness of the hydrated SPEEK membranes was on the order $\approx 120 \mu\text{m}$.

2.3. Degree of sulfonation (DS) of SPEEK membrane

Nuclear magnetic resonance (NMR) spectroscopy was used to measure the final degree of sulfonation (DS) of the SPEEK membranes. Specifically, ^1H NMR spectra were collected using a Bruker NEO 500 MHz spectrometer equipped with a Bruker SmartProbe (500 MHz, DMSO- d_6). For these experiments, a ≈ 3 mass % polymer solution was prepared in DMSO- d_6 .

2.4. Equilibrium water uptake (EWU)

After fabrication, each membrane was immersed in RO water and allowed to equilibrate for at least 24 h. Once the membranes were equilibrated, they were removed from the RO water, patted dry with a Kim Wipe, and the mass of the wet membrane, m_{wet} (in g), was taken. To obtain the dry mass of the membrane, m_{dry} (in g), the membranes were dried at 90 °C for 24 h. The following equation was used to calculate the equilibrium water uptake (in %)

$$\text{Equilibrium Water Uptake (EWU)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100. \quad (1)$$

2.5. Ion exchange capacity (IEC)

Ion exchange capacity (IEC) experiments were performed according to literature. [38,39] Briefly, the membrane was dried under vacuum at 90 °C for 24 h, massed, and immersed in 1 mol L $^{-1}$ NaCl for 24 h. Next, the membrane was removed from the NaCl solution, and the remaining solution was titrated with 0.01 mol L $^{-1}$ NaOH with phenolphthalein (1 % in a mixture of 1:1 water: ethanol by volume). The IEC for each membrane (in mmol g $^{-1}$) was calculated as follows

$$\text{Ion Exchange Capacity (IEC)} = \frac{V_{\text{NaOH}} C_{\text{NaOH}}}{m_{\text{dry}}}, \quad (2)$$

where V_{NaOH} is the volume of titrated NaOH solution (in L) and C_{NaOH} is the concentration of the NaOH solution (in mmol L $^{-1}$).

2.6. Pretreatment of membranes prior to battery flow battery tests

Prior to ZI RFB tests, both the SPEEK, prepared and characterized as described above (DS ≈ 73 % and thickness $\approx 120 \mu\text{m}$), and Nafion 212 membranes (thickness $\approx 50 \mu\text{m}$) were pretreated to convert these ionomer membranes from the H $^{+}$ to the K $^{+}$ form. Specifically, the Nafion 212 was refluxed at 90 °C for 1 h in each of the following: (i) RO water, (ii) 3 % (v/v) hydrogen peroxide, (iii) 0.5 mol L $^{-1}$ H $_2$ SO $_4$, and (iv) 1.0 mol L $^{-1}$ potassium chloride. Note, the membrane was refluxed in RO water in between each of the solvents. The SPEEK membrane was refluxed at 70 °C for 1 h each with 0.5 mol L $^{-1}$ sulfuric acid, RO water, and 1.0 mol L $^{-1}$ potassium chloride. Both membranes were stored in 1.0 mol L $^{-1}$ potassium chloride until use.

2.7. Zinc iodine redox flow battery construction and electrochemical characterization

Iron-containing carbon nanotube electrodes with a 9 cm 2 active area were used as the electrode material. Details on the their fabrication method can be found elsewhere. [40–42] The 1.0 mol L $^{-1}$ electrolyte

used for all electrochemical measurements comprises 1.0 mol L $^{-1}$ potassium iodide, 0.5 mol L $^{-1}$ zinc bromide, and 1.0 mol L $^{-1}$ potassium chloride. ZI RFBs were assembled with the carbon electrodes and the designated CEM in a Micro Flow Cell from ElectroCell Technologies (Towaco, NJ), and the electrolyte was circulated through the cell using a dual channel peristaltic pump (EQ-BK-380-2) from MTI Corporation (Richmond, California). The electrochemical performance of the ZI RFB was evaluated using galvanostatic charge-discharge (GCD) testing with an Arbin MSTAT Potentiostat (Arbin Instruments) and electrochemical impedance spectroscopy (EIS) with a Gamry Instruments Reference 600 Potentiostat. All measurements were performed at ambient conditions.

3. Results and discussion

To help the reader more easily follow the discussion of the results, a summary of the most important acronyms used in the remainder of the manuscript are provided in Table 1.

Fourier transform infrared (FTIR) spectroscopy was used to verify successful introduction of sulfonic acid groups along the backbone of PEEK. Fig. 1a shows the FTIR spectrum of a (dry) SPEEK membrane. Note that the wavenumber range from 1800 cm $^{-1}$ to 2700 cm $^{-1}$ has been omitted as there are no infrared bands of interest present in this region of the spectrum. As seen in Fig. 1a, several peaks are present in the SPEEK spectrum that were not there in the spectrum of dry PEEK. Specifically, the three infrared bands of interest – with peak maxima located at approximately 3445 cm $^{-1}$, 1400 cm $^{-1}$, and 1076 cm $^{-1}$ – can be assigned to the O–H stretching, asymmetric O=S=O stretching, and symmetric O=S=O stretching vibration from sulfonic acid (–SO $_3$ H) groups, respectively. [43] Next, the degree of sulfonation (DS) of the prepared SPEEK was quantitatively determined via ^1H NMR. The ^1H NMR spectrum of the SPEEK is shown in Fig. 1b. Notably, the –SO $_3$ H group causes a down field shift of the nearest neighboring proton (H $_{10}$; see chemical structure of SPEEK in Fig. 1b) compared with the protons of the unsubstituted ether-ether phenyl ring (H $_{12}$ and H $_{13}$). The DS can be calculated by taking the ratio of the relative integration of the H $_{10}$ peak to that of all the other proton peaks. From this analysis, the DS of the SPEEK used in this work was determined to be approximately 73 %.

As ion transport in these membranes can be classified as “water-facilitated transport” [44] and is considered to occur through the hydrophilic, water-filled domains formed by the aggregation of the sulfonic acid groups, it is important to characterize both the equilibrium water uptake (EWU) and ion-exchange capacity (IEC) of the SPEEK and Nafion. EWU is the ability of a membrane to absorb water, and thereby provides a qualitative measure of the relative volume of hydrophilic domains in a given mass of the membrane. IEC is a measure of the ability of the sulfonic acid groups to undergo displacement of ions, and therefore, provides some understanding of the ability of an ionomer to conduct (transport) ions, as it depends on the amount of the sulfonic acid groups within the hydrophilic channels that are in contact with, and connected to, the external electrolytes. That is, the EWU and IEC can provide insight into the phase segregated structure of the hydrated ionomer membranes, which is illustrated in Fig. 1d. The nanophase segregated structure of SPEEK contains both interconnected, continuous channels, as well as channels that terminate within the aromatic,

Table 1
List of relevant acronyms.

Full Name	Acronym	Full Name	Acronym
Poly(ether ether ketone)	PEEK	Cation exchange membrane	CEM
Sulfonated poly(ether ether ketone)	SPEEK	Energy efficiency	EE
Redox flow battery	RFB	Coloumbic efficiency	CE
Zinc iodine	ZI	Voltage efficiency	VE
Ion exchange capacity	IEC	Degree of sulfonation	DS
Equilibrium water uptake	EWU	Reverse osmosis water	RO water

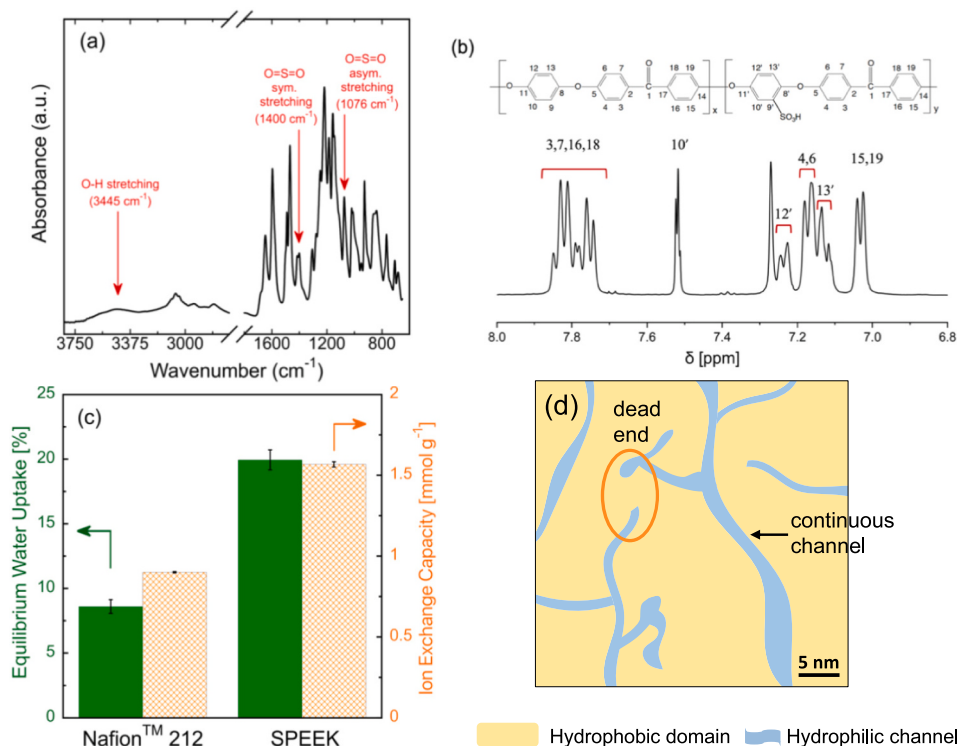


Fig. 1. (a) Fourier transform infrared attenuated total reflectance and (b) ^1H NMR spectra of (dry) SPEEK with a degree of sulfonation of approximately 73 %. The numbers in the NMR spectrum have been assigned to specific bonds in the SPEEK chemical structure. (c) Equilibrium water uptake (EWU) and ion exchange capacity (IEC) of Nafion™ 212 and SPEEK membranes, as well as (d) an illustrative schematic of the nanophase-segregated structure of ionomer membranes.

hydrophobic domain (i.e., a “dead end”). The results of these characterizations are summarized in Fig. 1c, where the EWU and IEC are shown with green and orange bars, respectively.

As shown in Fig. 1c, the equilibrium water uptake of the SPEEK membrane was over two-fold higher than that of the Nafion 212 (8.61 ± 0.53 % vs. 19.94 ± 0.77 %). In addition, the IEC of the SPEEK membrane, as measured by titration, was approximately 75 % higher than Nafion 212 (1.568 ± 0.016 mmol g $^{-1}$ vs 0.901 ± 0.004 mmol g $^{-1}$). It is important to note the method by which the values of IEC for these ionomers were determined as the value measured by titration will, in theory, always be lower than that calculated from NMR measurements. For example, if we assume that of all the sulfonic acid groups are available for ion exchange, the theoretical IEC of the SPEEK, with DS of 73 % (as measured by NMR), is calculated to be 2.105 mmol g $^{-1}$. This indicates that approximately 25 % of the sulfonic acid groups of the SPEEK are not accessible for ion exchange once the SPEEK is fabricated into a dense, free-standing membrane. As NMR is conducted on SPEEK dissolved in a solvent, it is sensitive to all sulfonic acid groups added to the backbone of PEEK. However, not all of these sulfonic acid groups will coalesce into the ionic channels when the membrane is hydrated, and thus, the IEC calculated from titration experiments is lower than that calculated from NMR measurements.

The higher value of EWU for SPEEK is not surprising given the increased value of IEC for these membranes, as it is known that increasing the number of hydrophilic sulfonic acid groups, thus increasing IEC, tends to lead to higher water absorption. These results potentially suggest that the SPEEK will have more facile transport of proton as ion transport in this class of membranes is strongly correlated with water content. [45] Traditionally, there is a tradeoff between EWU and the mechanical robustness of the ionomer membrane, where at a high enough DS, the SPEEK will become water soluble. [46] However, while the SPEEK was able to absorb a significantly higher amount of water, these membranes still remained mechanically robust, making them suitable candidates, at least mechanically, as the CEM in ZI RFBs.

A test-scale, zinc iodine redox flow battery was assembled as described above with iron-functionalized carbon electrodes, [40–42] 1.0 mol L $^{-1}$ electrolyte and either SPEEK or Nafion 212 membranes. The electrolyte was pumped through each electrode at a flowrate of 30 mL min $^{-1}$ and the cell was initially conditioned by galvanostatic charge discharge cycling with a current density of 5.6 mA cm $^{-2}$ and then a single complete cycle at 11 mA cm $^{-2}$ (voltage limits of 0.8 V and 1.42 V). At the same electrolyte flow rate, polarization curves were developed starting with a fully charged battery by charging and discharging for a period of 2 min with a rest time of 1 min between each current. Fig. 2a shows the average discharge voltage and associated power density of the ZI RFB over the range of current densities tested. The discharge voltages from cells with SPEEK membranes were routinely higher than those with Nafion 212, where this difference became increasingly more pronounced at higher current densities. The sustained higher voltages, especially at high current densities, is indicative of the lower internal resistance and polarization losses, which results from the higher ion conductivity and cation selectivity (lower rate of self-discharge) of the SPEEK membrane relative to Nafion. Specifically, the peak power obtained from ZI RFBs with the SPEEK membrane was 122 mW cm $^{-2}$ at a current density of 166 mA cm $^{-2}$ compared to 98 mW cm $^{-2}$ at 133 mA cm $^{-2}$ for those with Nafion 212. As all components in the ZI RFB were identical aside from the ionomer membrane, the 25 % increase in peak power can be attributed to the improved performance of SPEEK as the CEM. To the best of our knowledge, this is the first report of SPEEK membranes outperforming the current benchmark material Nafion in a ZI RFB energy conversion and storage device. As mentioned in the Introduction, there has only been one previous investigation on the use of neat SPEEK in ZI RFBs. However, in that study, the electrolyte concentration used was higher than the one used in our study. Further, the ionomer membrane thickness and DS were not reported. Thus, we are unable to directly compare our membrane’s performance to this prior work.

To further characterize the behavior of SPEEK as a CEM in flow

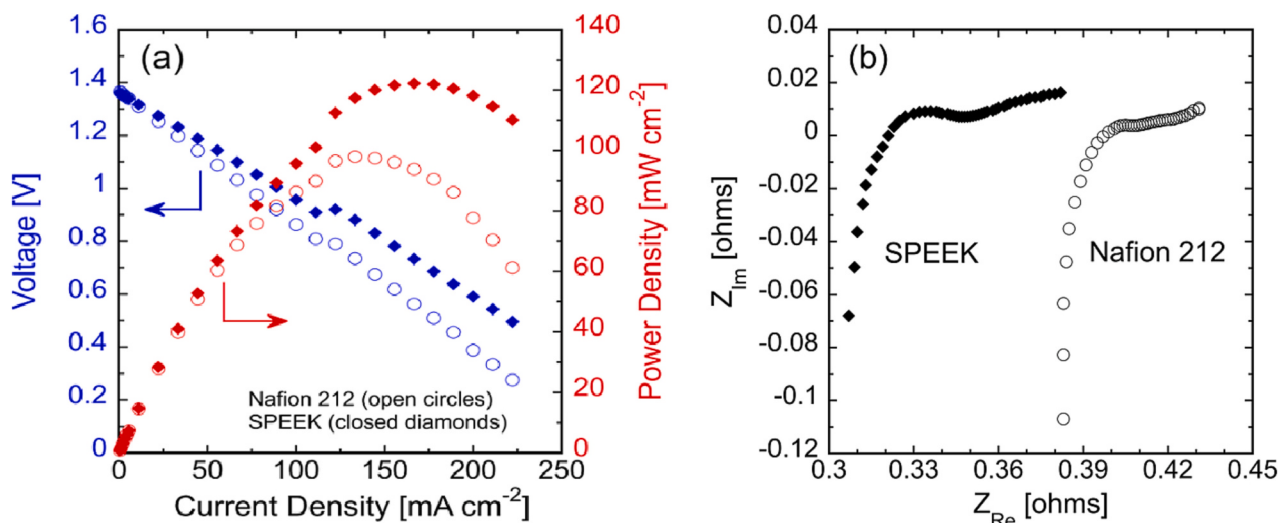


Fig. 2. (a) Discharge polarization curves (blue) and power density (red) of the ZI RFB with SPEEK (closed blue and red diamonds) and Nafion 212 (open blue and red circles) membranes. (b) Nyquist plot from EIS analysis of the ZI RFB with SPEEK (closed diamonds) and Nafion 212 (open circles) membranes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

battery applications, electrochemical impedance spectroscopy (EIS) was conducted to determine the internal resistances within the cell in the absence of electrolyte flow. The resulting Nyquist plots are shown in Fig. 2b, where the data obtained from RFBs with SPEEK and Nafion are shown in solid black diamonds and open black circles, respectively. Both membranes exhibited a low charge transfer resistance (R_{ct}) due to the presence of redox-active iron particles within the carbon electrodes, [42] 0.026Ω for Nafion 212 and 0.029Ω for SPEEK, with area specific

resistances (ASR) of $0.23 \Omega \cdot \text{cm}^2$ and $0.26 \Omega \cdot \text{cm}^2$, respectively. The 0.08Ω shift in the Nyquist plot away from the origin observed for RFBs with Nafion 212 arises from the lower ion conductivity through the Nafion membrane. Because the charge-transfer resistances of each RFB are similar, the lower discharge voltage observed in cells with Nafion 212 can be attributed to the difference in membrane properties (i.e. decrease in ion conductivity).

Next, galvanostatic charge-discharge cycling tests were performed to

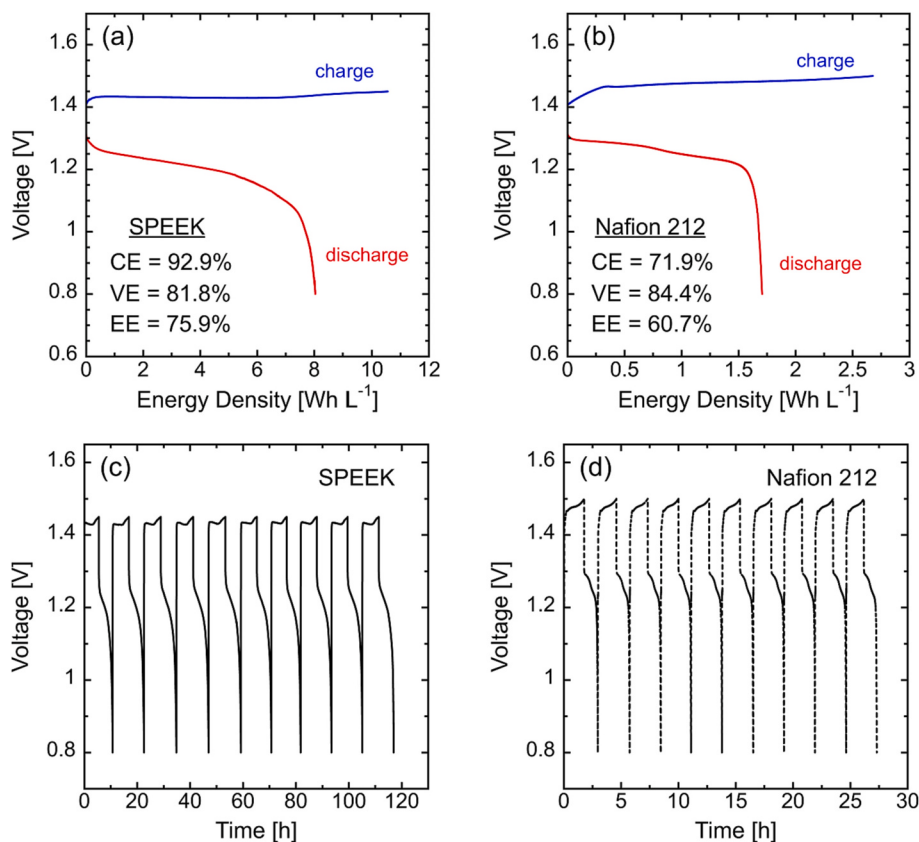


Fig. 3. The final charge-discharge cycle for ZI RFB with (a) SPEEK and (b) Nafion 212 membranes. Repeated cycling with (c) SPEEK (d) Nafion 212 membranes. All tests were performed in 1.0 mol L^{-1} electrolyte at a current density of 17 mA/cm^2 .

determine the charge-discharge behavior of the membranes during operation in the ZI RFB using a relatively low current density of 17 mA cm⁻². The charge voltage was limited to 1.45 V for SPEEK and 1.50 V for Nafion 212 – this was determined to be 100 % state of charge based on charge profile – and 0.8 V for the discharge voltage for both membranes. Fig. 3 shows the results from the battery analysis for repeated cycling, along with the final charge-discharge profile. Although the RFB with Nafion 212 exhibited a marginally higher discharge voltage, the battery with SPEEK had significantly higher discharge capacities, (Fig. 3a and b). To quantify this improved performance, the energy densities for the SPEEK and Nafion 212 were found to be 8 Wh L⁻¹ and 1.7 Wh L⁻¹, respectively, which is a 370 % increase in energy density when SPEEK is used as the CEM in the ZI RFB. Note, energy density calculations were based off the volume of the catholyte (in this case, 125 mL) as described in literature. [17] The relatively low values compared to the theoretical maximum (23.2 Wh L⁻¹ at an open circuit voltage of 1.3 V) are a result of using a low electrolyte concentration in the battery (1.0 mol L⁻¹). Another factor that limits the zinc iodine chemistry is the conversion of iodide to triiodide that often involves the formation of insoluble iodine. [15]

The coulombic efficiency (CE) and energy efficiency (EE), calculated from the 10th charge-discharge cycle, were notably higher in RFBs operating with SPEEK. For instance, the CE of the ZI RFB operating with SPEEK was 92.9 % compared to 75.9 % for the battery with Nafion 212, which results in a markedly higher EE of 71.9 % in comparison to 60.7 % for Nafion 212. The higher energy density, coulombic efficiency and energy efficiency can all be attributed to the improved cationic selectivity of SPEEK over Nafion in the neutral ZI electrolyte, and the reduction in ion-crossover (K⁺). The voltage efficiency, which is affected by membrane's resistance and thickness, [47] is slightly higher (<5 %) in the RFB with Nafion 212, which is likely due to the fact that the Nafion 212 membrane (~50 µm) is much thinner than SPEEK (~120 µm), which would result in lower overpotential under the low current density test conditions. [23,48] Finally, when comparing the charge-discharge cycles for RFBs with SPEEK (Fig. 3c) and Nafion 212 (Fig. 3d), there are two important behaviors to note: (1) there was no discernable capacity fading with time or number of cycles when the ZI RFB was operated with SPEEK (3 % capacity fade vs 5 % for Nafion 212) and (2) the total time to complete 10 charge-discharge cycles was significantly longer for SPEEK (~120 h) as compared to Nafion 212 (~27 h). In other words, RFBs with SPEEK membranes can sustain the given discharge current for a longer period of time at the given set of operating conditions (e.g. electrolyte concentration, flow rate). The higher charge retention and subsequently higher discharge capacities are likely a result of the greater number of sulfonic groups which allow for improved potassium cation transport (from KCl electrolyte) through the CEM. These results further underscore the improved performance of the ZI RFB when SPEEK is used as the CEM instead of Nafion, 212.

4. Conclusion

In conclusion, we fabricated a low-cost, sulfonated ionomer, i.e., SPEEK, was a degree of sulfonation of ~73 % for use as the CEM in a neutral ZI RFB. Compared to the current benchmark ionomer, Nafion, we observed an increase in power density of approximately 25 % when using a SPEEK membrane in the ZI RFB, and an impressive four-fold increase in the energy density. In addition, the SPEEK membrane shows lower polarization losses and higher coulombic efficiency, underscoring the improved ion exchange efficiency and cationic selectivity of these ionomers. These improved performance results, in combination with the reduced material costs achieved by using SPEEK (\$1700/m² vs \$80/m²) provides a clear pathway to achieving cost-effective RFBs with high energy and power, to support their adaptation into grid-scale electrical energy storage systems. Additionally, there is the prospect of further improving the performance properties of the ZI RFB by varying certain design parameters, such as the degree of

sulfonation of SPEEK membranes, the electrolyte concentration, to name a few.

CRedit authorship contribution statement

Abena Williams: Formal analysis, Investigation, Writing – original draft, Visualization. **Xueting Wang:** Formal analysis, Investigation, Writing – original draft, Visualization. **Eric M. Davis:** Validation, Writing – review & editing, Supervision. **Mark E. Roberts:** Conceptualization, Validation, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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