Research article

Development of Aqueous Organic Flow Battery Using SPEEK Membrane and Eco-Friendly Electrolytes

Sanphop Dumkrang[1,3], Kang Li[2], Likhasit Intakhuen[4], Konlayutt Punyawudho[4] and Sirichai Koonaphapdeelert[1,5]*

[1]*Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, Thailand*
[2]*Department of Chemical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom*
[3]*Graduate School, Chiang Mai University, Chiang Mai, Thailand, Thailand*
[4]*Department of Mechanical Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, Thailand*
[5]*Energy Research and Development Institute Nakornping, Chiang Mai University, Chiang Mai, Thailand*

Curr. Appl. Sci. Technol. 2024, Vol. 24 (No. 3), e0258288; https://doi.org/10.55003/cast.2024.258288

Received: 10 April 2023, Revised: 18 May 2023, Accepted: 18 October 2023,Published: 15 February 2024

Abstract

Keywords

sulfonated poly (ether ether ketone);

aqueous organic flow battery;

ion exchange membrane

Aqueous organic redox flow batteries (AORFBs) are a type of flow battery that offers a promising solution for energy storage, and one of the main issues is selecting low-cost membranes with high ion conductivity to enhance performance and efficiency. In this study, low-cost sulfonated poly ether ether ketone (SPEEK) membranes were fabricated using the casting method, with the polymer/solvent ratios of SPEEK and N,N'-dimethylformamide (DMF) being varied. The Nafion 117 membrane was used as a benchmark for comparison. The performance of aqueous organic redox flow batteries employing anthraquinone-2-sulfonic acid (AQS) and 1,2-benzoquinone-3,5-disulfonic acid (BQDS) as electrolytes was evaluated. The SPEEK membranes were determined to have dense, homogeneous surfaces with no flaws and a thickness of 60 microns. In addition, their physicochemical properties, such as water uptake, swelling ratio, ion exchange capacity, and degree of sulfonation, were investigated. The results showed that the SPEEK membranes had better rate performance and cycle stability when compared to the Nafion117 membrane during charge-discharge cycles. Additionally, the SPEEK membranes exhibited slower potential drops and higher power density during constant current mode operation, despite showing no significant differences in energy efficiency and power density. These findings demonstrate the potential of SPEEK membranes for use in AORFBs and as a benchmark for future research and development.

*Corresponding author: E-mail: sirichai@eng.cmu.ac.th

1. Introduction

Renewable energy is crucial for reducing greenhouse gas emissions and achieving the goal of net-zero emissions in the future. However, the randomness, low energy density, and intermittent nature of wind and solar energy make them difficult to store and distribute when compared to more reliable sources such as fossil fuels and biomass [1-6]. To improve power reliability, a redox flow battery (RFB) can be employed [7-9]. RFBs are energy storage devices that are capable of electrochemical conversion between chemical and electrical energy stored in electrolytes contained in external tanks. They have a good depth of discharge, excellent round-trip efficiency, a long lifespan compared to conventional Li-ion batteries and are scalable. Additionally, the output power of RFBs can be manipulated by changing the number of stack cells and electrolytes [7-9]. RFB comprise four main components: electrolytes, which store and release energy; ion exchange membranes, which separate the anolyte and catholyte compartments; electrodes, responsible for facilitating electrochemical reactions; and external tanks, which store the electrolytes.

Vanadium redox flow batteries (VRBs) have been used for large-scale energy storage, but their applications are limited due to the high cost, scarcity, and toxicity of vanadium. This has prompted the development of lower-cost, more environmentally-friendly technology as an alternative to VRBs [9-14]. Aqueous organic redox flow batteries (AORFBs) have the potential to serve as alternatives to VRBs and do not require expensive catalysts such as platinum. The electrolytes made of organic compounds are non-toxic and can be made from low-cost, abundant materials. Their electrochemical properties can also be improved by modifying functional groups [15-17]. In the context of AORFBs, the AQS/BQDS electrolyte system exhibits several unique advantageous features that make it an excellent candidate. First, both AQS and BQDS are highly soluble in water, thus increasing the energy density. Second, their redox potentials are well-separated, which contributes to a high cell voltage. Lastly, they show excellent electrochemical reversibility and stability, which is crucial for long-term operation of the battery. AORFBs operate in an acidic rather than alkaline system, and they involve only one type of cation (usually H^+) or anion (usually Cl^-) in the solutions. This allows for the use of low-cost membranes with high ion conductivity rather than ion selectivity, which is required in VRBs that involve three different cations [18-22].

Recently, many researchers have developed ion exchange membrane alternatives to Nafion, even though their excellent proton conductivity and chemical stability are considered less desirable due to their high cost and significant permeability. Anion Exchange Membranes (AEMs) have emerged as alternatives, providing good ionic conductivity and low vanadium ion crossover, but they often suffer from poor chemical stability, particularly under acidic conditions. Non-Ionic Porous Membranes like polybenzimidazole (PBI) membranes, characterized by their high thermal and chemical stability, have also been evaluated. However, their usage is often constrained by high production costs and relatively lower proton conductivity at ambient temperatures [23]. Among these alternatives, SPEEK membranes have received widespread attention for their low cost, excellent ion conductivity, stability in acidic environments, and ease of manufacture [24-34]. The key component under investigation in this work is the sulfonated poly ether ether ketone (SPEEK) membrane, which plays a crucial role in enhancing the performance and efficiency of the AORFB.

While previous studies have explored the application of SPEEK membranes in redox flow batteries, this study focuses on the impact of different solvent to polymer ratios on the physicochemical properties of the SPEEK membrane and its performance in aqueous-organic redox flow batteries. Through comparative analysis with the benchmark Nafion117 membrane, this study provides new insights into the role of the solvent to polymer ratio in enhancing the performance of SPEEK membranes, thus offering a different dimension to the ongoing research in the field. In this research, SPEEK membranes were fabricated by varying their polymer/solvent ratios, and their physicochemical properties, including water uptake, swelling ratio, ion exchange capacity, and degree of sulfonation, were examined. Additionally, the performance of the AORFB using the SPEEK membranes and AQS/BQDS electrolytes was investigated.

2. Materials and Methods

2.1. Materials

Nafion® 117 membranes were supplied by DuPont Inc. Anthraquinone-2-sulfonic acid sodium salt monohydrate and 4,5-Dihydroxy-1,3-benzenedisulfonic acid disodium salt monohydrate were purchased from Sigma-Aldrich while Amberlyst® 15(H), and N,N'-dimethylformamide 99% (DMF) were acquired from Alfa-Aesar.

2.2. Membrane preparation

The sulfonation of poly (ether ether ketone) (PEEK) (Vitrex Inc., USA) was conducted according to a previously reported procedure [35]. The membranes were prepared using the solution casting method. SPEEK powder was dissolved in DMF to give 10, 15, and 20 wt% solutions, which were designated as SPEEK10, SPEEK15, and SPEEK20, respectively. Magnetic stirring was used to obtain homogeneous casting solutions, and ultrasonication was applied to eliminate bubbles. The solutions were then filtered, cast onto dust-free glass plates, and dried at 60°C for 12 h followed by 110°C for 12 h in an oven. Afterwards, the membranes were peeled off from the glass plates and treated in 1 M H_2SO_4 solution for 24 h. The membranes were rinsed and stored in deionized water at room temperature before use.

2.3. Membrane characterization

The morphology of the membranes was examined using a scanning electron microscope (JSM-IT300) operating at 0.3-30 kV. The membranes were coated with gold and dried in an oven. Their weight and length were then determined. The dry membrane was soaked in DI water for 24 h, and its weight and length were measured to calculate the water uptake (WU) and swelling ratio (SR) using the following equations:

$$WU = \frac{W_{Wet} - W_{dry}}{W_{dry}} x100 \quad (1)$$

$$SR = \frac{L_{Wet} - L_{dry}}{L_{dry}} x100 \quad (2)$$

where W_{wet} and L_{wet} are the weight and length of the wet membrane: W_{dry} and L_{dry} are the weight and length of the dry membrane, respectively.

Ion exchange capacity (IEC) and degree of sulfonation (DS) were measured using the titration method. The membrane was soaked in a saturated sodium chloride (NaCl) solution for 24 h. The liquid that contains hydrogen ions (H^+) exchanged from the membrane was then titrated with a 0.01 M sodium hydroxide (NaOH) solution using phenolphthalein as an indicator. The IEC and DS were calculated using the following equation:

$$IEC = \frac{C_{NaOH}\ x\ V_{NaOH}}{W_{dry}} \quad (3)$$

where, C_{NaOH}, V_{NaOH}, and W_{dry} are the concentration of the NaOH solution (M), the titrated volume of the NaOH solution (mL), and the weight of the dry membrane (g), respectively.

$$DS = \frac{M_{PEEK}\ x\ \mathrm{IEC}}{1000 - M_{SO3H} x IEC} \quad (4)$$

where M_{PEEK} and M_{SO3H} represent the average molecular weight of the sulfonated poly(ether ether ketone) (SPEEK) repetitive unit and the molecular weight of the – SO_3H group, respectively.

2.4. Battery cell performances

The aqueous quinones redox system contained anthraquinone-2-sulfonic acid (AQS) at a concentration of 0.2M as the anolyte and 1,2-benzoquinone-3,5-disulfonic acid (BQDS) at a concentration of 0.2M as the catholyte, as shown in Figure 1. The quinone (NaAQS and Na_2BQDS) solution was dissolved in 100 mL of 1M sulfuric acid and stirred with Amberlyst H+ to replace sodium with hydrogen. The solution was then filtered using a GF/C glass microfiber filter to obtain the quinones solution. The endplates were assembled using a vinyl plastic composite gasket and a brass current collector with an o-ring to maintain the position of the compartments. The flow field was constructed using a gasket, a gas diffusion layer (GDL) made of carbon cloth, and the membrane, as shown in Figure 2. Polyurethane tubing was installed between the cell and external storage tanks using a diaphragm pump.

To test the redox flow battery, a single cell battery analyzer (TOB, CT4008) with multi-current range electronics load was used. The reactive area of the battery was 3.5x3.5 cm^2 and the flow rate was 300 mL/min. The tests were conducted at ambient temperature (around 25^{o}C). The charge-discharge behavior was evaluated at a constant current density of 10 mA/cm^2, with cut-off voltages set at 1 V and 0.01 V, respectively. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) were calculated. The polarization curves were determined using the constant current mode. The cell was first charged to obtain the open-circuit voltage (OCV), then discharged at a specific current and operating time. After the potential was recorded, the cell was recharged with the same current and operating time. This process was repeated, increasing the current until the cell potential reached the cut-off voltage at 0.1 V. The polarization curve and power density were measured. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) were calculated to assess the performance of the battery cell. The coulombic efficiency (CE) represents the proportion of electric charge transferred during discharge and charge. It can be calculated using the equation:

$$CE = \frac{I_d x t_d}{I_c x t_c} \quad (5)$$

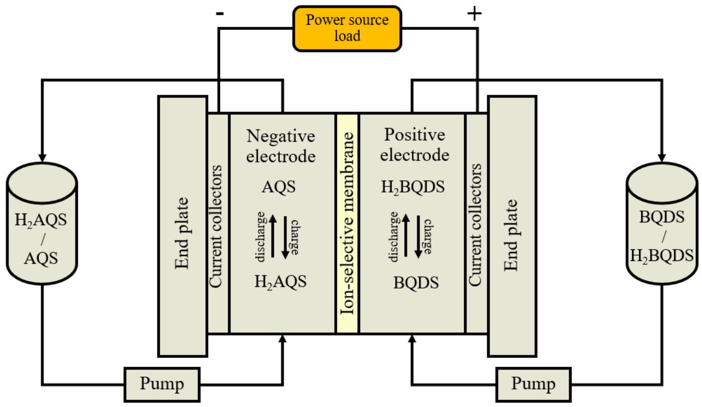


Figure 1. Schematic of the aqueous organic flow battery system

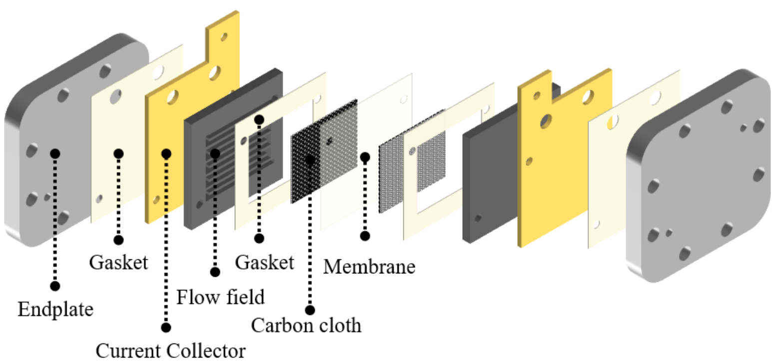


Figure 2. The components of the single battery cell

where, I_c and I_d are charging and discharging currents (A), t_c and t_d are the charging and discharging time(s), respectively.

The voltage efficiency (VE) is calculated by determining the average voltage generated during the discharge (V_d) and charge (V_c) processes. It is expressed as the ratio of the average discharge voltage to the average charge voltage, as shown in equation:

$$VE = \frac{\frac{\int_0^{t_d} V_d dt}{t_d}}{\frac{\int_0^{t_c} V_c dt}{t_c}} = \frac{\bar{V}_d}{\bar{V}_c} \tag{6}$$

where $\bar{V}_c$ and $\bar{V}_d$ are the voltages generated by charging and discharging (V), V¯_c and V¯_d are the average voltages during charging and discharging (V), respectively.

The energy efficiency (EE) represents the ratio of the energy output during discharge to the energy input during charge. It can be calculated by multiplying the coulombic efficiency (CE) by the voltage efficiency (VE), as shown in equation:

$$EE = \frac{I_d t_d \frac{\int_0^{t_d} V_d dt}{t_d}}{I_c t_c \frac{\int_0^{t_c} V_c dt}{t_c}} = CExVE \quad (7)$$

3. Results and Discussion

3.1. Physicochemical properties

The physicochemical properties of the SPEEK membranes and the Nafion117 membrane, including water uptake, swelling ratio, ion exchange capacity, and degree of sulfonation, are summarized in Table 1. The SPEEK membranes showed 25-52% higher water uptake than Nafion117, indicating better proton conductivity but less stability. Water uptake plays a significant role in proton conductivity, as it facilitates proton transport. Previous research [32] has shown that the optimal water uptake for both proton conductivity and stability is between 20% and 40%. Excess water uptake can lead to increased swelling, decreased mechanical and dimensional stability, and long-term performance issues. The water uptake of SPEEK membranes in this study was in the range of 19.15-23.69%, lower than the 38.00% and 35.67% achieved in previous studies using SPEEK membranes with DMF as a solvent [30, 34]. The lower water uptake may be due to inhomogeneous proton transport channels in the microstructure or differences in membrane thickness and water absorption.

Table 1. The physicochemical properties of SPEEK membranes with different polymer/solvent ratios

Membrane (%)	Thickness (nm)	Water Uptake (%)	Swelling Ratio (mmol/g)	IEC (%)	DS
Nafion117	187	15.70±2.30^{C}	9.94±1.68^{A}	1.01±0.25^{B}	-
SPEEK10	60	21.81±5.77^{A,B}	7.64±2.36^{B}	1.78±0.48^{A}	59.82
SPEEK15	60	19.15±2.13^{B,C}	6.82±1.21^{B}	1.50±0.21^{A,B}	49.21
SPEEK20	60	23.69±5.77^{A}	8.40±2.14^{B}	1.66±0.04^{A}	55.10

Note: A, B, and C mean data sets that do not share a letter are significantly different.

The SPEEK membranes had a swelling ratio (SR) in the range of 6.82-8.40%, significantly lower than that of Nafion117 by 14-27%. However, previous studies reported SR values of 13.60% [30] and 10.79% [34] for SPEEK membranes. The lower SR of the SPEEK membranes indicates higher mechanical stability during cell operation. Higher water uptake can lead to higher SR, resulting in a reduction in mechanical properties and decreased cell performance. The different SR values may be due to variations in membrane thickness, as in the case of the S-67 membrane (SPEEK with 67% DS), which had a similar water uptake, but lower SR compared to Nafion117 [30].

The ion exchange capacity (IEC) of the SPEEK membranes was in the range of 1.50-1.78 mmol/g, 48-76% higher than that of Nafion117. These results are consistent with previous reports of IEC values of 1.00-1.59 mmol/g [29, 30, 34] for SPEEK membranes, indicating sufficient ion exchange groups for proton transport as a functional ion exchange membrane in redox flow battery applications. The ionic transport capabilities of a membrane depend on the amount and type of ion exchange groups in the polymer structure. The difference between the SPEEK and Nafion membranes is the stronger acidity of ion exchange groups and the microstructure in the hydrated form. Generally, an increase in the IEC of a membrane leads to an increase in its ability to absorb more water, resulting in a transformation of the polymer into a hydrophilic form. This can improve cell performance but decrease membrane resistance and mechanical stability.

The degree of sulfonation (DS) of the SPEEK membranes was less than 60%, indicating that the proton conduction path may be composed of short, discontinuous channels, resulting in lower cell performance. This is consistent with the lower water uptake of the SPEEK membranes compared to other studies which reported DS values of 67% [30] and 52.62% [34] for SPEEK membranes. According to Winardi *et al*. [29], moisture contamination can significantly affect the DS of membranes. The properties of the SPEEK membrane may have been influenced by different experimental conditions. It is important to protect against moisture contamination. A DS range of 60%-80% is typically considered optimal for balancing mechanical properties and proton conductivity for long-term cell operation [24, 32].

Upon careful examination of the data in Table 1, several trends emerge when comparing SPEEK10, SPEEK15, and SPEEK20 membranes. The water uptake was observed to increase from SPEEK15 (19.15%) to SPEEK10 (21.81%), and then to SPEEK20 (23.69%). This suggests that the degree of sulfonation may influence water uptake. Moreover, the swelling ratio, which serves as an indicator of mechanical stability, decreases from SPEEK10 (7.64%) to SPEEK15 (6.82%), followed by a slight increase for SPEEK20 (8.40%). This trend, coupled with the fact that SPEEK15 has a lower water uptake than SPEEK10 and SPEEK20 but demonstrates the lowest swelling ratio, suggests a superior balance between water uptake and membrane cross-linking in SPEEK15. The ion exchange capacity, which is crucial for proton transport, was highest in SPEEK10 (1.78 mmol/g), was lower in SPEEK15 (1.50 mmol/g), and then showed a slight increase in SPEEK20 (1.66 mmol/g). This fluctuation points to a complex interplay between the degree of sulfonation, water uptake, and possibly membrane cross-linking. These observations highlight that controlling the degree of sulfonation significantly influences the water uptake, swelling ratio, and ion exchange capacity of SPEEK membranes. Interestingly, SPEEK15, with its lower degree of sulfonation, showed a balance in these properties, suggesting that a lower degree of sulfonation might be more beneficial for membrane stability. Future studies can focus on exploring these complex interactions and how they can be controlled to optimize SPEEK membrane performance. This could include varying the degree of cross-linking and investigating the impact of factors such as membrane porosity, surface roughness, and the balance between hydrophilic and hydrophobic properties on membrane performance.

3.2. Morphology

The physical characteristics of the SPEEK membranes were examined using scanning electron microscopy at 1000x magnification for surface morphology and 500x magnification for cross-section morphology. Figure 3 shows the dense surface morphology of the SPEEK membranes and displays SEM images of the cross-sectional area of SPEEK membranes with 60 µm thickness. It can be seen that the membrane thickness was less than that of the Nafion117, which had a thickness of 187 µm. The SPEEK20 membrane had the most homogeneous smoothness, indicating good

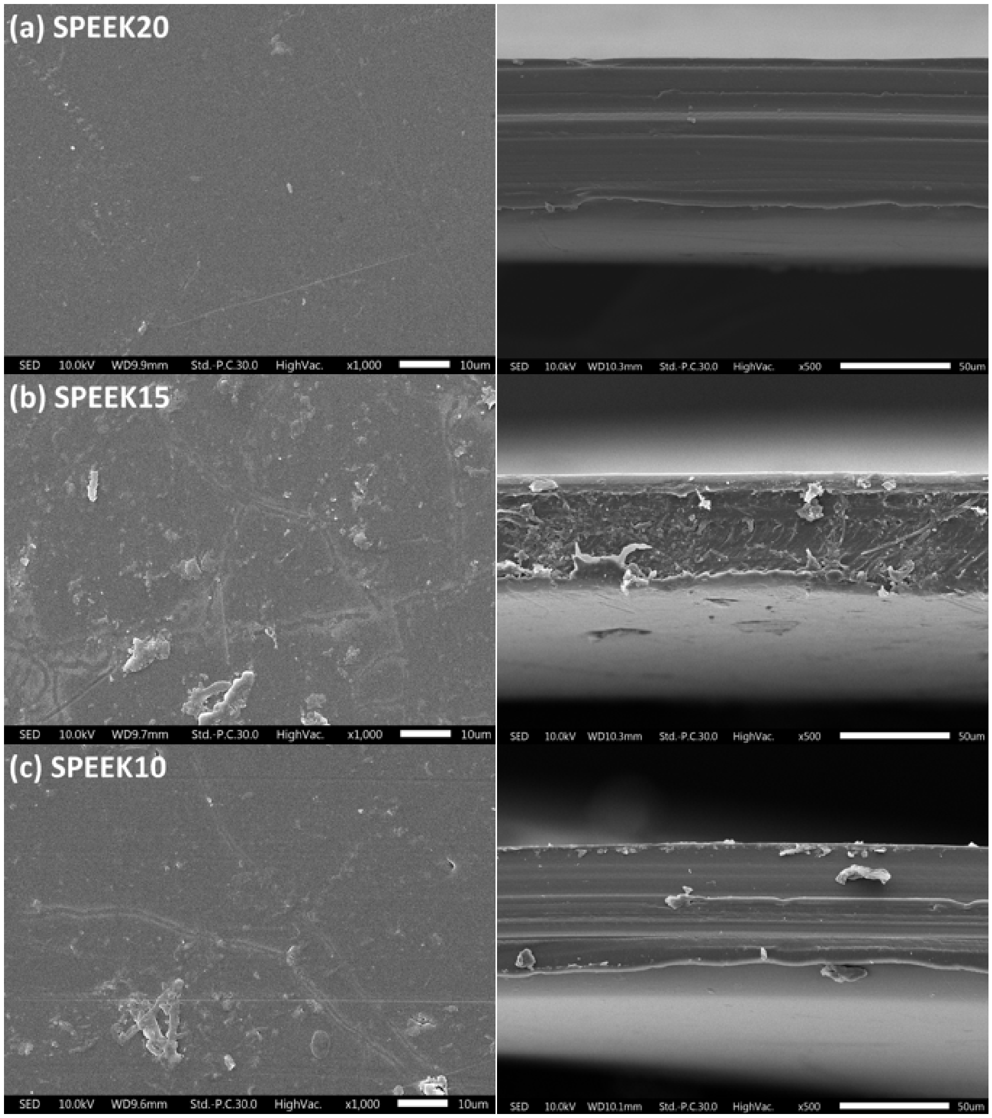


Figure 3. SEM images of the surface morphology (left) and cross-section morphology (right) of the (a) SPEEK20, (b) SPEEK15, and (c) SPEEK10, respectively

solubility and formability between SPEEK and solvent. This quality is beneficial for maintaining the integrity of the membrane and promoting stable operation of the battery. The SPEEK10 and SPEEK15 membranes were dense and non-porous with satisfactory smoothness. However, these membranes contained white fragments that had formed from PEEK polymers due to moisture contamination, which could potentially influence membrane performance. The morphology of the SPEEK membranes indicated that electrolyte leakage could be effectively prevented, making them suitable for use in redox flow battery applications.

3.3 Single-cell performance

Figure 4(a) shows the transformation of BQDS on the positive side during charging, before becoming a completely positive electrolyte. The coulombic efficiency (CE) reached up to 86% after the fourth cycle, which was lower than the 95-98% CE values reported by Intakhuen *et al*. [36] and Kakaen *et al*. [37] after around 20 cycles and the 95-99% CE reported by Zhang *et al*. [34]. The observed difference could be attributed to the absence of pre-treatment of the membranes in our study, which has been shown to impact CE positively. While our research primarily investigated the performance of non-pre-treated SPEEK membranes in AORFBs, it is worth noting that membrane pre-treatment could play a crucial role in improving coulombic and energy efficiency. Pre-treatment processes typically aim to boost ionic conductivity and selectivity by enhancing hydration and eliminating impurities. For instance, SPEEK membranes can be immersed in boiling water to amplify their hydrophilicity, thereby improving proton conductivity, and potentially, coulombic efficiency. Additionally, removing impurities might prevent the blockage of ionic channels, facilitating smoother ion transport. However, the choice of pre-treatment methods and conditions must be carefully optimized, as aggressive pre-treatment could lead to mechanical weakening or structural damage to the membrane. In any case, our study focused on the baseline performance of non-pre-treated SPEEK membranes. Figure 4(b) shows that the energy efficiency (EE) of the cell using SPEEK10, SPEEK15, and SPEEK20 membranes (38.56%, 39.44%, and 39.12%, respectively) was 5-6% higher than the cell with the Nafion membrane (33.11%). This indicates that the SPEEK membranes provided better performance in the AORFB, despite having virtually identical polymer/solvent ratios. In our study, the energy efficiency (EE) of SPEEK membranes demonstrated promising results. However, it was observed to be less than the EE values reported for SPEEK in previous studies [34] which ranged from 39.49% to 69.72% at 40-160 mA/cm^2. Similarly, the EE was documented to be 37.50% [36] and between 29.55% to 58.90% [37] when using Nafion117 with various electrodes. The lower values in our study could have been due to a relatively lower CE, and also possibly due to variations in experimental conditions, including the flow rate, electrolyte concentration, and electrode materials. It was reported that carbon cloth coated with an excessive amount of carbon black can have decreased efficiency due to a smaller reaction area and electrolyte transport pathway [37]. The energy efficiency (EE) of the redox flow battery depends on the physicochemical properties of the flow field and the electrochemical reactions of the electrolytes that occur on the flow field surface.

In Figure 4(c), SPEEK15 demonstrated that the highest average discharge capacity (0.349 Ah) was significantly different from that of Nafion which showed the lowest value. This indicates that the SPEEK15 membrane was able to support the highest level of battery discharge, contributing to greater battery performance. The average discharge capacities of the other membranes followed this sequence, from highest to lowest: SPEEK10 (0.340 Ah), SPEEK20 (0.335 Ah), and Nafion (0.321 Ah). On the other hand, the performances of SPEEK10 and SPEEK20 were not significantly different from any of the other membranes. This indicates that the discharge capacities of SPEEK10 and SPEEK20 fell within the performance range of the other membranes, and the differences observed were not statistically significant. From this, it is clear that SPEEK15 performed the best in terms of discharge capacity. This result is interesting as it could indicate a possible optimum SPEEK concentration for maximum discharge capacity of around 15%. However, this does not necessarily mean that SPEEK15 is the best overall membrane for AORFBs as other performance metrics such as ion conductivity, water uptake, chemical stability, and cost are also critical.

Moreover, the improved energy efficiency of the SPEEK membranes compared to Nafion117 could have been due to their optimal balance of water uptake, and mechanical and thermal stability. These characteristics enhance ionic conductivity, prevent self-discharge, and add

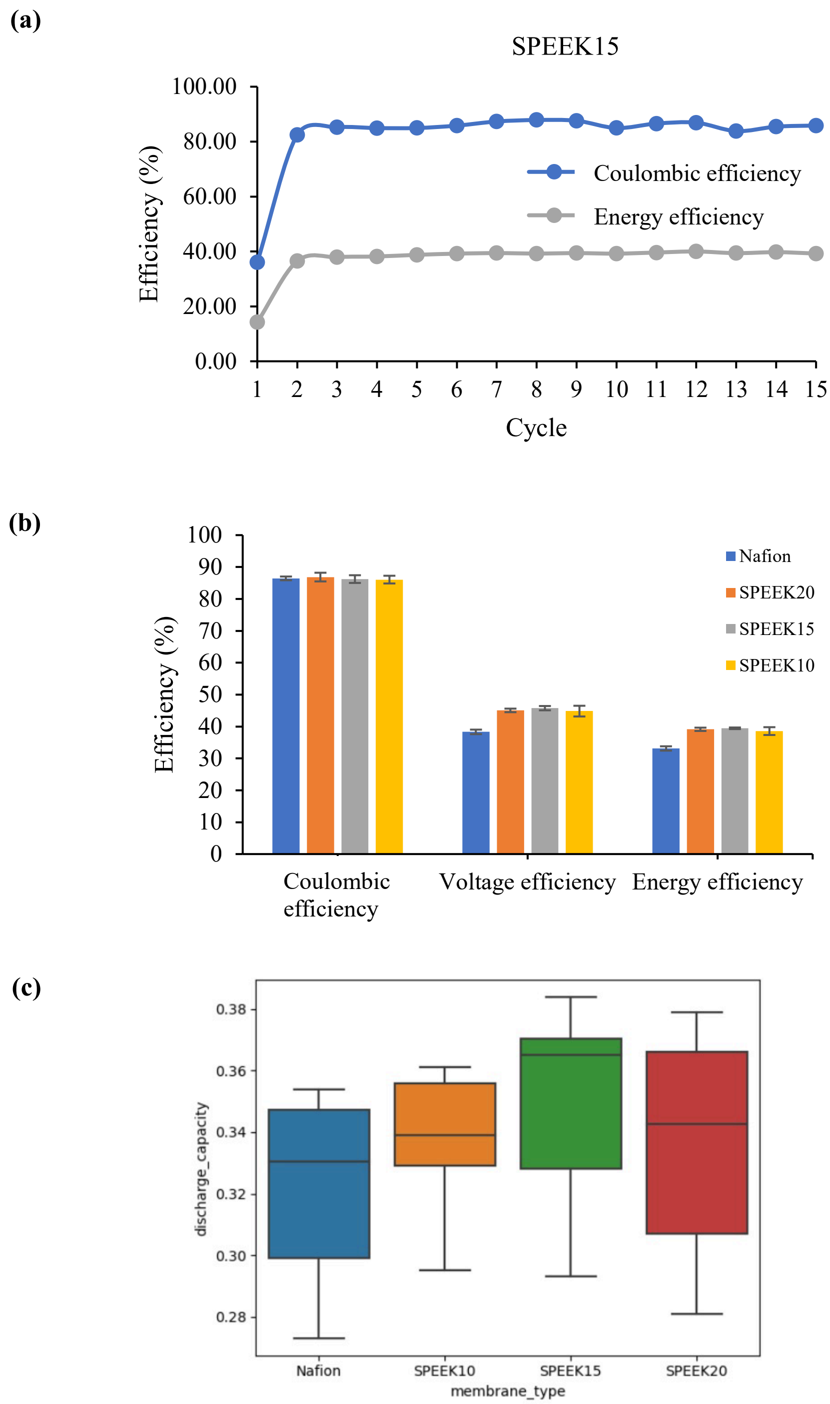


Figure 4. Single cell performance with difference membranes (a) Charge-discharge behavior of SPEEK15, (b) Coulombic, Voltage, and Energy efficiency and (c) Discharge capacity

to membrane durability, thus improving overall performance. As membrane thickness is a critical factor impacting these properties, control over this aspect during SPEEK membrane fabrication can lead to further enhancements in performance efficiency. It is also crucial to fine-tune membrane pre-treatment methods to maximize the coulombic efficiency of redox flow batteries.

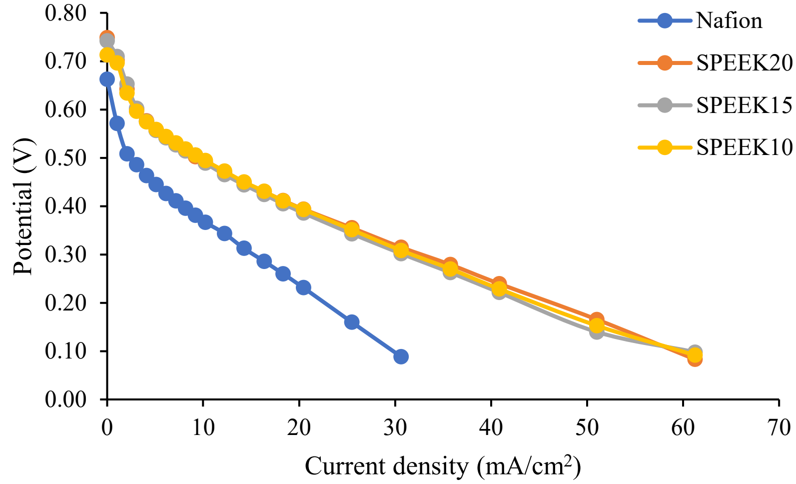
The polarization curve in Figure 5(a) showed the potential drop during the discharge process. Nafion membranes had a faster potential drop than SPEEK membranes, while the various SPEEK membranes had a similar drop rate. This indicates that the Nafion membranes have higher resistance to ionic flow due to their different thickness. The slope reflects both the operating resistance and the overall cell resistance. The SPEEK membranes clearly performed better, resulting in higher cell potential. In terms of the power density, as shown in Figure 5(b), our study found the SPEEK10, SPEEK15, and SPEEK20 membranes exhibited power densities of 8.34, 8.06, and 8.36 mW/cm^2, respectively, which were significantly higher than the Nafion at 4.22 mW/cm^2. This indicates that SPEEK membranes have higher charge/discharge performance and can distribute more current while maintaining a higher cell voltage. However, these values are lower than the power densities of 10.4 and 12.15 mW/cm^2 reported by Intakhuen *et al*. [36] and Kakaen et al. [37] both using Nafion 117. The lower power density in our study might have been due to the increased resistance during single-cell operation because of the non-pre-treated membrane, or potentially due to the reduction of the reactive area in the cell used in this study. Several factors can influence resistance during single-cell operation, including membrane properties, contact resistance, cell design and flow field, and operational conditions such as temperature and electrolyte concentration. Optimizing these factors could significantly enhance power density. For example, refining the membrane's physical characteristics, securing efficient contact between the membrane and electrodes, improving the cell and flow field design, and maintaining optimal operating conditions are potential strategies to reduce resistance and boost power density.

In terms of production costs, the SPEEK membrane has the advantage of being cost-effective and easy to fabricate. The cost of the SPEEK membrane in this study was calculated to be 67.95 USD/m^2 based on the market price of the chemicals and raw materials used in the lab. This is significantly lower than the cost of Nafion membrane at 2472.96 USD/m^2, as reported by Chang *et al.* [25]. The limitations of the SPEEK membrane in this study, such as lower performance compared to previous reports, may be due to moisture contamination during fabrication, different thickness, and lack of pre-treatment. These issues should be addressed for long-term and practical use.

4. Conclusions

In this study, SPEEK membranes for use in an AQS/BQDS redox flow batteries were fabricated with varying polymer/solvent ratios using a solution casting method. These membranes demonstrated remarkable characteristics compared to Nafion 117 in several aspects. For instance, they exhibited higher water uptake, ion exchange capacity, and a lower swelling ratio. Additionally, the SPEEK membranes featured smooth, non-porous surfaces, which made them suitable as ion exchange membranes in redox flow batteries. However, the degree of sulfonation in the SPEEK membranes was observed to be lower than optimum, and this was potentially due to factors such as moisture contamination during fabrication and differences in thickness. Addressing these issues in future studies should further improve the performance of SPEEK membranes. In the rate performance test, the SPEEK membranes achieved a coulombic efficiency of 86%, matching that of the Nafion membrane. Most notably, a cell with the SPEEK membrane achieved the highest energy efficiency of 39.44%, surpassing that of the Nafion in an AORFB cell. Furthermore, the

(a)



(b)

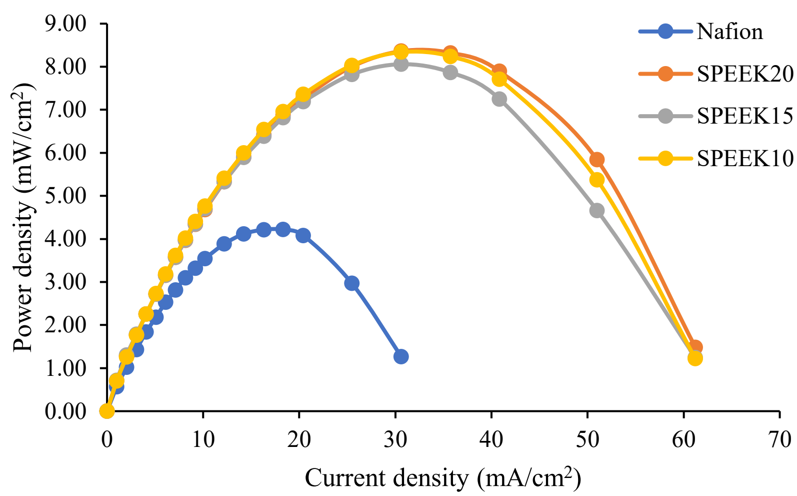


Figure 5. Single cell performance with difference membranes (a) Polarization curve and (b) Power density versus Current density

SPEEK membranes demonstrated superior power density, peaking at 8.36 mW/cm^2, compared to 4.22 mW/cm^2 for the Nafion in charge/discharge performance. The study's findings establish that, due to their high ion exchange capacity and compatibility with AQS/BQDS organic flow batteries, SPEEK membranes present a promising alternative to Nafion membranes for use in AORFBs.

Taking all factors into account, SPEEK15 appears to be the most optimal membrane in this work. While its energy efficiency was not significantly different from the other SPEEK membranes, it demonstrated the lowest water uptake and swelling ratio, indicating greater stability. Stability is critical in real-world applications of redox flow batteries, as they need to withstand long-term operation. Furthermore, the ion exchange capacity (IEC) of SPEEK15 fell within a comparable range to the other SPEEK membranes, indicating its good proton conductivity. This balance of properties - energy efficiency, stability, and good discharge capacity - suggests that SPEEK15 is the best-performing membrane among the ones studied. For future improvement of SPEEK membrane energy performance, strategies such as tuning the degree of sulfonation, incorporating composite materials, cross-linking, and conducting long-term stability tests could be considered. Notably, striking a balance between cross-linking and preserving ion conductivity is essential for achieving optimal performance. Future studies should also focus on the cost-effectiveness of these strategies, particularly for large-scale applications. These findings underline the promising potential of SPEEK membranes to replace Nafion in AORFBs, highlighting the effectiveness of the degree of sulfonation in enhancing the performance of redox flow batteries.

5. Acknowledgments

The authors acknowledge the Faculty of Engineering, Chiang Mai University, for financial support under a Research Assistant scholarship (RA); and the Graduate School of Chiang Mai University, for financial support under a Teacher Assistant and Research Assistant scholarship (TA/RA), respectively. This work was also partially supported by Chiang Mai University, Thailand and the Newton Fund, UK.

References

[1] Akinyele, D.O. and Rayudu, R.K., 2014. Review of energy storage technologies for sustainable power networks. *Sustainable Energy Technologies and Assessments*, 8, 74-91, https://doi.org/10.1016/j.seta.2014.07.004.

[2] Berger, M., Radu, D., Fonteneau, R., Henry, R., Glavic, M., Fettweis, X., Le Du, M., Panciatici, P., Balea, L. and Ernst, D., 2020. Critical time windows for renewable resource complementarity assessment. *Energy*, 198, https://doi.org/10.1016/j.energy.2020.117308.

[3] Groissböck, M. and Gusmão, A., 2020. Impact of renewable resource quality on security of supply with high shares of renewable energies. *Applied Energy*, 277, https://doi.org/10.1016/j.apenergy.2020.115567.

[4] Izadyar, N., Ong, H.C., Chong, W.T. and Leong, K.Y., 2016. Resource assessment of the renewable energy potential for a remote area: A review. *Renewable and Sustainable Energy Reviews*, 62, 908-923, https://doi.org/10.1016/j.rser.2016.05.005.

[5] Tarroja, B., Shaffer, B. P. and Samuelsen, S., 2018. Resource portfolio design considerations for materially-efficient planning of 100% renewable electricity systems. *Energy*, 157, 460-471, https://doi.org/10.1016/j.energy.2018.05.184.

[6] Saleem, M., 2022. Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source. *Heliyon*, 8 (2), https://doi.org/10.1016/j.heliyon.2022.e08905.

[7] Chalamala, B.R., Soundappan, T., Fisher, G.R., Anstey, M.R., Viswanathan, V.V. and Perry, M.L., 2014. Redox flow batteries: an engineering perspective. *Proceedings of the IEEE*, 102(6), 976-999, https://doi.org/10.1109/jproc.2014.2320317.

[8] Iwakiri, I., Antunes, T., Almeida, H., Sousa, J.P., Figueira, R.B. and Mendes, A., 2021. Redox Flow Batteries: Materials, Design and Prospects. *Energies*, 14(18), https://doi.org/10.3390/en14185643.

[9] Vanýsek, P. and Novák, V., 2017. Redox flow batteries as the means for energy storage. *Journal of Energy Storage*, 13, 435-441, https://doi.org/10.1016/j.est.2017.07.028.

[10] Choi, C., Noh, H., Kim, S., Kim, R., Lee, J., Heo, J. and Kim, H.-T., 2019. Understanding the redox reaction mechanism of vanadium electrolytes in all-vanadium redox flow batteries. *Journal of Energy Storage*, 21, 321-327, https://doi.org/10.1016/j.est.2018.11.002.
[11] Emmett, R.K. and Roberts, M.E., 2021. Recent developments in alternative aqueous redox flow batteries for grid-scale energy storage. *Journal of Power Sources*, 506, https://doi.org/10.1016/j.jpowsour.2021.230087.
[12] Lourenssen, K., Williams, J., Ahmadpour, F., Clemmer, R. and Tasnim, S., 2019. Vanadium redox flow batteries: A comprehensive review. *Journal of Energy Storage*, 25, https://doi.org/10.1016/j.est.2019.100844.
[13] Perry, M. L., Saraidaridis, J. D. and Darling, R. M., 2020. Crossover mitigation strategies for redox-flow batteries. *Current Opinion in Electrochemistry*, 21, 311-318, https://doi.org/10.1016/j.coelec.2020.03.024.
[14] Vinco, J.H., Domingos, A.E.E.d.C., Espinosa, D.C.R., Tenório, J.A.S. and Baltazar, M.d.P.G., 2021. Unfolding the Vanadium Redox Flow Batteries: An indeep perspective on its components and current operation challenges. *Journal of Energy Storage*, 43, https://doi.org/10.1016/j.est.2021.103180.
[15] Bamgbopa, M.O., Fetyan, A., Vagin, M., and Adelodun, A.A., 2022. Towards eco-friendly redox flow batteries with all bio-sourced cell components. *Journal of Energy Storage*, 50, https://doi.org/10.1016/j.est.2022.104352.
[16] Chen, R., 2020. Redox flow batteries for energy storage: Recent advances in using organic active materials. *Current Opinion in Electrochemistry*, 21, 40-45, https://doi.org/10.1016/j.coelec.2020.01.003.
[17] Leung, P., Shah, A.A., Sanz, L., Flox, C., Morante, J.R., Xu, Q., Mohamed, M.R., Ponce de León, C. and Walsh, F.C., 2017. Recent developments in organic redox flow batteries: A critical review. *Journal of Power Sources*, 360, 243-283, https://doi.org/10.1016/j.jpowsour.2017.05.057.
[18] Ruan, W., Mao, J. and Chen, Q., 2021. Redox flow batteries toward more soluble anthraquinone derivatives. *Current Opinion in Electrochemistry*, 29, https://doi.org/10.1016/j.coelec.2021.100748.
[19] Mao, J., Ruan, W. and Chen, Q., 2020. Understanding the aqueous solubility of anthraquinone sulfonate salts: The quest for high capacity electrolytes of redox flow batteries. *Journal of the Electrochemical Society*, 167(7), https://doi.org/10.1149/1945-7111/ab7550.
[20] Symons, P., 2021. Quinones for redox flow batteries. *Current Opinion in Electrochemistry*, 29, https://doi.org/10.1016/j.coelec.2021.100759.
[21] Xia, L., Huo, W., Gao, H., Zhang, H., Chu, F., Liu, H. and Tan, Z., 2021. Intramolecular hydrogen bonds induced high solubility for efficient and stable anthraquinone based neutral aqueous organic redox flow batteries. *Journal of Power Sources*, 498, https://doi.org/10.1016/j.jpowsour.2021.229896.
[22] Yang, B., Hoober-Burkhardt, L., Wang, F., Surya Prakash, G.K. and Narayanan, S.R., 2014. An inexpensive aqueous flow battery for large-scale electrical energy storage based on water-soluble organic redox couples. *Journal of the Electrochemical Society*, 161(9), A1371-A1380, https://doi.org/10.1149/2.1001409jes.
[23] Shi, Y., Eze, C., Xiong, B., He, W., Zhang, H., Lim, T.M., Ukil, A. and Zhao, J., 2019. Recent development of membrane for vanadium redox flow battery applications: A review. *Applied Energy*, 238, 202-224, https://doi.org/10.1016/j.apenergy.2018.12.087.
[24] Banerjee, S. and Kar, K.K., 2017. Impact of degree of sulfonation on microstructure, thermal, thermomechanical and physicochemical properties of sulfonated poly ether ether ketone. *Polymer*, 109, 176-186, https://doi.org/10.1016/j.polymer.2016.12.030.
[25] Chang, S., Ye, J., Zhou, W., Wu, C., Ding, M., Long, Y., Cheng, Y. and Jia, C., 2019. A low-cost SPEEK-K type membrane for neutral aqueous zinc-iron redox flow battery. *Surface and Coatings Technology*, 358, 190-194, https://doi.org/10.1016/j.surfcoat.2018.11.028.

[26] Khomein, P., Ketelaars, W., Lap, T. and Liu, G., 2021. Sulfonated aromatic polymer as a future proton exchange membrane: A review of sulfonation and crosslinking methods. *Renewable and Sustainable Energy Reviews*, 137, https://doi.org/10.1016/j.rser.2020.110471.

[27] Mohtar, S.S., Ismail, A.F. and Matsuura, T., 2011. Preparation and characterization of SPEEK/MMT-STA composite membrane for DMFC application. *Journal of Membrane Science*, 371(1-2), 10-19, https://doi.org/10.1016/j.memsci.2011.01.009.

[28] Parnian, M.J., Rowshanzamir, S. and Gashoul, F., 2017. Comprehensive investigation of physicochemical and electrochemical properties of sulfonated poly (ether ether ketone) membranes with different degrees of sulfonation for proton exchange membrane fuel cell applications. *Energy*, 125, 614-628, https://doi.org/10.1016/j.energy.2017.02.143.

[29] Winardi, S., Raghu, S.C., Oo, M.O., Yan, Q., Wai, N., Lim, T.M. and Skyllas-Kazacos, M., 2014. Sulfonated poly (ether ether ketone)-based proton exchange membranes for vanadium redox battery applications. *Journal of Membrane Science*, 450, 313-322, https://doi.org/10.1016/j.memsci.2013.09.024.

[30] Xi, J., Li, Z., Yu, L., Yin, B., Wang, L., Liu, L., Qiu, X. and Chen, L., 2015. Effect of degree of sulfonation and casting solvent on sulfonated poly (ether ether ketone) membrane for vanadium redox flow battery. *Journal of Power Sources*, 285, 195-204, https://doi.org/10.1016/j.jpowsour.2015.03.104.

[31] Ye, J., Cheng, Y., Sun, L., Ding, M., Wu, C., Yuan, D., Zhao, X., Xiang, C. and Jia, C., 2019. A green SPEEK/lignin composite membrane with high ion selectivity for vanadium redox flow battery. *Journal of Membrane Science*, 572, 110-118, https://doi.org/10.1016/j.memsci.2018.11.009.

[32] Yee, R.S., Zhang, K., and Ladewig, B.P., 2013. The effects of sulfonated poly (ether ether ketone) ion exchange preparation conditions on membrane properties. *Membranes (Basel)*, 3 (3), 182-95, https://doi.org/10.3390/membranes3030182.

[33] Zeng, L., Ye, J., Zhang, J., Liu, J. and Jia, C., 2019. A promising SPEEK/MCM composite membrane for highly efficient vanadium redox flow battery. *Surface and Coatings Technology*, 358, 167-172, https://doi.org/10.1016/j.surfcoat.2018.11.018.

[34] Zhang, L., Zhang, S., Li, E., Zhao, L. and Zhang, S., 2019. Sulfonated poly (ether ether ketone) membrane for quinone-based organic flow batteries. *Journal of Membrane Science*, 584, 246-253, https://doi.org/10.1016/j.memsci.2019.05.008.

[35] Jaafar, J., Ismail, A.F. and Matsuura, T., 2009. Preparation and barrier properties of SPEEK/Cloisite 15A®/TAP nanocomposite membrane for DMFC application. *Journal of Membrane Science*, 345(1-2), 119-127, https://doi.org/10.1016/j.memsci.2009.08.035.

[36] Intakhuen, L., Kakaen, W. and Punyawudho, K., 2020. Carbon catalysts, ionomer contents and operating conditions of an aqueous organic flow battery fabricated by a catalyst-coated membrane. *Journal of Energy Storage*, 30, https://doi.org/10.1016/j.est.2020.101472.

[37] Kakaen, W., Intakhuen, L., Siyasukh, A. and Punyawudho, K., 2021. The improvement of organic redox flow battery performance by spherical mesoporous carbon prepared by sol-gel polymerization in water-oil emulsification technique. *International Journal of Hydrogen Energy*, 46(9), 6448-6460, https://doi.org/10.1016/j.ijhydene.2020.11.149.