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Asymmetric supporting electrolyte strategy for electrolyte imbalance mitigation of organic redox flow batteries



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ABSTRACT

In alkaline quinone flow battery (AQFB) systems, the difference in the water amount between the anolyte and catholyte inevitably leads to water diffusion from the anolyte to the catholyte during operation, causing the volume imbalance issue. This volume imbalance results in the formation of salt in the anolyte, significantly hindering the long-term operation of AQFBs. To address this volume imbalance problem, a new operating strategy for AQFBs is proposed. By increasing the concentration of the supporting electrolyte (KOH) in the anolyte, it is possible to balance the water amount between the anolyte and the catholyte, thereby mitigating water diffusion. The effectiveness of this strategy in alleviating the volume imbalance was successfully demonstrated through both a three-dimensional AQFB model and experiments. Additionally, it was confirmed that this strategy can be applied under various operating currents and inlet flow rates.

1. Introduction

Over the last decades, a large number of efforts have been devoting to enable the critical transition of the conventional energy systems toward ones with a high portfolio of renewables such as wind and solar [1]. This necessitates the wide deployment of large-scale energy storage to migrate the fluctuations and intermittency in electricity production from renewables [2,3]. Redox flow batteries (RFBs) represent promising solutions for large-scale energy storage: their flexible capacity and energy configurations and long cycling lifespan allow them to maintain superior performance during repetitive charge-discharge cycles [4].

The first generation of RFBs that is usually metal based has encountered challenges in corrosivity [5,6], kinetics [7], materials cost [8], and particularly limited material resource [9]. To address these challenges, plenty of previous studies have focused on organic redox flow batteries (ORFBs) utilizing sustainable and abundant redox-active organic molecules [10]. Among legion flow battery techniques, quinone-based flow batteries utilizing an alkaline solution (short as alkaline quinone flow batteries, AQFBs), first proposed by Chen et al. in 2015, are of great interest because the quinone-based couples possess rapid redox kinetics, chemical tunability, and low cost [11,12]. Since then, many efforts have been devoted to this field. For example, the molecular designs of quinone-based couples were conducted to enhance their solubility or tune their reduction potential and further increase the batteries' energy density or power density [13,14]. Besides, kinds of economic and high-performance membranes were introduced to realize higher efficiency and lower batteries' cost for AQFBs [15]. In addition, new flow field designs were proposed to improve the performance of AQFBs particularly in terms of efficiencies [16,17].

Although the stability and cycling performance have been significantly enhanced over the last few years, operation of AQFBs remains challenging. Water migration is an important yet often overlooked challenge for enabling the long-term operation of RFB systems. Several previous studies reported that the preferential water transfer across the membrane was driven by multiple factors including osmotic pressure, hydraulic pressure, and the migration of charged species [18,19]. Therefore, many researchers primarily approached the problem from the engineering perspective otherwise through novel membrane material designs [20]. For example, Oh et al. studied the behavior of water transport through the membrane and volume imbalance during the operation of the VRFB [21]. Based on this research, we investigated the mitigation of volume imbalance in the VRFB through electrolyte rebalancing [22,23]. Poli et al. introduced a method to mitigate electrolyte concentration and volume imbalance in VRFBs by using a regeneration

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cell [24]. Chakraborty et al. proposed an approach for compensating ion migration by the addition of the extra solute to the catholyte to restrict water migration in zinc-iodide flow batteries [25]. Tan et al. further improved the cycling performance and significantly restricted water transfer in the selected RFB systems through the thickness optimization of the thin film composite membranes [26].

However, as far as we know, most of the above previous studies on the water migration through the membrane were served for conventional flow batteries, while less for ARFBs [21]. In particular, how the unique characteristics of AQFBs, such as the high viscosity of the electrolyte [27], the asymmetric chemical compositions of the positive and negative electrolyte [28], and the large molecular structure [29], simultaneously affect the water transfer behaviors have yet been deeply understood. And these characteristics are decisive factors in what specific methods should be taken to address the water transfer problem in AQFBs. Additionally, although some previous studies designed novel membrane materials to mitigate the impact of the water imbalance in AQFBs, the challenge of balancing battery performance and cost remained [30].

In the present study, the characteristics of water transmembrane in AQFBs are investigated, and a practical strategy for mitigating the water imbalance during the charge and discharge of the AQFB system is proposed. The net volumetric change of the electrolytes can result in the precipitation of redox species on the one side. These precipitates can deposit on the carbon felt, blocking the electrode and causing a rapid performance drop of the cell [31]. On the other side, it may lead to flooding of the electrolyte reservoir, resulting in operational difficulties and necessitating sophisticated water management in RFB systems [26]. Unlike VRFBs, AQFBs use different substances for the anolyte and catholyte, which means that electrolyte concentration and volume imbalance cannot be addressed through rebalancing electrolyte. Therefore, new operational strategies are required to mitigate volume imbalance during the operation of AQFBs. This study demonstrates that by varying the initial concentration of the supporting electrolyte in both the anolyte and catholyte, the electrolyte volume imbalance observed during long-term operation of the AQFB can be effectively mitigated. Additionally, simulations and experiments are performed under various inlet flow rates and operating current densities of the AQFB to validate the broad applicability of the proposed strategy. Last but not least, the proposed strategy has been shown to effectively mitigate electrolyte volume imbalance under various operating conditions (specifically, irrespective of applied current density or inlet flow rate) at a low cost.

2. Experimental details

2.1. Experimental setup

The experimental setup used in this study is shown in Fig. 1a, which consisted of an AQFB flow cell (Zhisheng Chemical, China), two peristaltic pumps (Cole Parmer Instrument Co., USA), two electrolyte tanks, and an electrochemical workstation (BioLogic, France). The AQFB flow cell used a Nafion® 212 proton exchange membrane (DuPont, USA) as a separator, and it was composed of two GF3 carbon felts (SGL Carbon, Germany) with the active area corresponding to 5 cm \times 5 cm and a thickness corresponding to 3.5 mm, as well as two current collectors. The cell dimensions are indicated in Table 1. The carbon felts used in the AQFB cell acted as porous electrodes, and gaskets were used to prevent the electrolyte leakage. Furthermore, to guarantee the effective contact among the various cell components, these elements were pressed together using two cell frames. This was achieved by applying a consistent clamping pressure of 45 kfg/cm². The compression ratio of the electrode was 87.5 %. Additionally, the two current collectors served as mediums to conduct electrons in the cell and complete the circuit. To avert electrolyte contamination due to the oxidation in the presence of air, nitrogen gas was introduced into the electrolyte reservoirs. The cell was then operated under the consistent and stable conditions, respectively, maintaining a temperature of 298.15 K.

2.2. Measurement of electrolyte imbalance

The electrolyte used in the experiments was prepared by directly manufacturing a supporting electrolyte solution to adjust its concentration. For the catholyte, 2.8 g of potassium hydroxide (KOH, purity \geq 85.5 %, Sinopharm Chemical Reagent Co., Ltd., China) and 8.44 g of potassium ferrocyanide (C₆FeK₄N₆, purity \geq 95.5 %, Shanghai Yuanye Bio-Technology Co., Ltd., China) were placed in a beaker, and distilled water was added up to 50 mL. As for the anolyte, 2.8 g of potassium

Table 1

Cell dimensions of AQFB components.

Symbols	Description	Value
t _E	Electrode thickness	3.5 mm
t _M	Membrane thickness	50.8 µm
t_C	Current collector thickness	2.5 mm
L	Electrode length	5 cm
W	Electrode width	5 cm
Α	Active area	$5~\text{cm}\times5~\text{cm}=25~\text{cm}^2$



Fig. 1. (a) Experimental setup of the AQFB system for the electrolyte volume imbalance measurements; and (b) mesh configuration of the AQFB single-cell geometry along with relevant cell dimensions.

hydroxide and 2.4 g of 2,6-Dihydroxyanthraquinone (C₁₆H₈O₄, purity ≥95.51 %, Leyan, China) were placed in a beaker, and distilled water was added up to 50 mL to produce an electrolyte solution. The electrolyte concentrations are listed in Table 2. In the following sections, these conditions at the mentioned concentrations will be referred to as Case KOH 1 M. In Case KOH 1 M, the AQFB cell was charged up to a cell voltage of 1.4 V and then discharged down to 1.0 V to avoid side reactions. The electrolyte volumes after a total of 10 cycles were measured under a current density of $i_{op} = 40$ mA/cm² and various flow rate of Q = 30, 45, 60 mL/min, respectively.

Considering that volume balance increases proportionally with operating time (that is, at low current densities, the operating time increases, while conversely, at high current densities, the operating time decreases), different charge-discharge cycles were applied in this study to examine the effects of the current density. To be specific, the electrolyte volume was measured after 5 cycles at the current density of $i_{op} = 20 \text{ mA/cm}^2$ and after 15 cycles at the current density of $i_{op} = 60 \text{ mA/cm}^2$, respectively.

To alleviate volume imbalance of the electrolyte, it is essential to decrease the water amount in the anolyte. To achieve a reduction in the water amount by increasing the amount of KOH in the anolyte, the following method was employed for the electrolyte preparation. Initially, 5.6 g of potassium hydroxide and 2.4 g of 2,6-dihydroxyanthraquinone were added to a beaker, and distilled water was added up to 50 mL to prepare an anolyte with the concentrations as listed in Table 2. In the following sections, these conditions at the mentioned concentrations will be referred to as Case KOH 2 M. The catholyte was prepared with the same concentration as that in Case KOH 1 M (pristine electrolytes). Subsequently, experiments were conducted under various flow rates and current densities as described in the previous experimental subsection, and the volume imbalance was measured accordingly. Prior to the start of the experiment, the electrolyte was filled inside the cell and tubes to ensure the smooth measurement of the volume imbalance. And 50 mL of anolyte and catholyte, respectively, were separately filled in two tanks, which were then connected to the flow cell for the experiment. The beaker has a measurement error of ± 1 mL, and the volumes of the electrolyte were measured before and after the charge and discharge cycles. Consequently, there is a possibility of an error of up to 1 mL during the measurement of the electrolyte volume.

3. AQFB model description

The three-dimensional, non-isothermal AQFB model has been developed based on the principles of conservation of mass and momentum. Furthermore, the present study incorporates the redox

Table 2

Operating conditions of AQFB model.

1 0	-	
Symbols	Description	Value
$C^{0}_{Fe(CN)_{6}^{4-}}$	Initial concentration of $Fe(CN)_6^{4-}$	0.36 mol/L
$C^{0}_{Fe(CN)_{6}^{3-}}$	Initial concentration of $Fe(CN)_6^{3-}$	0.04 mol/L
$C_{2.6-DHAQ}^0$	Initial concentration of $2, 6 - DHAQ$	0.18 mol/L
$C_{2.6-reDHAQ}^0$	Initial concentration of $2,6 - reDHAQ$	0.02 mol/L
$C_{KOH}^{0,cat}$	Initial catholyte concentration of KOH	1 mol/L in Case KOH 1 M 1 mol/L in Case KOH 2 M
$C_{KOH}^{0,ano}$	Initial anolyte concentration of KOH	1 mol/L in Case KOH 1 M 2 mol/L in Case KOH 2 M
$C_{Water}^{0,cat}$	Initial catholyte concentration of water	50.34 mol/L in Case KOH 1 M 50.34 mol/L in Case KOH 2 M
$C_{Water}^{0,ano}$	Initial anolyte concentration of water	52.22 mol/L in Case KOH 1 M 50.89 mol/L in Case KOH 2 M
i _{op}	Operating current density	20, 40, 60 mol/L
Q	Flow rate of inlet	30, 45, 60 mol/L

reactions of chemical species to explain the performance of the AQFB. It also includes the diffusion of water through the membrane and the electro-osmotic drag of water via potassium ion flux to describe the changes in the electrolyte volume.

3.1. Model assumptions

The assumptions made in the model are as follows:

- 1) Due to the relatively low pressure and flow velocities (maximum velocity 5.51×10^{-3} m/s), the electrolyte flow is considered laminar and incompressible.
- 2) Additional side reactions such as gas reactions are ignored.
- 3) The electrolyte is considered to be a dilute solution, and therefore interactions between ions within the electrolyte are neglected.
- 4) Mass transport within the AQFB cell is assumed to be isotropic.

3.2. Redox reaction and equations

The redox reactions occur at both electrodes, and can be expressed as follows.

Negative electrode:

$$2, 6 - DHAQ + 2e^{-} \stackrel{\text{charge}}{\Rightarrow} _{\text{discharge}} 2, 6 - \text{reDHAQ } E_{0,\text{PE}} = -0.33V \qquad (1)$$
Positive electrode:

$$\operatorname{Fe}(\operatorname{CN})_{6}^{4-} - \operatorname{e}^{- \stackrel{\operatorname{charge}}{\rightleftharpoons}}_{\operatorname{discharge}} \operatorname{Fe}(\operatorname{CN})_{6}^{3-} \operatorname{E}_{0,\operatorname{PE}} = 0.77 \mathrm{V}$$
 (2)

Eqs. (1) and (2) for the half-cell reaction involve the volumetric current density, denoted as j, which can be expressed using the standard Butler-Volmer equation. Eqs. (3) and (4) represent the volumetric current density of the electrochemical reactions at the negative and positive electrode, respectively.

For the negative electrode:

$$j_{NE} = aFk_{NE} \left(\frac{C_{2,6-reDHAQ}^{e}}{C_{2,6-DHAQ}^{e}} \right)^{1-2\alpha_{NE}} \left[C_{2,6-reDHAQ}^{s} e^{\frac{(1-\alpha_{NE})F}{RT}} \eta_{NE} - C_{2,6-DHAQ}^{s} e^{\frac{-\alpha_{NE}F}{RT}} \eta_{NE} \right]$$
(3)

For the positive electrode:

$$j_{PE} = aFk_{PE} \left(\frac{C_{Fe(CN)_{6}^{4-}}}{C_{Fe(CN)_{6}^{3-}}^{e}}\right)^{1-2\alpha_{PE}} \left[C_{Fe(CN)_{6}^{4}}^{s} e^{\frac{(1-\alpha_{PE})F}{RT}} \eta_{PE} - C_{Fe(CN)_{6}^{3-}}^{s} e^{\frac{-\alpha_{PE}F}{RT}} \eta_{PE}\right]$$

$$(4)$$

where, *a* denotes the electrochemical specific surface area per unit volume within the electrode $[m^2/m^3]$; *F* denotes the Faraday constant (equals 96,485 [C/mol]); k_i denotes the rate constant at the negative and positive electrode [m/s]; C_i^e denotes the bulk concentration of species *i* within the electrolyte $[mol/m^3]$; C_i^s denotes the surface concentration of species *i* at the interface between the electrolyte and electrode $[mol/m^3]$; $a_{\rm NE}$ and $a_{\rm PE}$ denotes the transfer coefficient at the negative and positive electrode, respectively; *R* denotes the universal gas constant (equals 8.314 [J/mol·K]); *T* denotes the temperature of the AQFB cell [K]; and $\eta_{\rm NE}$ and $\eta_{\rm PE}$ denotes the overpotential of the cell at the negative and positive electrode [V], respectively.

The concentration difference between C_i^e and C_i^s primarily arises due to the redox reaction of species *i* occurring at the electrode surface. The relationship between C_i^e and C_i^s can be further elaborated in Eqs. (5) and (6) as follows [32]:

For the charged species (2,6-*reDHAQ* or $Fe(CN)_6^{3-}$):

$$FD_{ch}\frac{C_{ch}^{e}-C_{ch}^{s}}{r_{p}}=Fk\left(\frac{C_{dch}^{e}}{C_{ch}^{e}}\right)^{1-2\alpha}\left[C_{ch}^{s}e^{\frac{(1-\alpha)F}{RT}\eta}-C_{dch}^{s}e^{\frac{-\alpha F}{RT}\eta}\right]$$
(5)

For the discharged species (2,6-*DHAQ* or $Fe(CN)_6^{4-}$):

$$FD_{dch}\frac{C_{dch}^{e} - C_{dch}^{s}}{r_{p}} = Fk \left(\frac{C_{dch}^{e}}{C_{ch}^{e}}\right)^{1-2\alpha} \left[C_{dch}^{s} e^{\frac{-\alpha F}{RT}}\eta - C_{ch}^{s} e^{\frac{(1-\alpha)F}{RT}}\eta\right]$$
(6)

where, *D* denotes the diffusion coefficient $[m^2/s]$; *ch* denotes the charged species; *dch* denotes the discharged species; *r_p* denotes the pore radius at the electrode [m]; and the other parameters are as defined above.

The overpotential, denotes as η , in Eqs. (3) to (6), arises from the half-cell reactions occurring at the electrode. It can be expressed as follows:

$$\eta = \phi_s - \phi_e - E_i \tag{7}$$

where, ϕ_s denotes the potential of the electronic [V]; ϕ_e denotes the potential of the electrolyte [V]; E_i denotes the equilibrium potential of the electrode [V], which can be expressed using the Nernst equation based on the half-cell reactions described in Eqs. (1) and (2), as follows:

For the negative electrode:

$$E_{NE} = E_{NE,0} + \frac{RT}{F} ln \left(\frac{C_{2,6-reDHAQ}^{e}}{C_{2,6-DHAQ}^{e}} \right)$$
(8)

For the positive electrode:

$$E_{PE} = E_{PE,0} + \frac{RT}{F} ln \left(\frac{C_{Fe(CN)_{6}^{4}}}{C_{Fe(CN)_{6}^{3}}} \right)$$
(9)

where, $E_{i,0}$ denotes the standard potential of the reactions at the electrode [V]; and the other parameters are as defined above.

3.3. Conservation equations

The AQFB model is developed based on four principles related to the conservation of mass, momentum, species, and charge. It is described as follows:

Mass conservation:

$$\frac{\partial \varepsilon \rho}{\partial t} + \nabla \cdot (\rho \, \vec{u}) = 0 \tag{10}$$

Momentum conservation:

$$\frac{1}{\epsilon} \frac{\partial \rho \vec{u}}{\partial t} + \frac{1}{\epsilon^2} \nabla \cdot (\rho \vec{u} \vec{u}) = -\nabla P + \nabla \cdot \tau + \rho \vec{g} + S_u$$
(11)

where, ε denotes the electrode porosity; ρ denotes the density of the electrolyte [kg/m³]; \vec{u} denotes the electrolyte velocity [m/s]; *P* denotes the pressure of the electrolyte [Pa]; τ denotes the viscous shear stress [N/m²]; *g* denotes the gravity acceleration [m²/s]; and *S*_u denotes the source term of the momentum conservation.

The density of the electrolyte denotes as ρ , In Eqs. (10) and (11), can be further elaborated as follows:

$$\rho = \sum_{i} \rho_i \cdot \nu f_i = \sum_{i} C_i \cdot M_i \tag{12}$$

where, ρ_i denotes the density of the species *i* [kg/m³]; vf_i denotes the volume fraction of species *i*; C_i denotes the molar concentration of the species *i* [mol/m³]; and M_i denotes the molecular weight of the species *i* [kg/mol].

To represent the flow of the electrolyte within a porous electrode, the source term can be expressed using Darcy's law as follows [33]:

$$S_u = -\left(\frac{\mu}{K}\right)\vec{u} \tag{13}$$

where, μ denotes the dynamic viscosity of the electrolyte [kg/m•s], and the other parameters are as defined above.

In Eq. (13), the effective permeability *K* is determined using the Kozeny-Carman equation as follows [34]:

$$\zeta = \frac{4r_{PM}^2}{C_{KC}} \frac{\varepsilon^3}{(1-\varepsilon)^2}$$
(14)

where, C_{KC} denotes Kozeny-Carman constant (equals 180), and the other parameters are as defined above.

Species conservation:

ŀ

$$\frac{\partial(\varepsilon C_i)}{\partial t} + \nabla \cdot \overrightarrow{N_i} = S_i \tag{15}$$

In Eq. (15), $\overline{N_i}$ represents the flux of species *i*, considering diffusion, migration, and convection, and it is expressed as follows:

$$\vec{N_i} = -D_i^{eff} \nabla C_i - \frac{z_i F}{RT} D_i^{eff} C_i \nabla \phi_e + \vec{u} C_i$$
(16)

where, z_i denotes the valence for species *i*, and the other parameters are as defined above.

In Eq. (16), the effective diffusion coefficient of species *i* within the porous electrode, D_i^{eff} , takes into account the porosity and tortuosity effects using the Bruggeman correlation, and it is expressed as follows [35]:

$$D_i^{eff} = \varepsilon^{\tau} D_i \tag{17}$$

Charge conservation:

$$\nabla \cdot \vec{i}_e = S_\phi \tag{18}$$

$$\nabla \cdot \vec{i}_s = -S_\phi \tag{19}$$

In Eqs. (18) and (19), \vec{i}_e and \vec{i}_s represent the flux of electrolyte ions and electronic, respectively, and they are expressed as follows:

$$\vec{i}_{e} = \sum_{i} \left(-z_{i} F D_{i}^{eff} \nabla C_{i} - \frac{z_{i}^{2} F^{2}}{RT} D_{i}^{eff} C_{i} \nabla \phi_{e} + z_{i} F \vec{u} C_{i} \right)$$
(20)

$$\vec{i}_s = \sigma^{eff} \nabla \phi_s \tag{21}$$

where parameters are as defined above.

In Eq. (21), σ^{eff} represents the effective electronic conductivity of various components in the AQFB. The electrode is considered as a porous region, and therefore the Bruggeman correlation is used as follows [35]:

$$\sigma^{eff} = \begin{cases} (1-\varepsilon)^{3/2} \sigma_s, \text{Prous electrodes} \\ \sigma_{cc}, \text{Current collectors} \end{cases}$$
(22)

3.4. Water transport equations

In this study, to explain the electrolyte volume imbalance between the anolyte and the catholyte, the governing equation for water has been derived as follows:

$$\frac{\partial(\varepsilon C_w)}{\partial t} + \nabla \cdot \left(-D_w^{eff} \nabla C_w + \overrightarrow{u} C_w \right) = S_w$$
(23)

where parameters are as defined above.

In Eq. (23), the source term S_w for water considers the transport of water due to electro-osmotic drag (EOD). In the charging/discharging process, according to the charge conservation, potassium ions move from the catholyte to the anolyte during charging and from the anolyte

to the catholyte during discharging. This transport of potassium ions induces the transport of water through the membrane. The source term for water related to the electro-osmotic drag can be expressed as follows [36]:

$$\mathbf{S}_{\mathrm{w}}^{\mathrm{EOD}} = -\frac{\nabla \cdot \left(n_{d} \, i\right)}{F} \tag{24}$$

where, n_d denotes the EOD coefficient; \vec{i} denotes the operating current density [A/m²]; and the other parameters are as defined above.

3.5. Boundary conditions and numerical implementations

The three-dimensional, transient AQFB numerical model was implemented using the COMSOL® Multiphysics software in this study. The computational domain and meshes were generated based on a laboratory-scale cell with an active cross-sectional area of 25 m², and a detailed schematic representation of this is shown in Fig. 1. Table 3 provides physical properties of its components. In the computational geometry, the no-slip and impermeable velocity condition were applied to all external walls except for the inlet and outlet regions of the electrodes. The inlet velocity u_{in} of the catholyte and anolyte was calculated using the given volumetric flow rate Q_{pump} of the pump as follows:

$$u_{in} = \frac{Q_{\text{pump}}}{eA_{in}} \tag{25}$$

where, Q_{pump} denotes the volumetric flow rate $[m^3/s]$; A_{in} denotes the inlet area $[m^2]$; and the other parameters are as defined above.

The electrolyte within the tanks is circulated using a pump, and the molar concentration and electrolyte volume within the tanks continuously change over time. Molar quantity of species $i(N_i^{tank})$ in each tank are calculated based on overall mass as follows:

$$\frac{\partial N_i^{\text{tank}}}{\partial t} = Q_{\text{pump}} \left(C_{i,out}^{cell} - C_{i,in}^{cell} \right)$$
(26)

where, $C_{i,out}^{cell}$ denotes the outlet concentration of the species *i* [mol/m³];

Table	3
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The properties of AQFB model.

Symbols	Description	Value	Ref.
n_d	EOD coefficient	5.6	[37]
D_{K^+}	K^+ diffusivity in the electrode	1.96×10^{-9}	[<mark>38</mark>]
		$m^2 \cdot s^{-1}$	
D_{OH^-}	OH ⁻ diffusivity in the electrode	$5.27 imes10^{-9}$	[38]
		$m^2 \cdot s^{-1}$	
$D_{2,6-DHAQ}$	2,6 - DHAQ diffusivity in the electrode	4.8×10^{-10}	[11]
_		$m^2 \cdot s^{-1}$	
$D_{2,6-reDHAQ}$	2,6 – <i>reDHAQ</i> diffusivity in the	4.8×10^{-10}	[11]
	electrode	m ² ·s ⁻¹	50.03
$D_{Fe(CN)_6^{4-}}$	$Fe(CN)_6^{4-}$ diffusivity in the electrode	6.89×10^{-10}	[39]
D	- / 3	$m \cdot s = 10^{-10}$	F007
$D_{Fe(CN)_6^{3-}}$	$Fe(CN)_6^{3-}$ diffusivity in the electrode	7.2×10 $m^2 c^{-1}$	[39]
~	Electronic conductivity of the electrode	$500 \text{ s} \text{ m}^{-1}$	[22]
σ_E	Electronic conductivity of the current	$1000 \text{ S} \text{m}^{-1}$	[32]
00	collector	1000 3.111	[40]
r_{n}	Pore radius of the electrode	$5 imes 10^{-6} ext{ m}$	[40]
ĸ	Kozeny-Carman constant: porous	180	[34]
	electrode		
k_{PE}	Rate constant at the positive electrode	$1\times 10^{-7}\ m{\cdot}s^{-1}$	[41]
k_{NE}	Rate constant at the negative electrode	$7\times 10^{-7}\ m{\cdot}s^{-1}$	[11]
а	Effective area/unit electrode volume	$3.5\times10^4~m^{-1}$	[40]
α_{PE}	Transfer coefficient in the positive	0.5	[41]
	electrode		
α_{NE}	Transfer coefficient in the negative	0.5	[11]
	electrode		
μ_{NE}	Dynamic viscosity of the anolyte	$1.17 imes10^{-3}$ Pa·s	[11]
μ_{PE}	Dynamic viscosity of the catholyte	$1.09 imes 10^{-3}$ Pa·s	[42]

 $C_{i,in}^{cell}$ denotes the inlet concentration of the species *i* [mol/m³]; and the other parameters are as defined above.

The volume of the electrolyte in the tank is expressed using a formula that assumes a dilute solution. The concentration of active specie *i* varies based on the volume of the corresponding electrolyte as follows:

$$\frac{\partial V^{\text{tank}}}{\partial t} = M_w \frac{Q_{\text{pump}}}{\rho_w} \left(C_{w,out}^{cell} - C_{w,in}^{cell} \right)$$
(27)

$$C_i^{\text{tank}} = \frac{N_i^{\text{tank}}}{V^{\text{tank}}} \tag{28}$$

where parameters are as defined above.

The AQFB cell was simulated to be charged/discharged under a galvanostatic mode, and the following conditions were applied to the side walls during the charge/discharge process.

$$-\sigma^{eff} \nabla \phi_{s} \cdot \vec{n} = \begin{cases} -i_{op} / A_{cc}(during \ discharge) \\ i_{op} / A_{cc}(during \ charge) \end{cases}$$
(29)

where, i_{op} denotes the operating current [A]; A_{CC} denotes the area of the current collector; and the other parameters are as defined above.

In Eq. (29), i_{op} represents the operating current. To ensure efficient and convergent solutions, the convergence criteria for the simulations were set with maximum residual magnitudes below 10^{-6} , and imbalances <0.01 % for mass and <1 % for energy.

The validity analysis to the AQFB model was provided in Section 4.1, where the voltage profiles obtained via simulations were compared against those via experiments (see Fig. 2). The total number of cells applied in the simulation was 3500. The grid independence tests were conducted for 7000 cells and 17,920 cells, and confirmed that the errors associated with voltage over time and volume changes of the anolyte and catholyte were within 1 % with respect to the applied grid.

4. Results and discussion

This study involves conducting AQFB experiments and simulations under different charging/discharging current densities and flow rates. The objective is to identify a major challenge in AQFB's operation, specifically the issue of the volume imbalance of the catholyte and the anolyte, and explore potential solutions. To uncover the cause of the volume imbalance and apply an appropriate operating strategy, the transport behavior of water inside the AQFB was simulated, and the obtained results were validated against experimental results (Section 4.1). In order to suppress the electrolyte volume imbalance, a strategy that applys asymmetric supporting electrolyte concentrations to the anolyte and the catholyte was devised and both simulative and experimental studies involving multiple charge/discharge cycles were conducted to verify the effectiveness of the proposed strategy (Section 4.2). Moreover, this strategy is confirmed through simulations and experiments to effectively mitigate electrolyte volume imbalance under various operating conditions (current densities and inlet flow rates) (Section 4.3). Last, the practicability and effectiveness of the proposed strategy is addressed in Section 4.4.

4.1. Electrolyte volume imbalance issue

The changes in the initial electrolyte volume (50 mL) can be observed at various charging/discharging current densities and flow rates. Fig. 2 shows the changes in the electrolyte volume and voltage during 10 cycles at a flow rate of Q = 45 mL/min and an operating current density of $i_{op} = 40$ mA/m², for Case KOH 1 M with varying symmetric supporting electrolyte concentrations (i.e., different amount of water). First, the simulation and experimental results regarding cell's voltage (Fig. 2c) and the volume change of the electrolytes (Fig. 2a and b) showed a good agreement. In this figure, it can be observed that when the symmetric supporting electrolyte is applied in the anolyte and



Fig. 2. Comparison of the electrolyte volume change and voltage profiles through experiments and simulations under the current density of $i_{op} = 40 \text{ mA/m}^2$ and the flow rate of Q = 45 mL/min after 10 cycles: (a) experimental results; (b) simulation results; (c) voltage profiles in the Case KOH 1 M; (d) experimental results; (e) simulation results; (f) voltage profiles in the Case KOH 2 M.

catholyte, water continuously diffuses across the membrane from the anolyte to the catholyte during charging and discharging, resulting in significant electrolyte volume changes after 10 cycles. The experimental results show a volume change of 4 \pm 1 mL in the catholyte and - 4 \pm 1 mL in the anolyte. Similarly, the simulation results indicate a volume change of 5.15 mL in the catholyte and - 5.15 mL in the anolyte (Fig. 2a and b).

The transport of water is further broken down into the EOD-driven

and diffusion driven parts (see Section 3.5). As shown in Fig. 3a and b, the water transmembrane transport due to EOD is almost negligible in terms of the volume imbalance between the positive and negative sides, as it is offset during the charging and discharging processes. Due to the initial higher water amount in the anolyte compared to that in the catholyte, water continuously diffuses from the negative to the positive side (Fig. 3a and b), until the water amount in the two electrolytes becomes equivalent (as indicated by the gradually reduced water



Fig. 3. The water mole flux through the membrane and reactant concentrations in the Case KOH 1 M, current density of $i_{op} = 40 \text{ mA/m}^2$, and flow rate of $Q = 45 \text{ mL/m}^2$ min during 10 cycles: (a) the water mole flux; (b) the water mole flux by diffusion. The reactant concentration: (c) $C_{2,6-reDHAQ}^e + C_{2,6-DHAQ}^e$; (d) $C_{Fe(CN)_{6}^{+}}^e + C_{Fe(CN)_{6}^{+}}^e + C_$

transmembrane flux). However, prior to the cessation of water diffusion, a substantial electrolyte volume imbalance can arise, resulting in a significant decrease of volume in the negative side and, conversely, a considerable increase of volume in the positive side. As the total molar quantity of chemical species remains constant, the reduction in the electrolyte volume leads to an elevation in the concentration of active species in the negative side. Consequently, this may give rise to the formation of salts in the negative side, leading to a decrease in the storage capacity of the AQFB and an associated increase in the inlet pressure. On the contrary, the increase of the volume reduces the concentration of active species in the positive side, potentially contributing to an escalation in the mass transport losses of active species [12]. Hence, the mitigation of the electrolyte volume imbalance is of paramount importance. As a result, it is also observed that the concentration of anolyte reactants continues to increase, while the concentration of catholyte reactants continues to decrease over time (Fig. 3c and d).

4.2. Impacts of asymmetric supporting electrolyte

The issue of the electrolyte volume imbalance in alkaline quinone flow batteries arises from the uneven diffusion of water due to the disparity in water amounts between the anolyte and the catholyte. Therefore, this study proposes a strategy to mitigate water diffusion by varying the concentration of KOH in the electrolytes of the catholyte and anolyte, aiming to achieve similar water amounts. When the same KOH concentration of 1 M is applied to the anolyte and the catholyte, the anolyte exhibits a higher water amount. Therefore, in order to achieve a more balanced water amount between the catholyte and the anolyte, it is necessary to increase the KOH concentration in the analyte. By setting the KOH concentration in the catholyte to 1 M and the KOH concentration in the anolyte to 2 M (Case KOH 2 M), it has been observed that the water amount in both electrolytes becomes more similar. Through simulations, it is confirmed that the unidirectional diffusion of water can be effectively suppressed (Fig. 4a and b), as seen in the reduced electrolyte volume change (Fig. 2d and e). This asymmetric supporting electrolyte strategy is then applied to the experiments, where a significant reduction in the electrolyte volume imbalance is observed after 10 cycles. The experimental results show a volume change of 1 ± 1 mL in the catholyte and -1 ± 1 mL in the anolyte. Similarly, the simulation results indicate a volume change of 1.12 mL in the catholyte and -1.12



Fig. 4. The water mole flux through the membrane and reactant concentrations in the Case KOH 2 M, current density of $i_{op} = 40 \text{ mA/m}^2$, and flow rate of Q = 45 mL/min during 10 cycles: (a) the water mole flux; (b) the water mole flux by diffusion. The reactant concentration: (c) $C_{2,6-reDHAQ}^e + C_{2,6-DHAQ}^e$; (d) $C_{Fe(CN)_{6}^{n-1}}^e + C_{Fe(CN)_{6}^{n-1}}^e$.

mL in the anolyte (Fig. 2d and e).

The alkaline quinone flow batteries utilize electrolytes at high pH levels to prevent proton-dependent reactions on the electrode. Elevating the pH value within the electrolyte shifts the thermodynamic potentials of proton reactions toward negative values. When the pH is above 12, all reduced species assume a fully deprotonated form, thereby inhibiting proton-dependent reactions. Additionally, the reduction potential of 2.6-DHAQ becomes independent of the pH value. Therefore, increasing the supporting electrolyte concentration in the anolyte to 2 M does not affect the reduction potential of 2,6-DHAQ. At the catholyte, the redox potential of ferro/ferricyanide remains unaffected by any pH value [43]. Therefore, even if asymmetric KOH concentrations are applied to the anolyte and the catholyte, it will not impact the equilibrium potential of the alkaline quinone flow battery [11]. Nevertheless, it was observed that an increase in the supporting electrolyte concentration at the anolyte led to a slight improvement in the performance (Fig. 2c and f). This enhancement can be attributed to the increased conductivity of electrolyte ions, as indicated in Eq. (20). There was a slight disparity in the electrolyte volume change between the simulative and experimental results after 10 cycles. This disparity could be attributed to side reactions such as gas evolution, air oxidation, chemical decomposition, electrolyte crossover, and leakage from the pumping system [11] which are not taken into account in the current AQFB model.

4.3. Impacts of applied current density and flow rate

Volume imbalance of the electrolyte is caused by unidirectional water diffusion. As the operating time increases, water diffusion intensifies, leading to a greater volume imbalance over time. Therefore, the imbalance is proportional to the operating time. Although the operating current affects the EOD, as mentioned in Section 4.1, the movement of water due to EOD during the charging and discharging of AQFB offsets one another, so it does not significantly impact the volume imbalance. And the diffusion of water through the membrane is mainly due to the difference in water amount between the anolyte and catholyte. However, since the inlet flow rate does not affect this difference in the water amount, the impact of the operating current and inlet flow rate on volume imbalance can be considered minor. Accordingly, the flow rate and operating current density do not affect the volume imbalance. Compared to the flow rate Q = 45 mL/min (Fig. 2a), a slight decrease in volume imbalance was observed after 10 cycles in a lower flow rate (Q = 30 mL/min), and Case KOH 1 M (Fig. 5a and b). However, this is attributed to the performance degradation due to the short operating time of AQFB rather than the direct impact of the flow rate. Even at a low flow rate, effective suppression of the electrolyte volume imbalance was achieved after 10 cycles in the Case KOH 2 M (Fig. 5d and e). On the other hand, Fig. 6 shows an increase in the water imbalance due to the higher flow rate Q = 60 mL/min and the increased operating time of AQFB. This results from the improved performance (Fig. 6a and b). At a higher flow rate, effective suppression of the electrolyte volume imbalance was still achieved after 10 cycles in the Case KOH 2 M (Fig. 6d and e).

The effect of the water imbalance at different operating currents is also shown in Fig. 7 ($i_{op} = 20 \text{ mA/m}^2$) and Fig. 8 ($i_{op} = 60 \text{ mA/m}^2$). At a low operating current density $i_{op} = 20 \text{ mA/m}^2$, the volume imbalance increased due to the longer operating time (Fig. 7a and b), while at a higher current density $i_{op} = 60 \text{ mA/m}^2$, the volume imbalance decreased due to the shorter operating time (Fig. 8a and b). However, effective suppression of the volume imbalance was achieved at both operating currents in the Case KOH 2 M (Figs. 7d, e, 8d and e).

4.4. Practicability

This study suggests a strategy that utilizes asymmetric supporting electrolytes between the anolyte and the catholyte to mitigate the volume imbalance. Due to the affordable price of potassium hydroxide, this



Fig. 5. Comparison of the electrolyte volume change and voltage profiles through experiments and simulations under the current density of $i_{op} = 40 \text{ mA/m}^2$ and the flow rate of Q = 30 mL/min after 10 cycles: (a) experimental results; (b) simulation results; (c) voltage profiles in the Case KOH 1 M; (d) experimental results; (e) simulation results; (f) voltage profiles in the Case KOH 2 M.



Fig. 6. Comparison of the electrolyte volume change and voltage profiles through experiments and simulations under the current density of $i_{op} = 40 \text{ mA/m}^2$ and the flow rate of Q = 60 mL/min after 10 cycles: (a) experimental results; (b) simulation results; (c) voltage profiles in the Case KOH 1 M; (d) experimental results; (e) simulation results; (f) voltage profiles in the Case KOH 2 M.

strategy allows for implementation at a low cost. Furthermore, as described in Section 4.2, it is observed that the introduction of an asymmetric supporting electrolyte does not significantly impact the AQFB performance. Moreover, it is confirmed that this strategy is applicable under various operating conditions (various flow rates and operating currents) in Section 4.3. By alleviating the volume reduction of the anolyte, it is possible to inhibit the concentration increase of the electrolyte and prevent salt precipitation within the electrolyte. Consequently, this strategy offers a resolution to the issues of capacity

reduction and inlet pressure elevation in the AQFB. And, by mitigating the volume increase of the catholyte, it is possible to suppress the decrease in electrolyte concentration and alleviate the substance transfer loss of the active species. This strategy is expected to be applicable to other RFBs experiencing electrolyte volume imbalance issues. It should be noted that the strategy should be employed cautiously in redox batteries where the supporting electrolyte plays a crucial role in stability or performance.



Fig. 7. Comparison of the electrolyte volume change and voltage profiles through experiments and simulations under the current density of $i_{op} = 20 \text{ mA/m}^2$ and the flow rate of Q = 45 mL/min after 5 cycles: (a) experimental results; (b) simulation results; (c) voltage profiles in the Case KOH 1 M; (d) experimental results; (e) simulation results; (f) voltage profiles in the Case KOH 2 M.



Fig. 8. Comparison of the electrolyte volume change and voltage profiles through experiments and simulations under the current density of $i_{op} = 60 \text{ mA/m}^2$ and the flow rate of Q = 45 mL/min after 15 cycles: (a) experimental results; (b) simulation results; (c) voltage profiles in the Case KOH 1 M; (d) experimental results; (e) simulation results; (f) voltage profiles in the Case KOH 2 M.

5. Conclusions

Through simulations and experiments, this study demonstrated that the electrolyte volume imbalance that occurs during AQFB operation can be effectively mitigated by increasing the initial supporting electrolyte concentration of the anolyte to 2 M KOH. This strategy is based on the suppression of the unidirectional diffusion of water caused by the water concentration difference between the anolyte and the catholyte, by adjusting the water concentration to be similar between the anolyte and the catholyte. In addition, simulations and experiments were conducted under various flow rates and operating current densities conditions of the AQFB, and it was found that the electrolyte volume imbalance of the AQFB increased proportionally with the operation time, regardless of the flow rate or operating current. Therefore, it was confirmed that this strategy can be applied under any operating condition by providing the same initial supporting electrolyte concentration of the anolyte, regardless of the flow rate or operating current. Furthermore, this strategy increased the concentration of the supporting electrolyte, which did not significantly affect the cell voltage. Moreover, the supporting electrolyte is relatively inexpensive, making it a practical solution to address the water transmembrane challenge in AQFBs. In addition, the current model can be used to apply this strategy to other types of ORFBs and confirm the mitigation of electrolyte volume imbalance.

CRediT authorship contribution statement

Jeongmin Shin: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. Jing Sun: Validation, Investigation, Writing – original draft. Menglian Zheng: Investigation, Writing - review & editing, Supervision, Project administration, Funding acquisition. Jie Sun: Investigation, Writing review & editing.

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

Data will be made available on request.

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