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Research paper



Electrochemical Studies on Alizarin Red S as Negolyte for Redox Flow Battery: a Preliminary Study

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Abstract

Redox flow battery (RFB) has received tremendous attention as energy storage system coupled with renewable energy sources. In this paper, a low-cost alizarin red S (ARS) organic dye is proposed to serve as the active material for the negative electrode reaction for organic redox flow batteries. Cyclic voltammetry has been conducted under a number of operating conditions to reveal the electrochemical performance of this molecule. The results suggest that ARS is highly reversible at low electrode potential (c.a. 0.082 V vs. standard hydrogen electrode), indicating that ARS is a promising negative electrode material for organic redox flow batteries. The diffusion coefficient of ARS is calculated in the range of 6.424 x 10^{-4} cm^2 s^{-1}, This has indicated fast diffusion rate and electrochemical kinetics for oxidation and reduction in higher concentration of ARS. It has been found out that the higher concentration of ARS in base electrolyte cause lowest diffusion coefficient due to solubility issue of ARS.

Keywords: *Alizarin red S ; Negolyte ; Organic redox flow battery ; Renewable energy storage ; Redox material*

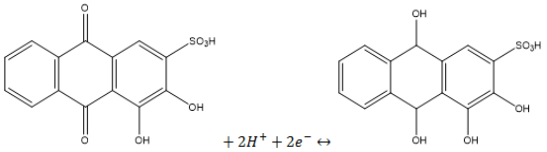
1. Introduction

Constantly expanding global industrial development and rapid growth of world human population has issued toward drastic increase of energy demand. Enerdata reported a total of 82 % energy derived from fossil fuel resources (coal, oil and gas) in 2015 [1]. Also in the similar year, worldwide energy consumption for G20 countries was reported as 10.9 Gtoe, in contrast to 8.1 Gtoe in 2000; this indicated an increment of 34 % [1]. The percentage of increment of energy consumption attributed to the growth of world population with the estimation number provided by United Nation is 7.35 billion in 2015 compared with 6.13 billion in 2000 [2] and industrial demands over years. International Energy Outlook 2016 (IEO2016) reported total industrial energy consumption projection on non-OECD (China, India, Middle East, Russia and Brazil) and OECD countries (US, Canada, Mexico, Chile, Japan, South Korea, Australia and New Zealand) from 2012 until 2040 [3], [4]. For non-OECD countries, 149.0 quadrillion Btu was consumed in 2012, the number are increasing with an annual percentage of 1.5 yearly with to expectation of 224.5 quadrillion Btu. By taking account of these numbers, energy sector was seen as a huge economical market growing by years.

Due to the environmental impacts and depletion of fossil fuel, these scenarios elevates the exploration of intermittently-available renewable energy such as wind, tidal and solar energy. To solve the fluctuation issue in electricity grid, sustainable energy storage is a reliable component for growing use of renewable energy sources by storing energy in large scale. Thus, the excellent system scalability of RFBs, along with large capacity and cycle life, inherent safety, decoupling power and energy have received increasing attention recent years to be serve as one of the most promising large scale energy storage systems [5]–[7]. In redox flow battery, electrical energy is stored in electrolyte and can be instantly converted to chemical potential according to demand. External electrolyte tank with unlimited fuel is another key difference of RFBs that offering infinite life cycle [8]. Unlike the dependent capacity of lithium ion battery, energy and power capacity of RFBs are independently scalable. Emphasizing on the advantage of being decoupled, RFBs pledged a tremendous design flexibility to fit the energy and power criterion well suited for large scale applications such as remote area supplier, backup power supplier [9], generation and distribution [10], power quality optimization and in future HEV application [11]. The cost limitation of existing conventional RFB such as vanadium [12] and zn [5], [13] based RFB challenged the extension of RFB application.

At the point for full scale operating RFBs, reduction in cost of electrolytes is significant. Since the introduction of RFBs, a series of electrochemical redox couple have been applied in the studies of RFBs aiming to propose a better and cheaper RFBs technology to real time applications [14]. Redox reaction tends to happen in both electrolyte compartments. To address this challenges [15]–[17] faced by most in-organic RFBs, recent evidences suggests that the introduction of organic redox couples elevate the possibility of cost reduction (> USD $35 per kW h) [18]–[22]. Alizarin red s is widely used as dye and is reported to have good stability as negolyte [23]. More importantly, the price for ARS is said to be low (USD $35 per kilogram) which it can be extracted from cheap quinone compare to vanadium (~USD $40 per kilogram). The equation of ARS is as follow:

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(1)

The electrode potential of ARS, E_0 is 0.082 V referring to literature [19], [23]. ARS has lowest electrode potential value compare to anthraquinone-2-sulfonic acid, AQS (0.187 V) and 1,8-dihydroxyanthraquinone-2,7-disulfonic acid, DHAQDS (0.120 V) making ARS a good candidates as negolyte for redox flow battery application. Previous studies are focus in low concentration of ARS investigation. In present study, a preliminary finding on abundant organic redox material - alizarin red s in acidic has been demonstrated. The essential goal of this paper is to investigate the possibility of ARS as negolyte for RFB application. In this study, the are two main investigations which are i) investigation on the effect of ARS concentration in 1 M H_2SO_4 and ii) investigation on the effect of base electrolyte concentration in ARS electrochemical kinetics. The behaviour of alizarin red S was evaluated and compared in cyclic voltammetry (CV) results.

2. Experimental

2.1. Materials Preparation

Alizarin red s (powder, Sigma Aldrich) was used as received without further purification.

2.2. Electrochemical Measurement

The investigated electrolyte solutions consisted of i) 0.05 M ARS ii) 0.15 M ARS in 1 M or 2 M H_2SO_4 as base electrolyte. A three electrodes half-cell system was utilized with potentiostat (AUTOLAB, 101N) for electrochemical measurement purpose for alizarin red s investigation. Three electrode system was employed which glassy carbon electrode as working electrode (CHI 104) with an area of 0.2475 cm^2 , while platinum (CHI 115) and Ag/AgCl (CHI 111) were use as the counter and reference electrodes. Before the measurement, glass carbon electrode was cleaned with alumina and rinse with de-ionized water. Cyclic voltammetry (CV) was conducted at 10 mV s^{-1} scan rate. All the measurement were complete at room temperature.

2.2. Electrochemical Kinetics

The diffusion coefficient ratio (*D*) was calculated and tabulated in Table 2 by using Randles-Sevcik equation, the equations are as follows:

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} S_A D^{\frac{1}{2}} C v^{\frac{1}{2}} \quad (2)$$

$$i_p = 7.61 \text{ x } 10^5 S_A D^{\frac{1}{2}} C v^{\frac{1}{2}} \quad (3)$$

where i_p is the anodic peak of reduction peak of electroactive material, *n* is the number of electrons in the redox reaction (n = 2 [24]), S_A is the electroactive surface area (0.2475 cm^2), *v* is the scan rate (V s^{-1}), and *C* is the concentration (mol cm^{-3}) of the electroactive species at the electrode.

$$D = \left[\frac{i_p}{7.61 \times 10^5 S_A C v^{\frac{1}{2}}}\right]^2 \quad (4)$$

3. Result and Discussion

3.1. Cyclic Voltammetry Characteristics

The peak separation of potential ($\Delta E_p = E_{pa} - E_{pc}$), anodic and cathodic peak current are used to estimate the reversibility of alizarin red s reaction in sulfuric acid.

a) Effect of ARS concentration

Fig. 1 illustrates cyclic voltammetry of 0.05 M and 0.15 M ARS in two different concentration (1 M and 2.5 M) H_2SO_4. CV peak potential separation (ΔE_p) for 0.05 M ARS in 1 M H_2SO_4 of -173.35 mV as calculated diffusion rate is 6.424 x 10^{-4} cm^2 s^{-1} with cathodic peak current of 749.86 mA at 10 mV s^{-1} scan rate. The diffusion rate is faster compare to literature [19] which has a higher calculated diffusion value of 2.14 x 10^{-6} cm^2 s^{-1}. This indicate higher concentration of ARS allow faster ion diffusion and higher electrochemical kinetics activity in redox reaction. By referring to Table 1, 0.05 M ARS achieved higher anodic current and higher diffusion coefficient compare to 0.15 M ARS.

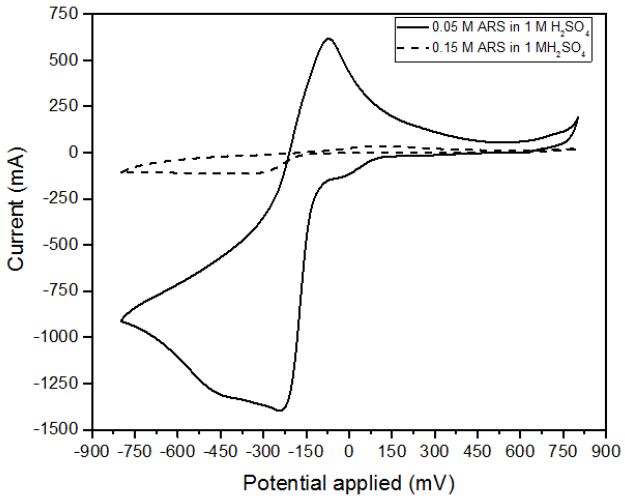


Fig. 1: Cyclic voltammetry of 0.05M and 0.15M ARS in different concentration (i.e 1M and 2.5M) of H2SO4 with scan rate of 10 mV s^{-1}

Table 1: Comparison on anodic current and diffusion between 0.05 M ARS and 0.1 M ARS in 1 M H_2SO_4

ARS concentration, mol cm^{-3}	I_{pa}, mA	*Diffusion coefficient , cm^2 s^{-1}
0.05	-1193.4	6.424 x 10^{-4}
0.15	-96.61	4.677 x 10^{-7}

**calculated*

b) Effect of different base electrolyte concentration

By comparing the voltammetries of four solutions as shown in Fig. 2, the curve of 0.05 M ARS in 1 M H_2SO_4 clearly illustrated the highest cathodic of 764.22 mA while 0.15 M ARS in 1 M H_2SO_4 achieved the highest value for anodic of – 96.61 mA . Although the theory stated that higher concentration of sulphuric acid, the higher ionic conductivity but the diffusion rate is low with limited solubility of ARS in base electrolyte. This statement is support by the result reported in literature [19] which ARS has poor experimental stability. Therefore, the finding suggested that suitable modification on the chemical compound is necessary. Table 2 indicated the measured and calculated value for investigated solution.

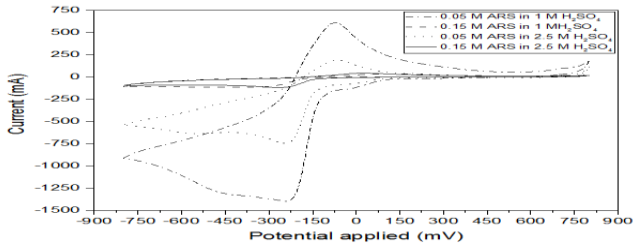


Fig. 2: Cyclic voltammetry of 0.05M and 0.15M ARS in different concentration (i.e 1M and 2.5M) of H_2SO_4 with scan rate of 10 mV s^{-1}

CV peak potential separation (ΔE_p) for 0.05 M ARS in 2.5 M H_2SO_4 of -191.06 mV and the diffusion rate of 2.045 x 10^{-4} cm^2 s^{-1} were presented at 10 mV s^{-1} scan rate. The result indicated that the diffusion of ARS is depends on optimum acidity value and solubility in base electrolyte. The average peak separation in cyclic voltametric of ARS is -273.9 mV, which is lower than 59 mV/n (where n is 2) showing ARS undergoes multi electron quasi-reversible process [19]. The comparison for two different concentration of ARS was reported in Table 3, the result indicated that diffusion rate for higher concentration of ARS is lower compare to lower concentration of ARS due to the limitation of ARS solubility. The result also illustrated higher anodic current, I_{pa} can be achieved in higher concentration of sulphuric acid. However, the concentration of ARS is necessary to define with respect to the solubility of ARS in sulphuric acid. The result shown that the highest concentration for ARS without modification is less than 0.15 M.

Table 2: Measured data for 0.05 M and 0.15 M ARS in 1.0 M and 2.5 M of H_2SO_4 in term of anodic current (I_{pa}), cathodic current (I_{pc}) and potential (E_p)

Concentration, mol cm^{-3}		I_{pa}, mA	I_{pc}, mA	E_{pa}, mV	E_{pc}, mV	*ΔE_P
ARS	H_2SO_4					
0.05	1.0	-1193.4	749.86	-245.83	-72.48	-173.35
0.15	1.0	-96.61	38.77	-350.21	93.48	-443.69
0.05	2.5	-675.34	260.57	-248.97	-57.91	-191.06
0.15	2.5	-109.28	49.80	-267.21	20.52	-287.73

Table 3: Calculated diffusion value from measured value for 0.05 M and 0.15 M ARS in different concentration of H_2SO_4

ARS concentration, mol cm^{-3}	I_{pa}, mA	*Diffusion value, cm^2 s^{-1}
0.05	-1193.4	6.424 x 10^{-4}
0.05	-675.34	2.045 x 10^{-4}
0.15	-96.61	4.677 x 10^{-7}
0.15	-109.28	5.985 x 10^{-7}

**calculated*

4. Conclusion

This paper presented a preliminary analysis on ARS as potential redox material for organic redox flow battery. It has been found out that ARS suitable as negative electroactive species for flow batteries. Good electrochemical reversibility of ARS was demonstrated in cyclic voltammetry with two redox peaks. However, the improvement for ARS solubility and stability by additives and synthetic modification are necessary. With proper functional molecule modification and additives, this will lead to developing ARS as one of the potential negolyte candidates for RFB application. This work is currently continuing under several testing process in order to improve the solubility of selected quinone and will be further testing in optimized redox flow cell.

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