Electrochimica Acta 105 (2013) 584–592

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Preparation of silica nanocomposite anion-exchange membranes with low vanadium-ion crossover for vanadium redox flow batteries

P.K. Leung, Q. Xu, T.S. Zhao*, L. Zeng, C. Zhang

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

ARTICLE INFO

Article history:
Received 6 October 2012
Received in revised form 28 April 2013
Accepted 30 April 2013
Available online 20 May 2013

Keywords:
Flow battery
Vanadium redox flow battery
Anion exchange membrane
Silica sol–gel reaction

ABSTRACT

Crossover of vanadium ions through the membranes of all-vanadium redox flow batteries (VRFB) is an issue that limits the performance of this type of flow battery. This paper reports on the preparation of a sol–gel derived silica nanocomposite anion exchange membrane (AEM) for VRFBs. The EDS and FT-IR characterizations confirm the presence and the uniformity of the silica nanoparticles formed in the membrane via an in situ sol–gel process. The properties of the obtained membrane, including the ion-exchange capacity, the area resistance, and the water uptake, are evaluated and compared to the pristine AEM and the Nafion cation exchange membrane (CEM). The experimental results show that the permeability of the vanadium ions through the silica nanocomposite AEM is about 20% lower than that of the pristine AEM, and one order of magnitude lower than that of the Nafion CEM. As a result, the rates of self-discharge and the capacity fading of the VRFB are substantially reduced. The Coulombic and energy efficiencies at a current density of 40 mA cm^{-2} are, respectively, as high as 92% and 73%.

1. Introduction

The redox flow battery (RFB) is considered to be an attractive energy storage device for load-leveling and other off-grid applications, such as integration with renewable energy sources [1–4], as it offers obvious advantages in cost, cycle-life, safety and flexibility compared to other energy storage technologies. Among different types of RFB, the all-vanadium redox flow battery (VRFB) is the most studied system and has been demonstrated globally at large scale. Typical charge–discharge reactions of an VRFB involve two vanadium redox couples, V(II)/V(III) and V(IV)/V(V), in the negative and positive half-cells, respectively. In a fashion similar to most batteries, electrons are transferred between the two electrodes through the external circuit during the charge and discharge processes [5]. At the negative electrode, the redox reaction between V(III) and V(II) during charge and discharge are:

$$V^{3+} + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} V^{2+} \qquad E_{-VE} = -0.26\,\text{V vs. SHE} \tag{1}$$

Similarly, V(V) and V(IV) active species as a form of VO_2^+ and VO^{2+} are reduced and oxidized at the positive electrode. Water molecules and protons are involved in the cathodic reaction to maintain the charge balance and the stoichiometry as:

$$VO^{2+} + H_2O - e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftarrows}} VO_2{}^+ + 2H^+ \qquad E_{+VE} = +1.0\,\text{V vs. SHE} \tag{2}$$

In a VRFB, the ion exchange membrane is a key component that not only provides an ionic conduction pathway between the two electrolytes but also prevents mixing of the negative and positive electrolytes. The crossover of ions through the membrane will result in self-discharge and thus the loss of the chemical energy. As reported elsewhere [6], the self-discharge of VRFB is mainly associated with the diffusion of vanadium ions from one half-cell to the other due to the concentration gradients between the two electrolytes. For instance, V(II) and V(III) ions diffused from the negative half-cell can reduce V(IV) and V(V) ions in the positive electrolyte, while the V(II) and V(III) ions in the negative half-cell are oxidized by V(IV) and V(V) ions from the positive side. Crossover of vanadium ions gives rise to a reduction in the Coulombic efficiency and an imbalance of state of charge (SOC) between the two half-cell electrolytes, resulting in a capacity fading after prolonged cycling.

State-of-art VRFBs use perfluorosulfonic cation exchange (CEM) membranes (such as Nafion). However, the high cost (up to 40% of the entire cell cost [7]) and significant crossover of vanadium ions through Nafion membranes are the two barriers that hinder the commercialization of VRFB [8]. Recent studies suggested that the anion exchange membrane (AEM) is an attractive candidate to replace Nafion as the AEM tends to have lower permeability of

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* Corresponding author. Tel.: +852 2358 8647.
E-mail address: metzhao@ust.hk (T.S. Zhao).

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http://dx.doi.org/10.1016/j.electacta.2013.04.155

vanadium ions than Nafion does due to the electrostatic repulsion between the positive functional groups of the membrane and the vanadium cations in the electrolyte. As proposed by some recent works [9], AEMs could transport both proton and sulfate anions in an acidic VRFB system.

Compared to VRBs using Nafion membranes, the VRFBs equipped with several AEMs were reported to have improved Coulombic and energy efficiencies [10–15]. Despite this, most AEMs in the market are used for alkaline electrolytes. In order to ensure a long-term stability, a recent AEM designed for acidic VRFB system (Fumasep FAP, Fumatech GmbH, Germany) was used in this work, which costs (€0.12 cm^{-2} [16]) only 20% of that of Nafion membranes (€0.57 cm^{-2} [17]).

The objective of this work is to minimize the crossover of vanadium ions by modifying an AEM via in situ sol–gel synthesis method. The silica nanoparticles serve as physical barriers to block the permeation of vanadium ions across the membrane as some vanadium cations may still penetrate through the AEM [18]. Prior to this work, commercial AEMs (Tokuyama Corp., Japan) have been modified via in situ polymerization [19,20] and sol–gel modified Nafion CEMs have been used in various applications, including VRFBs [18,21–23]. As reported elsewhere [18], the VRFBs equipped with the Nafion/silica membranes exhibit improved self-discharge performance and show higher Coulombic and energy efficiencies than the system using Nafion CEM. In this work, a silica nanocomposite AEM was tested and compared with Nafion CEM by measuring the ion-exchange capacity (IEC), the area resistance, the water uptake and the vanadium ion permeability. It is demonstrated that the self-discharge and the capacity fading of the VRFB with the prepared membrane are substantially reduced. The energy efficiency of the VRFB in a typical charge–discharge cycle is as high as 73% at 40 mA cm^{-2}.

2. Experimental

2.1. Silica nanocomposite AEM preparation

The method for preparing a silica nanocomposite AEM was based on the in situ sol–gel synthesis method developed by Mauritz et al. in the 1990s [18], which has been used and further modified in various works. In this work, an AEM used for acidic media was Fumasep FAP, which was purchased from Fumatech GmbH (Germany) and designed for the all-vanadium redox flow battery. For comparison purpose, Nafion 115 cation exchange membrane (Dupont, USA) was also used. As-received AEM was pretreated by first cleaning in a 3 wt.% H_2O_2 solution (Aldrich, USA) at 70–80 °C for 30 min. Subsequently, the membrane was immersed in a 1 mol dm^{-3} H_2SO_4 solution (Sigma–Aldrich, USA) at the same temperature for another 30 min and further rinsed with deionized water several times to remove any remaining trace of H_2O_2 and H_2SO_4. It should be noted that the membrane may decompose when the temperature is higher than 80 °C. Such pretreatment procedures are crucial to swell the membrane (linear swelling ratio c.a. 6.2%) and to allow easier absorption of the solutions during the fabrication process.

Before the in situ sol–gel synthesis, the pretreated membrane was cut into the size of 4.5 cm × 2 cm (9 cm^2) and the weight was measured accordingly. The silica nanocomposite AEM was prepared by a conventional in situ sol–gel approach using tetraethyl orthosilicate (TEOS, $Si(OCH_2CH_3)_4$) (Sigma–Aldrich, USA) as a silicon alkoxide precursor to react with water in methanol solvent (Aldrich, USA). For the preparation of the silica nanocomposite AEM, the pretreated AEM was soaked in a 30 cm^3 MeOH/TEOS solution (1:1 volumetric ratio) for 12 h. The use of methanol is to facilitate the permeation of the TEOS solution and the subsequent water, into the channel network of the AEM. Since it is miscible with water and the TEOS solution, an efficient sol–gel reaction can be ensured. The soaked membrane was then immersed in a solution (30 cm^3) with 50 vol.% methanol and 50 vol.% 0.2 mol dm^{-3} ammonia (Aldrich, USA) for a specified period of time under vigorous stirring to initiate the hydrolysis/condensation reaction for the formation of the silica nanoparticles inside the AEM. A small amount of ammonia was used as the catalyst and to provide a slightly alkaline medium. After that, the resulting silica nanocomposite AEM was dipped immediately in anhydrous methanol for several times to remove the surplus reactants and then dried under ambient air for 24 h. Prior to any testing, the prepared silica nanocomposite AEM was stored in deionized water to establish certain level of hydration [18]. The silica content (w) of the nanocomposite AEM is obtained from:

$$w = \frac{m_{SiO_2,\,dry}}{m_{AEM}} = \frac{m_{SiO_2/AEM} - m_{AEM}}{m_{AEM}} \times 100\% \tag{3}$$

where m_{AEM}, $m_{SiO_2/AEM}$ and $m_{SiO_2,\,dry}$ are the mass of the pristine AEM, silica nanocomposite AEM and the dry silica nanoparticles, respectively.

The distribution of the silica content in the nanocomposite AEM was examined by Energy-Dispersive X-ray spectroscopy mapping (EDS-mapping, JEOL-6300F). Fourier transform infrared (FT-IR) spectra of the membranes were obtained using attenuated total reflection (ATR) accessory. The silica xerogel was prepared in a similar approach by mixing the same sol–gel solutions used in silica nanocomposite AEM fabrication. The solutions were 4 cm^3 MeOH/0.2 mol dm^{-3} ammonia solution (1:1 volumetric ratio) and 6 cm^3 MeOH/TEOS solution (1:1 volumetric ratio). With a small addition of ammonium fluoride (0.15 g) as a catalyst, a wet gel was formed within 30 min. The silica xerogel was hence formed by removing the water content through vacuum drying at 110 °C for 24 h.

2.2. Membrane characterization

2.2.1. Ion-exchange capacity

The ion-exchange capacity (IEC) of the AEMs was measured by following the procedures reported elsewhere [10]. The dried AEM was first cut into the size of 1 cm × 1 cm and then accurately weighted. The AEM was initially immersed in 1 mol dm^{-3} KOH solution (Sigma–Aldrich, USA) for 48 h to exchange into OH^- form, which was then immersed in a 0.05 mol dm^{-3} HCl solution (30 cm^3) for another 48 h. The amount of the OH^- exchanged by the AEM would further neutralize with the H^+ ions available in the 0.05 mol dm^{-3} HCl solution. To determine the amount of OH^- exchanged by the AEM, the HCl solution for soaking the membrane was back titrated with 0.05 mol dm^{-3} KOH solution using phenolphthalein (Sigma–Aldrich, USA) as a colorimetric indicator. The IEC value (mmol g^{-1}) was then calculated as the ratio of the titrated amount of OH^- to the weight of the dried membrane. Similarly, the IEC of the Nafion CEM was measured by immersing a dried membrane in a 30 cm^3 0.05 mol dm^{-3} KOH solution first, followed by a back titration with 0.05 mol dm^{-3} HCl solution.

2.2.2. Area resistance

The area resistance of the membrane was measured in a conventional method described elsewhere [18–24]. A conductivity cell with two compartments separated by a membrane was used, in which 4 mol dm^{-3} H_2SO_4 solution (20 cm^3) was filled in each compartment. The area of the membrane exposed to the solution, S, was 4.5 cm × 2 cm, while the two graphite electrodes were placed at a distance of 2 cm from each other. The ionic resistances of the conductivity cell with and without membrane, were determined by the real axis intercept of the Nyquist plot using electrochemical