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A two-dimensional porous electrode model for designing pore structure in a quinone-based flow cell

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ABSTRACT

A two-dimensional porous electrode model for designing a pore structure in a quinone-based flow battery was developed and validated by using experimental data from a metal-free quinone-based flow battery. The effects of porosity and pore size distribution on electrode performance and concentration fields were analyzed, the appropriate porosity and pore size distribution were obtained. In addition, the comprehensive effect of pore volume, specific surface area and pore size were considered, the dimensionless number shape factor SF was introduced to characterize the morphology, and the effect of morphology on the electrode performance was also investigated. This model was expected to understand the effect of morphology on the electrode performance and guide the preparation of the electrode. Extensions to the model in actual tests and future work were suggested.

1. Introduction

High demands for efficient energy delivery and renewable energy have generated impressive interest in energy storage technologies. One of the most promising of such technologies is the redox-flow battery. Redox flow batteries have shown impressive performance in medium- and large-scale energy storage. Compared with conventional batteries, redox flow battery (RFB) technologies can achieve high energy efficiencies, low cost per kWh for large storage capacities and a long cycle life [1–3]. Redox flow batteries store energy in solutions containing different redox couples and the charge and discharge processes occur at the surfaces of either porous or non-porous electrodes [1,4]. In a redox flow battery, the energy storage capacity of the system is determined by the volume of the electrolyte tanks, while the system power is determined by the size of the stacks and the active electrode surface area [4,5].

In the past few decades, many types of redox flow batteries (RFBs) have been proposed, such as all vanadium redox flow batteries (VRBs), iron/chromium flow batteries (ICB), and polysulfide/bromine flow batteries (PSBs). One of the most popular types of RFBs was the all-vanadium redox flow battery (VRFB), which was first patented by Skyllas-Kazacos et al. [6] in 1986. The great challenge for all-vanadium flow batteries, however, was the high cost [7,8]. Compared with inorganic electrode materials, organic electrode materials showed sustainable and overwhelming advantages in cheap, green and versatile characteristics [9–12]. Quinone-based materials as a type of organic active material for RFBs were studied in the 1980s, when researchers used quinones as positive materials and Pb or Li as negative materials [13,14]. Huskinson et al. [15] investigated a quinone-bromide flow battery with a high power density and storage capacity retention. 9,10-Anthraquinone-2,7-disulfonic acid (AQDS) was used as the negative electrolyte, the advantage of the system being that chemicals and electro-chemicals do no need metal catalysts. AQDS/H_2AQDS as an organic redox couple also had many advantages including low toxicity, good reversibility and a faster rate constant [5,15–17]. Here, we introduced 3,4-Dihydroxy-9,10-anthraquinone-2-sulfonic acid (ARS) as the negative electrolyte in the flow cell. It belongs to the quinone species and is usually used for dyeing [18]. ARS was an abundant chemical compound that could be synthesized from cheap commodity chemicals [19] and it was cheaper than the AQDS used in the flow battery. Fig. 1 shows the electrochemical reaction of quinone/hydroquinone in a porous electrode.

The rapidly improving cell performance of RFBs sets a series of new challenges for developers of the technology, notably electrode morphologies and channel configurations [20]. Ferrigno et al. [21] utilized vanadium species for both half-cells in a Y-shaped microchannel. Cohen et al. [22] introduced the planar or F-shaped microchannel, which increased the contact area between the electrolyte and electrodes. Kjeang et al. [23–25] reported a model of vanadium species in half-cells, including graphite rod arrays and porous carbon paper as electrodes; the results showed that the flow-through architecture was related to utilization of the three-dimensional active area inside the

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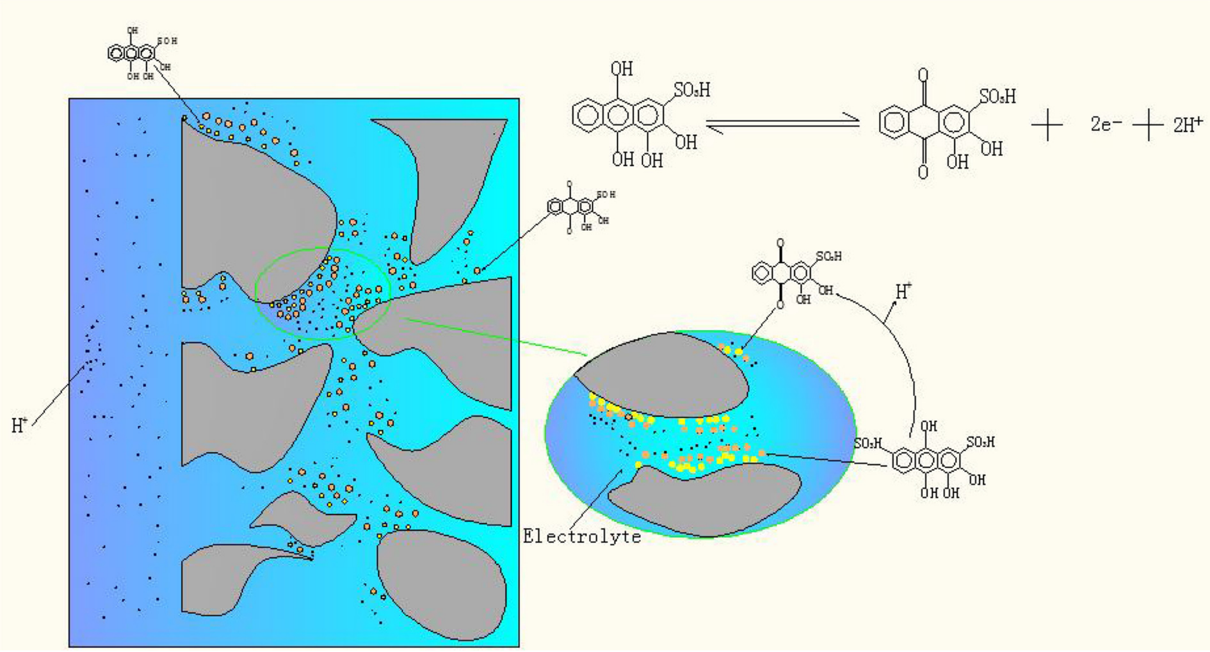

Fig. 1. Schematic of the electrochemical reaction of quinone/hydroquinone in a porous electrode.

porous electrodes. Noriaki Sano et al. [26] modified electrodes from different carbon sources and demonstrated that the pore size distribution had an important influence on the electrodes by experimental means; however, they did not investigate how the pore structure affect the performance of porous electrode. Shah et al. [27] proposed a two-dimensional isothermal dynamic model to investigate the volumetric porosity on cell performance but did not take the electrode structure into account.

In this paper, we approached the study of the current density for porous electrode in a quinone-based flow battery through a 2D model, in which the relationship among the current density, the pore size distribution and the electrode morphology was investigated. Mass transfer phenomenon in pores with different tortuosity was analyzed to account for the results. Two important keys are presented: (1) the appropriate range in different pore size distributions can be predicted based on this model; and (2) for the first time, pore volume, specific surface area and pore size to a new unified structural descriptor named the shape factor (SF) are proposed, which can be quantified via common experimental techniques.

2. Model developments

2.1. Geometry of the model and assumptions

A two-dimensional model of the quinone-based redox with the electrolyte flow through a porous electrode was formulated to analyse the electrochemical reaction in the porous electrode. The geometry of model is shown in Fig. 2, in which the major components are pore channels and the solid electrode. The pore diameter is determined by controlling the size of the solid electrode. In the two-dimensional model, the gap between solid electrodes indicates the pore channel, and the circular region indicates the solid electrode. The total area of the electrode isL× L(μm), and L_p is the particle distance. Thus, the pore diameter is defined by the following:

$$d_p = L_p - d_f \tag{1}$$

where d_p is the pore diameter(m), and d_f is the fibre diameter of solid electrode. The surface area S is defined by the following:

$$S = \pi d_f n \tag{2}$$

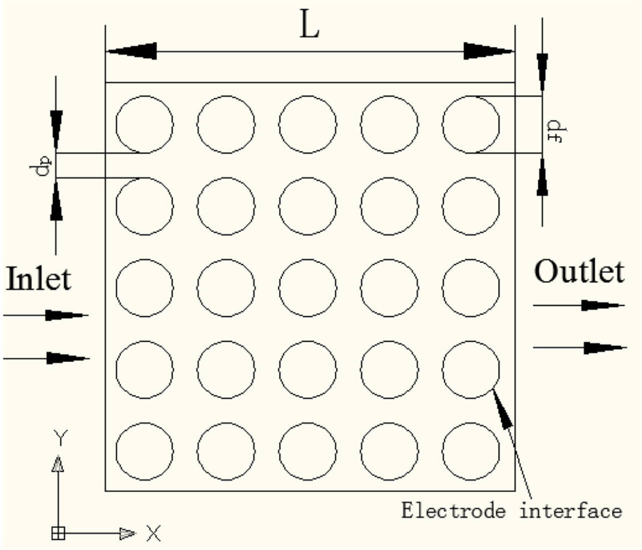

Fig. 2. Schematic of the 2D electrode modelling domains.

where n is the number of solid electrodes (in this model, n = 25). The porosity εis defined by the following:

$$\varepsilon = 1 - \frac{\pi}{4} d_f^2 n \Big/ L^2 \tag{3}$$

The pore volume per unit depth V is defined by the following:

$$V = L^2 \varepsilon \tag{4}$$

Meanwhile, when the electrolyte comes into contact with the porous electrode, electrons will be gained and lost at the electrode surface to achieve the charge and discharge of the battery, respectively. Sulfuric acid and ARS solution are used as the negative electrolyte. The reaction of the negative electrode during charging or discharging can be expressed as the following equation [28]:

$$\text{ARS} + 2e^- + 2H^+ \rightleftharpoons H_2ARS \tag{5}$$

By diffusion, migration and convection, each charged species