Applied Energy 180 (2016) 386–391

Contents lists available at ScienceDirect

Applied Energy

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

Copper nanoparticle-deposited graphite felt electrodes for all vanadium redox flow batteries

L. Wei, T.S. Zhao *, L. Zeng, X.L. Zhou, Y.K. Zeng

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

HIGHLIGHTS

- Copper nanoparticle is proposed as electrocatalyst for VRFBs for the first time.
- Propose a binder-free copper nanoparticle decorated electrode.
- The energy efficiency is up to 80.1% at 300 mA cm^{-2}, enhancing more than 17%.
- High stability and capacity retention are achieved by battery with copper catalyst.

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 5 July 2016
Accepted 30 July 2016

Keywords:
Vanadium redox flow battery
Electrode
Catalyst
Copper nanoparticle
Energy efficiency

ABSTRACT

A copper nanoparticle deposited graphite felt electrode for all vanadium redox flow batteries (VRFBs) is developed and tested. It is found that the copper catalyst enables a significant improvement in the electrochemical kinetics of the V^{3+}/V^{2+} redox reaction. The battery's utilization of the electrolyte and energy efficiency are found to be as high as 83.7% and 80.1%, at a current density of 300 mA cm^{-2}, which are 53.1% and 17.8% higher than those of the battery without the catalyst. Moreover, the present battery shows a good stability during the cycle test. The results suggest that the inexpensive copper nanoparticle catalyst without tedious preparation process offers a great promise for VRFB application.

1. Introduction

With increasingly pressing concerns over environmental issues and energy sustainability due to the consumption of fossil fuels, renewable energy sources such as solar and wind have been attracting more and more attentions [1–4]. However, the fluctuant and intermittent nature of the electricity generated from these renewables make them challenging for practical use [5–9], due to that introducing more than 20% intermittent electricity from current renewable sources without assistant storage facilities could lead to the voltage disturbance and frequency fracture of the grid [10]. One effective approach to address this issue is to employ the use of large-scale electrical energy storage technologies [11]. The redox flow battery would be one such system, and has already been regarded as a promising large-scale storage technology due to its inherent safety, moderate cost, ease of scalability and flexible operation [2]. In particular, the vanadium redox flow battery (VRFB) proposed by the Skyllas-Kazacos group is perhaps the most studied and promising one because its reduced cross-contamination effect by employing the same element in both electrolytes and long service life [12–14].

Although significant developments have been made over the past few decades, the VRFB technology has yet to meet the stringent cost and performance requirements for broad penetration of the energy storage market [10,15–18]. According to the recent cost and performance model built by Pacific Northwest National Laboratory [19], it is reported that the power stack alone accounts for around 35% of a 4 MW h VRFB's entire cost. To reduce the cost of the power stack as well as the whole system, one approach is to operate the VRFBs at high current densities without sacrificing energy efficiency, best expressed as high power density [20]. Herein, improving the power density is tantamount to decreasing the size of the power stack for the given power requirement, thus reducing the component materials such as bipolar plates, electrodes and membranes [21]. The issue with enhancing operating

* Corresponding author.
E-mail address: metzhao@ust.hk (T.S. Zhao).

http://dx.doi.org/10.1016/j.apenergy.2016.07.134
0306-2619/

current density, however, is that it typically induces large polarization, sacrificing the battery's performance. Thus, it is of great importance to enhance the rate performance and efficiencies of VRFBs.

In the flow battery, polarization consists of kinetic polarization, ohmic loss and mass transport limitation. As a critical component of VRFBs, electrode provides electroactive surfaces, conduct electrons for redox reactions. It contributes to the system through not only the ohmic loss, but also kinetic loss [10,22]. The battery's performance, which is denoted by its power density and stability, is highly determined by the type of material used for the electrode and its surface properties. Graphite felt has been most widely used as electrode for VRFBs due to its wide operating potential range, satisfactory chemical and mechanical stability, high electrical conductivity and low cost [23]. However, the pristine graphite felt is plagued by its poor electrochemical activity towards vanadium redox reactions. Therefore, conventional VRFBs installed with pristine graphite felt electrodes usually exhibit low current densities below 100 mA cm^{-2} [10]. In an effort to address this issue, a variety of electrode treatment methods, including acid treatment, thermal treatment and nitrogen doping have been investigated [24]. In addition, a variety of nanostructured electrocatalysts [25–27], including metal-based (metal and metal oxide) and carbon-based materials, were also introduced on the surface of graphite felt to improve the electrochemical activity for the redox reactions [28,29]. However, their performance is highly dependent on the distribution uniformity and preparation process. On this occasion, it is essential to develop advanced catalysts with superior catalytic activity as well as low cost [30,31].

Herein, we report on the first use of inexpensive and highly conductive Cu nanoparticles as catalysts to enhance the electrochemical activity of the graphite felt electrode. A tiny amount of Cu salts was introduced into the electrolyte and the Cu nanoparticles were synchronously electrodeposited onto electrode surface during charge without any pretreatment procedures or binder (as depicted in Fig. 1). This process yields a battery energy efficiency of 80.1% at a current density of as high as 300 mA cm^{-2}. Besides, extended cycling test results also demonstrate that the battery installed with the proposed electrode exhibits a significantly improved rate capability and capacity retention compared to that of the battery with the pristine electrode. These superior results suggest that Cu nanoparticles are effective catalysts in improving the electrochemical activity of V^{3+}/V^{2+} redox reaction and graphite felts decorated Cu nanoparticles have great potential application as high-performance electrodes for VRFBs.

2. Experimental

2.1. Preparation of the battery

20 mL solution containing 1 M V^{3+} + 3 M H_2SO_4 and another 20 mL solution containing 1 M VO^{2+} + 3 M H_2SO_4 were used as the negative and positive electrolytes, respectively. $CuSO_4$ (Aldrich, 99.5%) was added into the electrolyte with varying Cu^{2+} concentrations of 0, 0.0025, 0.005 and 0.01 M. Commercially available graphite felt (SGL company, GFA series) with an uncompressed thickness of 1.5 mm (active area of 4.7 cm^2) was used as positive and negative electrode, respectively. Nafion® 212 (Dupont, USA) was employed as the membrane. The performance of the battery was tested in a zero-gap serpentine flow-field structured battery, which is detailed in previous work [32–34]. The electrolytes in the batteries were circulated at a fixed flow rate of 0.6 mL s^{-1} with a peristaltic pump (N6-3L, Baoding Shenchen Precision Pump). Before each measurement, nitrogen gas (high purity) was bubbled to exhaust any entrapped air in the electrolyte and reservoirs. All measurements were conducted at room temperature.

2.2. Electrochemical measurements

Cyclic voltammograms were obtained on the Autolab (PGSTAT30) workstation. A traditional three electrode electro-

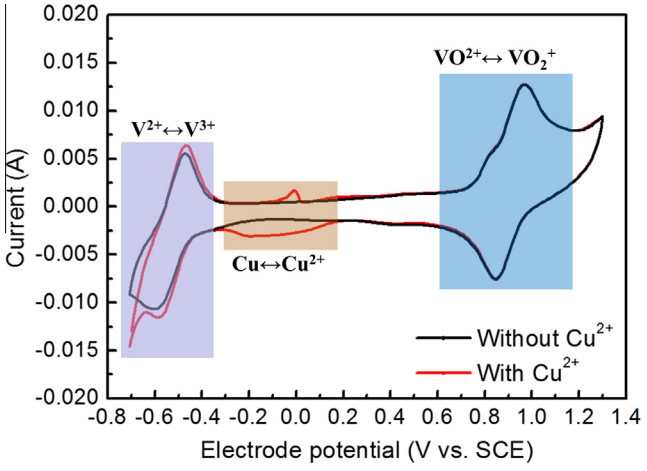

Fig. 2. CV curves of the graphite electrode with and without 0.005 M Cu^{2+} at a scan rate of 50 mV s^{-1}.

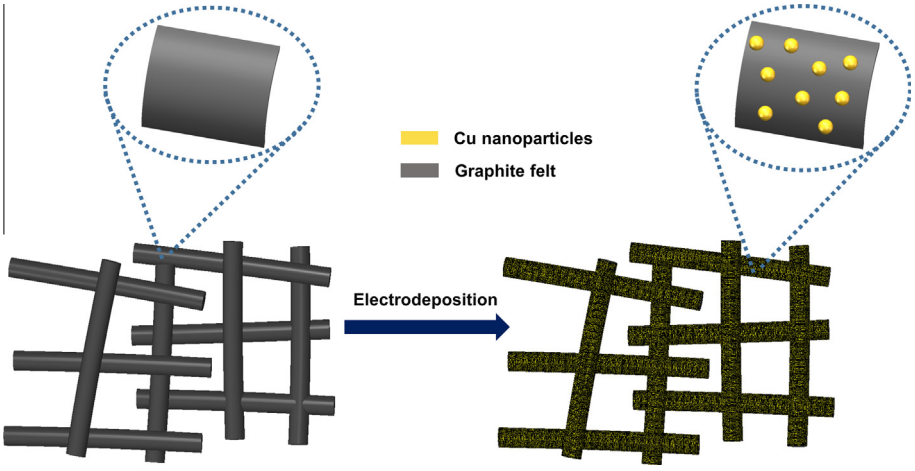

Fig. 1. Schematic diagram of the electrodeposition process: Cu nanoparticles sourced from the electrolyte containing Cu ions decorating on the surface of graphite felt.