Novel Cobalt Coated Carbon Felt as High Performance Negative Electrode in Sodium Polysulfide/bromine Redox Flow Battery

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The first use of cobalt coated carbon felt (Co-CF) as high performance negative electrode in sodium polysulfide/bromine battery (PSB) is presented. The Co-CF was prepared by electroless plating and evaluated by polarization tests and cycling experiment in a PSB single cell at room temperature. At current density of 40 mA cm⁻², the cathodic overpotential of the Co-CF for polysulfide/sulfide couple was -22 mV. When using Co-CF as negative electrode and CF as positive electrode, an energy efficiency up to 82.4% was achieved.

Key Words : Carbon Felt, Cobalt, Polysulfide/bromine Redox Flow Battery, Energy Efficiency

1 Introduction

Polysulfide/bromide battery (PSB) employs polysulfide/sulfide and bromine/bromide redox couple as anolyte and catholyte, respectively. The reversible electrochemical reactions during the operation of PSB may be represented, in simple terms, by the equation

$$2\text{NaBr} + (n-1) \text{Na}_2\text{S}_n \Leftrightarrow \text{Br}_2 + n\text{Na}_2\text{S}_n-1 \quad n = 2 \sim 4$$

This is based on the oxidation/reduction of non-metals rather than cations. The open-circuit voltage of the cell is about 1.54~1.61 V depending on the concentration of electrolyte. Like other redox flow batteries, the most attractive feature of PSB is the separation of output power rating and capacity, which makes it can be easily scaled up and is most suitable for utility scale energy storage. Moreover, the chemical reagents used in the electrolytes of PSB are not only plentiful and available at low cost, but also readily soluble in aqueous media and relatively safe, which makes it more economical for scaling-up of energy storage capacity. Now, VRB Power Systems Inc. acquired the intellectual property rights and assets to the Regenesys Energy storage system developed by Regenesys Technologies Ltd. They decided to make continuous development and commercialization of PSB intended for applications from 10-100MW’s with duration of 8 to 12 hours. However, the energy efficiency of PSB needs further enhancement to make this technology more competitive in the energy storage field.

For polysulfide/sulfide couple, flow-by type electrode consists of activated carbon (AC) and polymeric binder is the only electrode has been applied in PSB. The original aim was to utilize the high surface area of AC. However, at 60 mA cm⁻², only 56% energy efficiency and 50% voltage efficiency were obtained. Due to the properties of high external surface and porosity favorable for electrochemical reactions and good chemical and electrochemical stability, CF has been successfully applied in all-vanadium battery. Unfortunately, as a promising electrode material, CF has not been sufficiently utilized in PSB. In this work, based on CF, Co was selected as catalyst for its better activity and stability for polysulfide/sulfide redox reactions. A novel Co coated CF (Co-CF) was prepared by electroless plating and first employed in PSB at a practical current density and room temperature.

2 Experimental

Before electroplating, polyacrylonitrile (PAN)-based CF (Shanghai Xinxing Carbon Corp., China) was tailored into rectangular pieces of 0.5 cm in thickness and submitted to the following treatments: (i) boiling in 1 M NaOH for 1 h; (ii) washing with deionized water until pH ≈ 7; (iii) being dried and preserved for use. Pretreated CF samples were presensitized in a 40 g L⁻¹ SnCl₂·H₂O + 100 mL L⁻¹ HCl solution for 4 min at 30°C to adsorb Sn⁺ on the fiber surface. Then, the samples were placed in a 1 g L⁻¹ PdCl₂ + 300 mL L⁻¹ HCl solution for 8 min at 30°C to form palladium catalytic nuclei on the fiber surface. The preactivated pieces were washed with deionized water and introduced into an electroless plating bath. The composition of the cobalt plating solution and the conditions are given in Table 1. During plating, the bath was maintained at a temperature of 80 ± 1°C by a constant temperature bath. Besides, the pH of the bath also maintained constant during the plating process with the addition of NH₃ solution. The catalyst loading was co-

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Concentration/g L⁻¹</th>
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<tbody>
<tr>
<td>CoCl₂·6H₂O</td>
<td>30</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>50</td>
</tr>
<tr>
<td>Na₃C₁₂H₁₄O₁₄·2H₂O</td>
<td>30</td>
</tr>
<tr>
<td>NaH₂PO₄·3H₂O</td>
<td>20</td>
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controlled by plating time and determined by weight method.

A custom-designed multi-channel battery testing system, BT2000 as well as MITS Pro software (Arbin Instruments Corp., USA) were used to measure the electrode electrochemical performances. A saturated calomel electrode was applied to reference the negative electrode potential. Nafion® 117 was employed as the separator of the flow cell.

The surface morphologies of CF were examined by scanning electron microscope (SEM) in a JEM-1200EX (JEOL Ltd., Japan). Its physical details were summarized in Table 2. The specific surface area is estimated through filamentary analog as described in literature. Real-to-geometric area ratio means how much times of surface area could be gained from the apparent area of CF.

The operating conditions were as follows: electrode geometric area is 5 cm²; average thickness of electroless cobalt films is 66, 131 and 263 nm corresponds to 5, 10 and 20 mg cm⁻² loading, respectively; anolyte, 1.3 M Na₂S₅ catholyte, 4.0 M NaBr; constant current density of 40 mA cm⁻² during charging/discharging the cell; for polarization tests, charge to state of charge (SOC) 50%, record polarization curves, then discharge; for cycling experiment, charge to SOC of 20%, then discharge to 1.0 V.

3 Results and Discussion

The morphologies of CF before and after being deposited with catalyst are illustrated in Fig. 1. From the photographs of × 100 magnification in Fig. 1 (a) and (b), the CF shows an anisotropic medium consists of randomly dispersed fibers. No bridging and jointing of the fibers due to coating was observed (shown in Fig. 1 (b)).

Moreover, the coated carbon felt remained pliable and soft, which allows keeping the original compressibility of the felt. As can be seen in Fig. 1 (c), the original single fibers have a flat, cylinder shape, with shallow grooves along the long axis. After plating a cobalt deposit is formed as spherical grains that appear as very closely packed crystallites on the fiber surface, as shown in Fig. 1 (d). This irregular deposit further increased the active surface area compared with planar deposit case, thus may lead to lower overpotential, in return, higher energy efficiency of the battery. In fact, the deposit is the Co-P alloy not pure Co. Because the electroless solution contains, besides cobalt salts, reducing agent (NaH₂PO₃·H₂O), other complexing agent, and buffers (NH₄Cl, to maintain pH at 9.5) as shown in Table 1. After coating, an obvious bright metal layer containing phosphorous (P) under about 5 wt.% with cobalt metal in the layer, can cover firstly dispersed Pd for initiating the deposition of cobalt layer on the fiber surface of CF, and would become a continuous film if the plating time were longer enough (above 20 min.). We consider that the P containing in Co metal layer has no influence on the application performance of the material. The above results show the electroless plating is an effective method to deposit catalyst on CF. With the unchanged structure, increased active surface area and uniformly dispersed catalyst, the Co-CF was expected to be a high performance electrode material for polysulfide/sulfide couple.

Figure 2 illustrates the effects of catalyst loading on the negative electrode polarization. As can be seen from the curves of pure CF, the cathodic reaction is difficult to take place than the anodic reaction, which may due to the different reaction mechanisms in anodic and cathodic directions. The overpotential dropped significantly when felts coated with catalyst were employed, which can be assigned to the better electrochemical activity of
As shown in Fig. 3 (a), when using the Co-CF of 10 mg cm$^{-2}$ loading and the pure CF as negative and positive electrodes, respectively, average coulombic, voltage and energy efficiency were achieved by 97.0, 85.0 and 82.4%, respectively. The overall energy efficiency of the cell succeeded in remaining over 80%, which is really a great advancement upon activated carbon based electrode.$^{6,7}$

As shown in Fig. 3 (b), a cycling curve obtained demonstrates that the electrode succeeded in maintaining a stable voltage performance throughout the whole cycling test. Although a longer cycling test is needed, we can still draw a conclusion that the Co-CF is an efficient negative electrode material for PSB.

4 Conclusion

The Co coated carbon felt prepared by electroless plating was first applied in PSB and succeeded in meeting the design goal for high energy efficiency > 80%. The Co-CF seems to be a promising negative electrode material for PSB.

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References