Study of a high power density sodium polysulfide/bromine energy storage cell

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Abstract

Nickel catalyst supported on carbon was made by reduction of nickelous nitrate with hydrogen at high temperature. Ni/C catalyst characterization was carried out by XRD. It was found that the crystal phase of NiS and NiS₂ appeared in the impregnated catalyst. Ni/C and Pt/C catalysts gave high performance as the positive and negative electrodes of a sodium polysulfide/bromine energy storage cell, respectively. The overpotentials of the positive and negative electrodes were investigated. The effect of the electrocatalyst loading and operating temperature on the charge and discharge performance of the cell was investigated. A power density of up to 0.64 W cm⁻² (V = 1.07 V) was obtained in this energy storage cell. A cell potential efficiency of up to 88.2% was obtained when both charge and discharge current densities were 0.1 A cm⁻².

1. Introduction

The sodium polysulfide/bromine energy storage cell is based on regenerative fuel cell (RFC) technology. Two electrolytes flow through the cell on either side of a cation exchange membrane. The cell can work at room temperature. It has high efficiency, long life, low cost and is environmentally benign. It is modular and comparatively easy to site. These features make it suitable for large-scale energy storage applications [1–3].

The sodium polysulfide/bromine cell was first reported by Remick [4]. It was developed largely by the UK company Innogy. Using the sodium polysulfide/bromine cell technology, a 120 MWh, 15 MW energy storage plant is expected to be completed in 2003 [2]. The sodium polysulfide/bromine cell technology could be developed for submarine and ship applications as an alternative to the lead-acid battery [5].

Most of the electrodes for the polysulfide redox system are based on metallic sulfide [4, 6–9], carbon composition [10–12] and novel metals [13–15]. Only a modest current density of 10–20 mA cm⁻² at less than 50 mV overpotential was obtained for catalytic electrode surface layers of cobalt and MoS₂ [7]. To improve the electrochemical reaction area, reticulated copper sulfide or nickel sulfide for use as an electrocatalytic material of the polysulfide redox system was reported [9]. When operated at a current density of 40 mA cm⁻², the overpotential was 100 and 30 mV on charging and discharging the cell, respectively [9]. A carbon based electrode also showed modest performance. For the reduction of sulfur at 40 mA cm⁻² the overpotential was 40–75 mV [11]. Elemental sulfur may be formed during the oxidation of polysulfide ions and the deposited sulfur has a considerable effect on the electrode performance [13–15]. The electrodes for the Br₂/Br⁻ redox couple are mainly based on carbon [16, 17] and platinum [18]. The Br₂/Br⁻ electrode reaction is a version of a chemical–electrochemical (C–E) reaction [19]. The chemical reaction has little effect on the electrode kinetics at very slow homogeneous reaction rates, but has a more drastic effect on the electrode kinetics at faster homogeneous reaction rates [19].

2. Experimental

2.1. Electrode preparation and characterization

Ni/C catalyst for the negative electrode was made by reduction of nickelous nitrate with hydrogen at high temperature. Carbon powder (Vulcan XC-72, Cabot Corp.) was mixed with nickelous nitrate. The weight ratio of Ni to carbon was 1:1. The mixture was dried at 353 K. Then H₂ (flow of 200 cm³ min⁻¹) was fed to the dried mixture and heated at a rate of 2 K min⁻¹, to a final temperature of 773 K. After maintaining the temperature at 773 K for 30 min, it was cooled to room temperature in a H₂ atmosphere.

The negative electrode was prepared as follows: (i) Ni/C catalyst was added to ethanol and treated with ultrasonic agitation for 30 min; (ii) the prepared Ni/C in 50 wt.% ink and Nafion in 50 wt.% solution were mixed with ultrasonic agitation for 20 min; (iii) polyacrylonitrile graphite felt was boiled in 1.0 mol l⁻¹ sodium hydroxide solution, rinsed and dried; (iv) the mixture of
the nickel-dispersed carbon powder and Nafion solution was impregnated in the pretreated polyarylonitrile graphite felt and then dried in an oven at 393 K for 30 min under nitrogen atmosphere.

The preparation procedure of the positive electrode was the same as for the negative electrode. The mixture of Pt/C (10 wt.% Pt on XC-72 carbon powder) and Nafion solution was impregnated in the polyarylonitrile graphite felt and then dried.

The impregnated Ni/C catalyst was prepared by heating Ni/C in Na$_2$S$_4$ solution at 353 K for 6 h, rinsing in boiling water, boiling in NaOH solution, rinsing in boiling water and drying.

X-ray diffraction (XRD) was performed on a Rijaku D/MAX2400 diffractometer equipped with Cu K$_\alpha$ radiation operated at 40 kV and 100 mA. The scan speed was 4° min$^{-1}$ and the scan step was 0.02°.

2.2. Membrane pretreatment

A Nafion membrane was pretreated by boiling in 1 mol l$^{-1}$ H$_2$O$_2$ solution, rinsing in boiling water, boiling in 0.5 mol l$^{-1}$ sulfuric acid solution, rinsing in boiling water, boiling in 1.0 mol l$^{-1}$ sodium hydroxide solution and finally rinsing in boiling water.

2.3. Test station and cell configuration

Figure 1 is a schematic diagram showing the principles of the sodium polysulfide/bromine energy storage cell. During charging or discharging the cell, the electrolytes are pumped through two separate chambers of the cell and then flow into the storage tanks.

Figure 2 shows the cell configuration with reference electrode. The negative and positive electrodes were on two sides of Nafion membrane (Du Pont). The reference electrode consisted of a Pt/C catalyst layer and a diffusion layer near the working electrode. The polar plates were waterproof and carved parallel grooves served as flow channels. The frames, gaskets, tie-ins and pipelines were all made of polytetrafluoroethylene. Humidified hydrogen was fed to the reference electrode.

Some tests were carried out using a cell without a reference electrode. Its configuration was similar to that with the reference electrode. The difference between these two cells is that electrode area of the usual cell (5 cm$^2$) was slightly larger than that of the cell with a reference electrode (2 cm$^2$).

The negative and positive storage tanks were filled with nitrogen gas to negate the influence of oxygen. Unless otherwise mentioned, the operating conditions were as follows:

- The initial negative electrolyte was 2.0 mol l$^{-1}$ Na$_2$S$_2$ solution.
- The initial positive electrolyte was 1.0 mol l$^{-1}$ Br$_2$ dissolved in 2.0 mol l$^{-1}$ NaBr solution.
- The flow rates of two electrolytes were about 30 cm$^3$ min$^{-1}$.

3. Results and discussion

3.1. The principles of the sodium polysulfide/bromine energy storage cell

When the sodium polysulfide/bromine energy storage cell is discharging, the sulfide and lower polysulfide compounds are oxidized to corresponding higher polysulfide compounds on the surface of the negative electrode. The simplified electrochemical reaction on the negative electrode is

$$\begin{align*}
(x + 1)\text{Na}_2\text{S}_x & \rightarrow 2\text{Na}^+ + x\text{Na}_2\text{S}_{x+1} + 2\text{e}^- \quad x = 1 \sim 4
\end{align*}$$

(1)

Positive ions of sodium pass through the cation selective membrane from the negative to the positive side. Bromine is reduced to bromide ions:

$$\text{Br}_2 + 2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{NaBr}$$

(2)

The overall chemical reaction is as follows:

$$\begin{align*}
(x + 1)\text{Na}_2\text{S}_x + \text{Br}_2 & \rightarrow x\text{Na}_2\text{S}_{x+1} + 2\text{NaBr}
\end{align*}$$

(3)