Core-shell rhodium sulfide catalyst for hydrogen evolution reaction / hydrogen oxidation reaction in hydrogen-bromine reversible fuel cell

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HIGHLIGHTS

- Rh_xS_y-shell and Pt-core catalyst was synthesized for HOR/HER in H_2-Br_2 fuel cell.
- ECSA/mass of core-shell catalyst is 7 times that of commercial Rh_xS_y catalyst.
- The core-shell catalyst is more durable than Pt catalyst in H_2-Br_2 fuel cell.
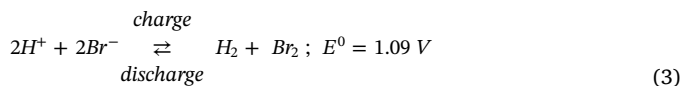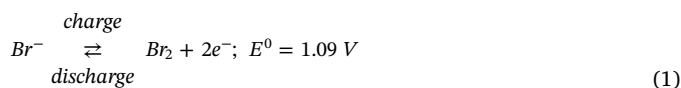
ARTICLE INFO

ABSTRACT

Synthesis and characterization of high electrochemical active surface area (ECSA) core-shell Rh_xS_y catalysts for hydrogen evolution oxidation (HER)/hydrogen oxidation reaction (HOR) in H_2-Br_2 fuel cell are discussed. Catalysts with Rh_xS_y as shell and different percentages (5%, 10%, and 20%) of platinum on carbon as core materials are synthesized. Cyclic voltammetry is used to evaluate the Pt-equivalent mass specific ECSA and durability of these catalysts. Transmission electron microscopy (TEM), X-ray Photoelectron spectroscopy (XPS) and Energy-dispersive X-ray spectroscopy (EDX) techniques are utilized to characterize the bulk and surface compositions and to confirm the core-shell structure of the catalysts, respectively. Cycling test and polarization curve measurements in the H_2-Br_2 fuel cell are used to assess the catalyst stability and performance in a fuel cell. The results show that the catalysts with core-shell structure have higher mass specific ECSA ($50\,m^2\ gm$-Rh^{-1}) compared to a commercial catalyst (Rh_xS_y/C catalyst from BASF, $6.9\,m^2\ gm$-Rh^{-1}). It also shows better HOR/HER performance in the fuel cell. Compared to the platinum catalyst, the core-shell catalysts show more stable performance in the fuel cell cycling test.

1. Introduction

Electrical energy storage technologies are needed when a significant fraction of intermittent renewable energy sources such as wind and solar are integrated into the electrical grids [1,2]. Compared with slower mechanical-to-electrical energy processes used in flywheel and compressed air storage system, the chemical-to-electrical energy conversion processes in electrochemical devices are almost instantaneous and much more efficient. Among the flow battery systems, the hydrogen-bromine (H_2-Br_2) regenerative fuel cell system is one of the promising technologies because of its high round-trip conversion efficiency, high power density capability and low cost [3]. The H_2-Br_2 fuel cell consists of three parts: the negative H_2 electrode, proton-conductive membrane and the positive Br_2 electrode. During charge, bromide ions from a solution of HBr are oxidized to bromine at the positive electrode. The H^+ ions from the HBr solution migrate across the proton

conducting membrane to the negative electrode and are reduced to hydrogen. The charge, discharge and overall reactions in this regenerative fuel cell are as follows:

$$Br^- \underset{discharge}{\overset{charge}{\rightleftarrows}} Br_2 + 2e^- ; \ E^0 = 1.09\ V \tag{1}$$

$$2H^+ + 2e^- \underset{discharge}{\overset{charge}{\rightleftarrows}} H_2 ; \ E^0 = 0\ V \tag{2}$$

$$2H^+ + 2Br^- \underset{discharge}{\overset{charge}{\rightleftarrows}} H_2 + Br_2 ; \ E^0 = 1.09\ V \tag{3}$$

In a hydrogen bromine fuel cell, while carbon can be used for the bromine reactions, a noble metal catalyst such as platinum is needed for

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the hydrogen reactions. While platinum is a highly active catalyst for hydrogen reactions, it is not stable in HBr/Br_2 environment [4,5]. Since HBr and Br_2 are expected to cross from the bromine electrode to the hydrogen electrode during operation, a more durable and active catalyst is needed. Rh_xS_y catalysts have been found to be stable in the HBr/Br_2 environment and shown similar specific areal activity as platinum [6–10]. Furthermore, due to the large particle sizes and broad particle size distributions (12–40 nm), commercial Rh_xS_y catalysts have low mass specific ECSA ($< 10\, m^2\, g^{-1}$) and activity for HOR [6,11]. To address this problem, we explored the core-shell approach used by others as a way to increase the mass specific ECSA of these Rh_xS_y catalysts [10]. In this work, platinum core-rhodium sulfide shell catalyst was synthesized and characterized by transmission electron microscopy (TEM), X-ray Photoelectron spectroscopy (XPS) and Energy-dispersive X-ray spectroscopy (EDX) techniques. Cyclic voltammetry (CV) was used for electrochemical characterization and electrochemically active surface area (ECSA) measurement. A hydrogen-bromine fuel cell was also assembled to test the HOR/HER activity of catalyst.

2. Experimental

2.1. Synthesis of rhodium sulfide catalyst with core-shell structure

The rhodium sulfide precursor synthesis process by Gulla and Allen [12] was used to synthesize the rhodium sulfide precursor shell. The rhodium (III) chloride hydrate ($RhCl_3 \cdot 3H_2O$) (Alfa Aesar) was dissolved in deionized water (DI water) and refluxed at 100 °C for 2 h. Pt/C powders with different percentages of Pt (5%, 10%, and 20%) were then added to the solution. The 5% Pt/C material was from Alfa Aesar and its carbon substrate was activated carbon. The 10% Pt/C material also was from Alfa Aesar and used graphite carbon substrate. The 20% Pt/C coming from E-TEK uses XC72r, a widely used graphite carbon substrate for fuel cell catalyst, as carbon substrate. The weight ratio of rhodium to platinum was 1.7:1. The mixture was sonicated for 2 h to disperse the solid. The sulfur source, $(NH_4)_2S_2O_3$, was added to the mixture, and the solution was refluxed at 100 °C for 2 h. During this time, Rh^{3+} cation and S^{2-} anion, which were generated from the dissociation of rhodium chloride and ammonia thiosulfate respectively, precipitated on the Pt cores. The Pt core-Rh_2S_3 shell precursors on carbon support were washed in DI water and dried at 100 °C overnight. Then it was converted to active phases by thermal treatment with purge of argon. The temperature of the thermal treatment was varied from 650 °C to 700 °C to obtain the most suitable composition.

2.2. Characterization

The morphology and chemical compositions of the samples were determined by a FEI Tecnai F20 XT Field Emission Transmission Electron Microscope (TEM) coupled with an energy-dispersive X-ray

spectrometer (EDX) at an acceleration voltage of 200 kV. The line-scans for the core-shell particles were measured during HAADF-TEM. The step intervals of the line-scans were 0.662 and 0.263 nm, respectively, and the resolutions of HAADF-TEM were 20 and 10 nm, respectively. X-ray powder (XRD) patterns were obtained using monochromated Cu-Kα radiation (λ = 1.54178 Å) on a Bruker Proteum diffraction system equipped with Helios high-brilliance multilayer optics, a Platinum 135 CCD detector and a Bruker Microstar microfocus rotating anode X-ray source operating at 45 kV and 60 mA. The scanning was done from 5 to 90° (2θ) with step size of 0.5°. In XPS measurements, the prepared catalysts were analyzed by a PHI 5000 Versa Probe II electron spectrometer with Monochromated Al as X-ray source. The XPS binding energies were measured with a precision of 0.2 eV. The analyzer pass energy was set at 23.5 eV. The take-off angle was 45° and the beam size was 100 μm. For each measurement, the XPS spectra were corrected to the internal reference spectra of C 1s at 284.5 eV to compensate for electrostatic charging.

2.3. Electrode preparation

A gas diffusion layer (GDL) was used as the support for the catalyst for cyclic voltammetry. The GDL (SGL-10AA) was cut into a 2 cm by 1 cm piece and then soaked in 2M HNO_3 solution to make it hydrophilic. After rinsing with DI water, the GDL was dried in an oven at 80 °C overnight and then weighed. A catalyst ink was prepared by sonicating a mixture of catalyst powder and isopropanol alcohol (IPA), ∼4 mg catalyst powder and 2 mL of IPA. The catalyst ink was applied onto one of the surfaces of the GDL with a brush. The gas diffusion electrode (GDE) was dried at 80 °C for 1 h and weighed. The weight difference between the GDE and GDL is the weight of catalyst coated on the electrode. Finally, 2%-wt Nafion solution was applied on the surface of the catalyst layer. Nafion was used as a binder for the catalyst layer. The GDE with Nafion coating was annealed at 135 °C for 5 min and allowed to cool to room temperature.

2.4. Cyclic voltammetry

All electrochemical measurements were made with a Gamry Instrument (G300 Potentiostat/Galvanostat/ZRA). Electrochemical measurements were carried out in a glass beaker filled with 1M H_2SO_4 with the GDE made in the above-mentioned procedure as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. The working electrode was held by the fixture shown in Fig. 1. Nitrogen gas was passed through the solution continuously during the CV scan. All measurements were at room temperature (∼22 °C) unless otherwise stated. The electrochemical active surface area (ECSA) of catalyst was calculated in comparison with platinum. The equation used to calculate the Pt equivalent ECSA is [13,14]:
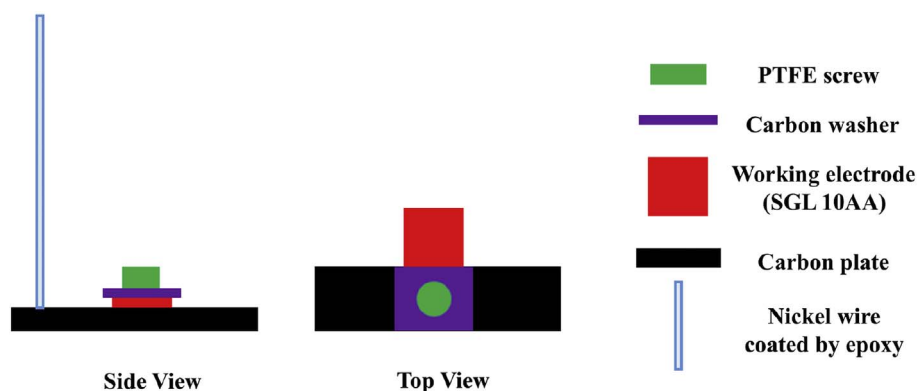

Fig. 1. Schematic of the fixture used to hold the working electrode.