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The effect of cobalt ion on the hydrogen evolution reaction in sulfate solution

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ABSTRACT

The effects of cobalt ion on the hydrogen evolution reaction (HER) in sulfate solution were studied by several electrochemical measurements, such as linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry. The charge transfer resistance and the apparent activation energy can be decreased with the cobalt ion adding into the sulfate solution. The calculated values of apparent activation energy are 43.4 kJ mol⁻¹ and 31.9 kJ mol⁻¹ for HER in the MnSO₄–(NH₄)₂SO₄ solution without and with cobalt ion respectively. At the same temperature, the charge transfer resistances become smaller when the cobalt ion present in the solution. The charge transfer resistance of HER decreases with the increasing concentration of cobalt ion. The results of X ray diffraction (XRD), Energy Dispersive Spectrometer (EDS) and scanning electron microscopy (SEM) indicate that metallic cobalt electrodeposited on the surface of the electrode. As a result of the cobalt electrodeposition, the surface property of the cathode is changed significantly and thus the hydrogen evolution reaction is promoted.

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Introduction

Due to the increased energy and environmental issues, hydrogen (H₂), as a potential candidate for the clean and sustainable energy, has attracted much attention of many researchers [1–3]. More and more researchers focus on its production methods [4]. In order to produce hydrogen, the materials with stable and low hydrogen over-potential properties are necessary [5–8]. In recent years, as an interesting non-noble metal, cobalt has shown its excellent catalytic power for hydrogen evolution [9,10]. Considerable research

efforts have been devoted to making cobalt as electrode materials or electro-catalysts for producing hydrogen [11–18]. The electrocatalytic activity for the hydrogen evolution reaction (HER) depended on the composition of the cobalt composite electrode, morphology and phase structure. The sphere-like Co₃S₄ exhibits better electrocatalytic activity than the dandelion-like Co₉S₈ for HER [16]. The hydrogen evolution efficiency from the cobalt cocatalyst can be comparable to those of systems containing the well-known platinum cocatalysts [18]. Cobalt composite electrode and cobalt electro-catalyst have both exhibited excellent performances.

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For some hydrometallurgical processes, such as electrolytic manganese and zinc, hydrogen evolution reaction is unavoidable. However, the current efficiencies of electrodeposited metals are always decreased due to the HER. In addition, the presence of impurities can further decrease the current efficiency of the electrodeposited metal, because the impurities, such as cobalt, zinc, nickel and copper, can be leached into aqueous solution from the metallic ore [19]. For the effect of cobalt on the current efficiency of manganese, Zosimovich et al. [20] pointed out that the manganese current efficiency decreased quickly for a stationary electrode, but slowly for a rotating disk. The similar results were obtained when we investigated the effect of impurities on the manganese electrodeposition. With the increasing concentration of cobalt ion, the current efficiency of manganese decreased dramatically. On the contrary, there was a marked improvement of current efficiency of hydrogen evolution reaction. Cobalt ion is bad for manganese electrodeposition, but it may be benefit for hydrogen evolution reaction. More attentions were paid on the current efficiency of manganese deposition and its quality at present [19]. However, the effect of cobalt ion on the hydrogen evolution in the electrolyte of manganese has not been given proper attentions.

In this paper, the effects of cobalt ion on HER in the sulfate solution were studied. At specified concentration of cobalt ion and temperature, the electrochemical parameters and the apparent activation energies of HER were calculated. In order to better understand the catalysis process of cobalt ion on the HER in the sulfate solution, the morphology and composition of the cathode were determined by scanning electron microscopy (SEM) and Energy Dispersive Spectrometer (EDS) and X ray diffraction (XRD).

Experimental

Electrochemical measurement

A CHI608D electrochemistry workstation and conventional three-electrode system were employed to carry out all the electrochemical experiments. A stainless steel (0.50 cm², 314L) electrode was used as the working electrode. The working electrode was polished by using sandpapers and degreased in alkaline solution (Na₂CO₃ 20 g L⁻¹, NaOH 20 g L⁻¹) and acetone, cleaned with ultrasonic washer for 20 min in purified water. A Pb/Sb/Sn/Ag quaternary alloy substrate (3 cm²) was used as a counter electrode. A saturated Hg/Hg₂SO₄ electrode was used as the reference electrode. This three-electrode system was always used to study the electrodeposition of manganese. In this paper, the aforementioned three-electrode system was used to study the hydrogen evolution reaction. The main components of the sulfate solution were (NH₄)₂SO₄ (100.0 g L⁻¹), MnSO₄ (55.0 g L⁻¹) and CoSO₄. The concentrations of CoSO₄ were 0.0 g L⁻¹, 1.0 × 10⁻³ g L⁻¹, 3.0 × 10⁻³ g L⁻¹, 5.0 × 10⁻³ g L⁻¹ respectively. Before the start of experiments, N₂ was used to get rid of oxygen. The pH of electrolyte was adjusted to 7.0 by using ammonium hydroxide or sulfuric acid. Linear sweep voltammetry (LSV) curves were recorded at 2.5 mV s⁻¹ scan rate in range of -1.0 V to -1.7 V. Cyclic voltammetry (CV) curves were recorded at 20 mV s⁻¹ scan rate in

range of -0.2 V to -1.7 V. The EIS was carried out at various frequencies in range of 1 Hz–10⁵ Hz with AC voltage amplitude of 5 mV peak-to-peak. The chronoamperometry experiment was carried out at -1.5 V for 100 s. Then the potential was switched to -0.8 V and maintained for 100 s. The temperature and pH value were 313 K and 7.0 respectively.

Morphology and crystal measurement

Scanning electron microscopy was used to examine the surface of stainless steel electrode. Crystallographic structure was determined by X ray diffraction with graphite monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV) in the 2 θ range of 20°–80° at a scan rate of 8.0000° min⁻¹.

Results and discussion

Polarization measurements

Effect of temperature

The effect of temperature on the HER at the stainless steel electrode in MnSO₄–(NH₄)₂SO₄ solution was investigated by steady polarization curves. In the range of studied potential, only the HER occurred on the cathode. Fig. 1 shows that the relationship between the current density and temperature. As shown in Fig. 1, it is easy to know that the HER is promoted by temperatures. The values of exchange current densities at different temperatures were extrapolated. The Arrhenius plot is shown in Fig. 2. The apparent activation energy for the hydrogen evolution reaction can be calculated by using the Arrhenius equation [21,22].

$$E_a = -2.303R[d(\lg i_0)/d(T^{-1})] \quad (1)$$

where E_a , i_0 and T are the apparent activation energy, exchange current density and absolute temperature, respectively. R is the gas constant (8.314 J (mol K)⁻¹).

The activation energy of the HER in the MnSO₄–(NH₄)₂SO₄ solution on stainless steel, which can be calculated from Eq. (1), was 43.4 kJ mol⁻¹. The calculated value of E_a is higher than

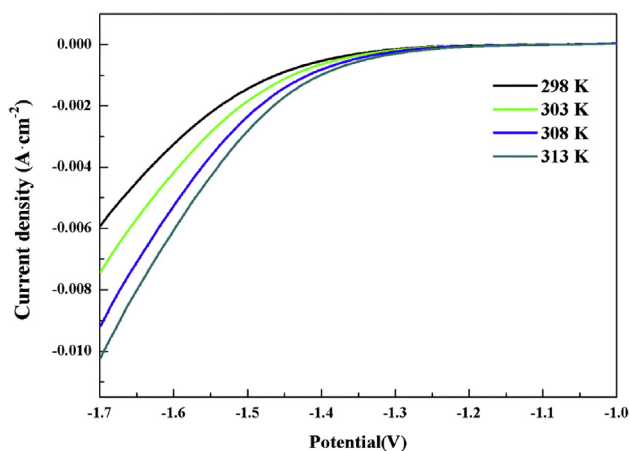


Fig. 1 – LSVs for the HER at different temperatures in MnSO₄–(NH₄)₂SO₄ solution.

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