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Electrochemical oxide sulfide in an air-cathode fuel cell with manganese oxide/graphite felt composite as anode

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ABSTRACT

Sulfide found in wastewaters and industrial off-gases is a toxic and highly corrosive pollutant. The air-cathode fuel cell has great potential for simultaneous elemental sulfur (S_0) and electricity recoveries from sulfide. Here, manganese oxide (MnO_x) is in-situ synthesized on graphite felt (GF) surface in a solvothermal system at different ethanol/water (E/W) volume ratios, and the prepared MnO_x/GF composites are used as the anodes of air-cathode fuel cell for spontaneous sulfide electrochemical oxidation. The performance of these MnO_x/GF composite anodes is comprehensively evaluated in term of sulfide removal, sulfur recovery and electricity production efficiencies. The results show that the manganese oxide loading on the GF presents as MnO_2 at E/W ratio of 0/10. When the E/W ratio is greater than 3/7, the obtained manganese oxides are all Mn_3O_4 and its particle size and loading on the GF decrease with the increase of ethanol concentration. The Mn_3O_4/GF composite prepared at E/W ratio of 3/7 has a great potential in catalyzing the electrochemical oxidation of sulfide in the air-cathode fuel cell. Compared with GF, the Mn_3O_4/GF composite anode shortens the time for complete sulfide oxidation from 120 h to 60 h. Meanwhile, the sulfur recovery efficiency and coulombic efficiency are as high as 78.4% and 71.5%, respectively.

1. Introduction

Sulfide is ubiquitously present in wastewaters and as gaseous hydrogen sulfide in waste gases. The removal of sulfide is necessary due to its corrosivity and toxicity. Sulfide is typically removed via precipitation or oxidation processes, which are effective in reducing sulfide concentration to satisfy the stringent water and gas discharge standards [1–4]. However, these approaches demand a substantial energy and chemical agents. The recovery of valuable element sulfur (S_0) and the capture of chemical energy stored in sulfide are therefore pursued to offset the energy and chemicals consumption in sulfide treatment.
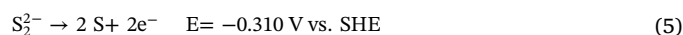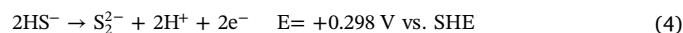
The spontaneous electrochemical oxidation of sulfide by air-cathode fuel cell technology is desirable for simultaneously recovering S_0 and producing electricity at ambient temperature [5–7]. The working principle of such a device is based on the spontaneous electron transfer from the sulfide at the anode to the oxygen at the cathode via an external circuit [8]. Ideally, in order to recover S_0 from sulfide the reactions occurring at the anode and cathode should follow Eqs. (1) and (2):

$$HS^- \rightarrow S + H^+ + 2e^- \quad (1)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (2)$$

Thus the overall reaction is:

$$O_2 + 2H^+ + 2HS^- \rightarrow 2H_2O + 2S \quad (3)$$

However, sulfur has many possible oxidation states which are involved in several parallel or consecutive electrochemical equilibriums that can occur simultaneously [9,10]. Eqs. (4)–(7) summarize other side reactions that might occur at the anode of air-cathode fuel cell:

$$2HS^- \rightarrow S_2^{2-} + 2H^+ + 2e^- \quad E= +0.298 \text{ V vs. SHE} \quad (4)$$

$$S_2^{2-} \rightarrow 2S + 2e^- \quad E= -0.310 \text{ V vs. SHE} \quad (5)$$

$$2S + 3H_2O \rightarrow S_2O_3^{2-} + 6H^+ + 4e^- \quad E= +0.165 \text{ V vs. SHE} \quad (6)$$

$$HS^- + 4H_2O \rightarrow SO_4^{2-} + 9H^+ + 8e^- \quad E= +0.252 \text{ V vs. SHE} \quad (7)$$

Therefore, an array of products involving S_0, polysufide or sulfur oxyanions can be produced from the electrochemical oxidation of sulfide in the air-cathode fuel cell. The distribution of final products is highly dependent upon the type of electrode as well as electrolytic conditions. The electrochemical oxidation of sulfide at the carbon anode could produce S_0, polysufide, thiosulfate ($S_2O_3^{2-}$) and tetrathionate ($S_4O_6^{2-}$) [11], while SO_4^{2-} is the main product from sulfide oxidation at boron-doped diamond electrode [12]. In our previous work, the effect of pH on the electrochemical oxidation of sulfide was investigated, and the results showed that neutral pH was optimum for

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recovering both the S_0 and electricity [8].

The transition metal manganese can exist in a variety of readily oxidation states ranging from 0 to +7. The flexible variations in its local bonding configuration give rise to manganese oxides as diverse as MnO, Mn_2O_3, Mn_3O_4 and MnO_2 [13]. Notably, the facile inter-conversion between Mn (II), Mn(III) and Mn (IV) valences endows these manganese oxides with exceptional catalytic activities in the field of electrochemistry [14–16]. Therefore, in this work the feasibility of manganese oxides in catalyzing the electrochemical oxidation of sulfide is evaluated. Manganese oxide-loaded graphite felt (MnO_x/GF) composites were fabricated in a solvothermal system. MnO_2/GF and Mn_3O_4/GF composites with different structures, compositions and morphologies were obtained at different ethanol/water (E/W) ratio. The performance of these MnO_x/GF composites as the anode of air-cathode fuel cell for sulfide oxidation is comprehensively evaluated in terms of sulfide removal, sulfur recovery and electricity production. The results demonstrate the great potential of Mn_3O_4/GF composite in catalyzing the electrochemical oxidation of sulfide into S_0 in the air-cathode fuel cell.

2. Experimental

2.1. Fabrication of MnOx/GF composite

Manganese oxide was loaded on the GF by solvothermal method. Briefly, the GF ($4 \times 2.5\,cm^2$, 2 mm in thickness) was pretreated in a mixed acid solution (HNO_3: H_2SO_4, 1:1, v/v ratio) at 100 °C for 1 h, and then immersed in 40 mL of ethanol water which contained 0.4 g of $KMnO_4$. According to experimental design, the E/W volume ratio in ethanol water was 0/10, 3/7, 6/4, 9/1 and 10/0, respectively. The solvothermal reaction was conducted in a 50 mL sealed Teflon-lined stainless steel autoclave at 120 °C for 24 h. Next, the GF loaded with manganese compound was thermally treated at 350 °C for 2 h to obtain the MnO_x/GF composite. The resulting products are denoted as E0, E3, E6, E9 and E10, respectively.

2.2. Characterization of the MnOx/GF composite

Crystalline phase of the MnO_x/GF composite was identified by X-ray diffractogram (XRD) using a Bruker D8 advance-X-ray diffractometer equipped with graphite-monochromated Cu Kα radiation ($\lambda = 1.54178\,\text{Å}$). Valence states of manganese in the composite were determined using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250 spectrometer (Thermo, USA) equipped with a monochromatic Mg Kα X-ray source (1253.6 eV). The C1s electron binding energy corresponding to graphitic carbon was set at 284.6 eV and used as a reference to position the other peaks on the XPS spectra. Loading weight of MnO_x on the GF was determined by thermogravimetry (TG) on a TGA DT-50 apparatus (Sahimadzu, Japan). The TG was performed from room temperature to 1000 °C at a heating rate of $10\,°C\,min^{-1}$ under air atmosphere. Microscopic images of the composite were obtained using a Sirion 200 scanning electron microscope (SEM) (FEI Co., Netherlands). Element distribution on the surface of GF was characterized by field emission scanning electron microscopy (FESEM) (Zeiss SIGMA, Germany). The composites was cut into $5 \times 5\,mm^2$ pieces for SEM and XRD analyses, and were ground into powders for TG and XPS analyses.

2.3. Oxidation of sulfide in an air-cathode fuel cell

Sulfide was electro-oxidized at the anode of a 175 mL single-chamber air-cathode fuel cell as previously described [8]. The MnO_x/GF composite was used as the anode electrode and a $2 \times 2\,cm^2$ Pt-coated carbon paper ($0.05\,mg\,cm^{-2}$ Pt catalyst on one side) was the cathode electrode. The coated side of the cathode was positioned facing the proton-exchange membrane (GEFC-10N, GEFC Co., China), and the
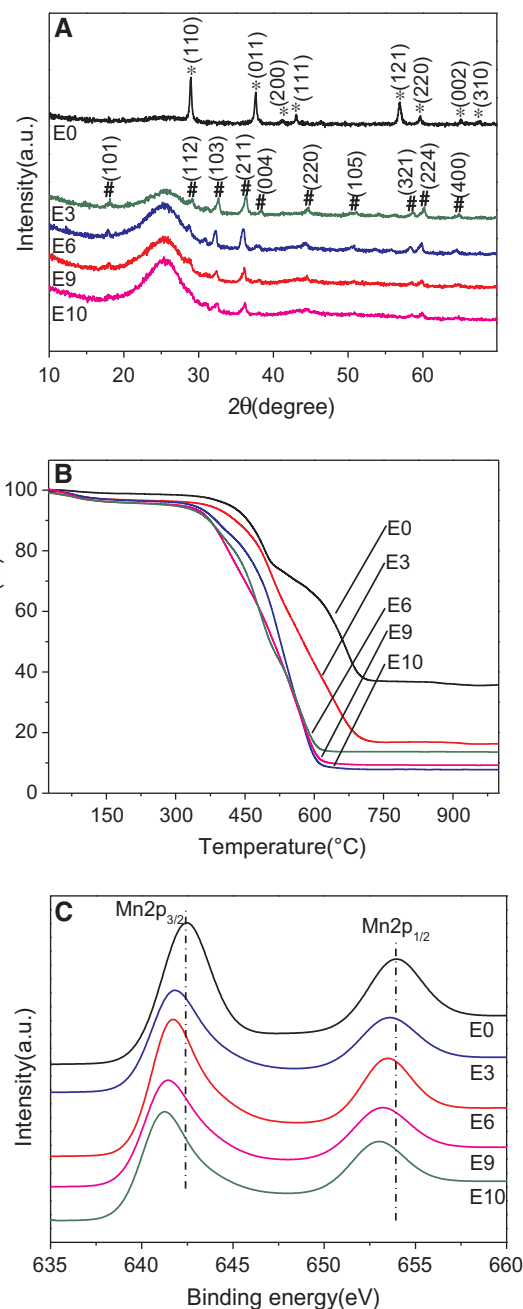

Fig. 1. The XRD patterns (A), TG curves (B) and XPS spectra of MnO_x/GF composites prepared at different E/W volume ratios.

uncoated side was directly exposed to air. The anodic chamber was filled with 150 mL of solution containing 0.20 M NaCl electrolyte and 0.05 M phosphate buffer, and then purged with nitrogen to remove dissolved oxygen. Solution pH was adjusted to 7.0 and the Na_2S stock solution (iodometrically standardized) was added into the chamber at 10 mM. The fuel cell was started by connecting the circuit with a 100 Ω resistor. Voltage across the resistor was recorded at 10 min intervals by an Agilent 34972A data acquisition system. The current was calculated using Ohm's law, and the total number of charges was obtained by integrating the current over time. The coulombic efficiency (CE) was determined based on the assumption that 2 mol of electrons were available from the oxidation of 1 mol of sulfide with S_0 as the product.