



Short Communication

Studies on polymer modified metal oxide anode for oxygen evolution reaction in saline water



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ABSTRACT

Since most of the water source on the earth surface is saline in nature, hydrogen generation from saline water is of great importance. In this paper, we have developed a membrane protected anode, using anionic backbone of sulfonated polystyrene-block-(ethylene-ran-butylene)-block-polystyrene polymer (S-PSEBS) over the anode (IrO₂/Ti) which is capable of electrostatically repelling the chloride ions (Cl⁻) from the electrode surface and thereby enhancing the oxygen evolution rather than the chlorine evolution. The electrochemical behavior of both polymer modified and bare IrO₂/Ti electrodes were characterized by electrochemical polarization studies and the gas evolution efficiencies were calculated. The surface morphology of the electrodes was investigated using scanning electron microscope (SEM). The results suggest that nearly 95% oxygen evolution efficiency could be achieved when the surface of IrO₂/Ti electrode was modified with a permselective membrane.

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1. Introduction

Hydrogen has great potential as an environmentally clean energy fuel. When hydrogen is utilized as fuel (either in fuel cells or internal combustion engines) the only by-product generated will be water. Hydrogen is available in both renewable (water) and non-renewable (fossil fuel) forms. However, the existing hydrogen production from non-renewable sources is inadequate to sustain its extensive use for energy purposes. Hence, effective generation of hydrogen from renewable sources is essential for the so-called hydrogen economy [1,2]. While hydrogen can be produced by several methods, water electrolysis is a clean and simple way of producing hydrogen from renewable energy sources such as solar, wind and hydroelectric power. Water electrolysis can be classified based on their electrolytes, namely, alkaline, acidic (using proton exchange membrane {PEM}) and solid oxide electrolyte. Alkaline electrolysis is a well established method for producing hydrogen and research and development efforts are focused to improve the efficiency of such electrolyzers to minimize the use of electricity and to increase the current density to reduce the investment cost [3–6]. PEM electrolysis is less common and normally utilizes expensive materials such as noble metal catalysts and

sulfonated polymers as electrolyte [7–10]. PEM based steam electrolysis could also reduce the energy cost compared to liquid electrolysis [11]. Solid oxide electrolysis is operated at elevated temperatures, and it is too premature to compare it with other systems [12]. The main obstruction for the development of solid oxide electrolyzer is poor stability of the electrolysis cell [13] and research and development is focused to minimize the electrolyte aging and electrode deactivation.

Recently, manganese dioxide coated IrO₂ anodes for saline water electrolysis that preferentially evolve oxygen over chlorine have been developed [14,15–17]. The reason for the selective oxidation of water by the manganese dioxide coated electrode is yet unclear. However, it appears that the MnO₂ film may act as a diffusion barrier layer for chloride ions. Therefore, we speculated that if we could prevent chloride anions from accessing to the electrode surface by electrostatic repulsive forces, this might be effective in enhancing oxygen evolution and suppressing chlorine evolution. This could be possible by applying a cation selective (i.e. anionic backbone) coating on the electrode surface. In this paper, we have explored the anionic backbone of the sulfonated polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (S-PSEBS) polymer as a permselective layer on IrO₂/Ti anode to prevent chloride anions to the anode surface. The performances of both polymer coated and uncoated IrO₂/Ti anode have been compared for saline water electrolysis.

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2. Experimental

2.1. Preparation of sulfonated PSEBS polymer

Polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (PSEBS) was obtained from (Aldrich, Germany) and sulfonated form of the polymer was synthesized by adopting our previous method [18]. Briefly, PSEBS polymer was sulfonated using chlorosulfonic acid (CSA) as a sulfonating agent. The required amount of polymer was dissolved in chloroform and the solution was allowed to cool in an ice bath. The required amount of tri-butyl phosphate (to moderate the reaction) was added. Then CSA was added drop-wise with continuous stirring. The reaction was carried out in nitrogen atmosphere for 3 h, and it was terminated using methanol. The polymer was dried by solvent evaporation method. The ion exchange capacity (IEC) of the polymer was estimated to be about 0.01–0.02 meq/g (Ion conductivity- 10^{-3} S/cm). The degree of sulfonation (DS) was found to be 13%. The structure of the polymer is shown in Fig. 1.

2.2. Preparation of IrO₂/Ti and S-PSEBS/IrO₂/Ti electrodes

IrO₂/Ti electrode was prepared by etching titanium anode in boiling aqueous oxalic acid (10 wt.%) for 10 min and then de-greased with isopropanol. Chloroiridic acid (0.1 mol/dm³) in propanol was applied on this pretreated titanium substrate (area 2.0 cm²). The solvent was evaporated by heating at 90 °C and the resulting electrode was calcinated at 450 °C for 10 min under air stream. The polymer coated iridium oxide (S-PSEBS/IrO₂/Ti) electrode was prepared by dissolving S-PSEBS (concentration 2.7×10^{-2} mol/dm³), in tetrahydrofuran (THF) and 250 μ L of this solution was coated on prepared IrO₂/Ti electrode and dried for 10 min.

2.3. Electrochemical characterization of IrO₂/Ti and S-PSEBS/IrO₂/Ti electrodes

The electrochemical behavior of the electrodes were examined by cyclic voltammetry and potentiodynamic polarization method in a three electrode cell assembly using Ag/AgCl as reference electrode and platinum foil as counter electrode respectively. Electrolysis was performed in an undivided glass cell of 100 mL volume using IrO₂/Ti and S-PSEBS/IrO₂/Ti electrodes as anodes and platinum gauze as the cathode in 0.5 M sodium chloride electrolyte maintained at 30 °C and pH 8.3 for 30 min for various current densities. The oxygen evolution efficiency was determined by subtraction of the chlorine evolution efficiency from 100% and was estimated by conventional iodometric titration method [19].

3. Results and discussion

The surface morphology of the prepared electrodes was examined by scanning electron microscope [SEM; Hitachi model S-3000H]. Fig. 2 shows SEM image of polymer coated IrO₂/Ti before electrolysis. As can be seen the polymer coating is uniform since

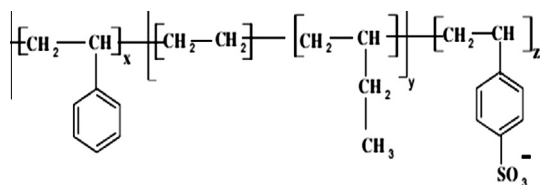


Fig. 1. The structure of sulfonated polystyrene-block-(ethylene-ran-butylene)-block-polystyrene (S-PSEBS) polymer.

cracks are not to be observed, IrO₂ surface is completely covered with S-PSEBS polymer layer.

Fig. 3 shows a typical cyclic voltammogram recorded at a scan rate of 50 mV/s for IrO₂/Ti and S-PSEBS/IrO₂/Ti electrodes. The voltammetric curves of both the electrodes show two broad humps due to the redox processes of Ir(III)/Ir(IV) and Ir(IV)/Ir(V) as detailed in reference [20]. The marginal decrease in current was observed with S-PSEBS/IrO₂/Ti electrode is due to the electrical resistance offered by the S-PSEBS film on IrO₂/Ti electrode. Except decrease in current the electrochemical behavior of the S-PSEBS polymer coated electrode was similar to bare IrO₂/Ti electrode. Therefore, the redox behavior of the IrO₂ was not affected by S-PSEBS coating. Fig. 4 shows the potentiodynamic anodic polarization curves of IrO₂/Ti and S-PSEBS/IrO₂/Ti electrodes. It is observed that the polarization current density of a bare IrO₂ electrode (IrO₂/Ti) is higher than S-PSEBS coated IrO₂ electrode (S-PSEBS/IrO₂/Ti). The decrease in current density of the S-PSEBS coated electrode is due to the intercalation of ions being impeded from the solution [below the thermodynamic water splitting potential (1.23 V)] [21–22]. However, gas evolution in the case of polymer modified anode is predominantly oxygen. In the case of bare iridium oxide coated electrode, evolution of oxygen and chlorine take place. The chlorine and oxygen evolution efficiencies of IrO₂/Ti electrode as a function of operating current densities is shown in Fig. 5. The oxygen evolution efficiency of IrO₂/Ti is 26%

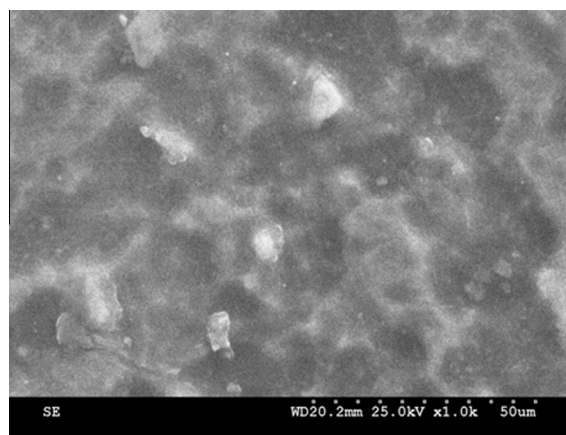


Fig. 2. SEM image of S-PSEBS coated IrO₂/Ti electrode (S-PSEBS/IrO₂/Ti).

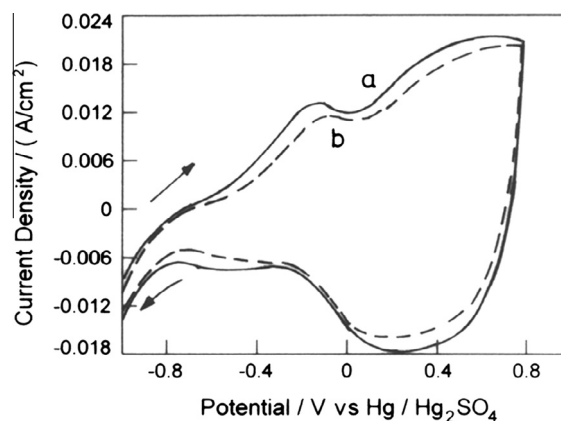


Fig. 3. Cyclic voltammogram curve of IrO₂ electrodes (a) IrO₂/Ti (black solid line) and (b) S-PSEBS polymer coated on IrO₂/Ti electrode (black dashed line) in 0.5 M H₂SO₄ recorded at a scan rate of 50 mV s⁻¹.

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