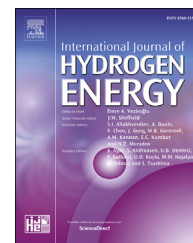




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Electrochemical hydrogenation of organic sulfides



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ABSTRACT

Electrochemical reduction desulfurization is a low cost, environmental friendly technology which is capable of achieving a high degree of automation. Electrochemical coupling reactions of organic sulfur hydrogenation and water electrolysis on the C/Nafion electrodes were performed. The electrochemical desulfurization was determined by cyclic voltammetry (CV), bulk electrolysis with coulometry (BEC) and electrochemical impedance spectroscopy (EIS) techniques. Thiophene and benzyl mercaptan were used as model organic sulfur compounds. The results of cyclic voltammetry showed that the electrochemical hydrogenation reduction reaction of thiophene occurred at about -0.35 V. The process included proceeding chemical reaction and electrochemical reaction. The currents generated from thiophene hydrogenation reactions increased with the reaction temperature and the H^+ concentration of the electrolyte acidity of anode. Under the same reaction conditions, the desulfurization efficiency of benzyl mercaptan was significantly higher than that of thiophene. From the products of electrolytic reactions, the mechanisms of electrochemical hydrogenation of thiophene were proposed, consisting of two pathways: ring opening followed by hydrogenation and directly hydrogenation followed by ring opening. The proposed reaction mechanisms were consistent with the EIS results, indicating the predominant reactions were ring opening followed by hydrogenation. The reaction products and EIS results suggested that the reaction mechanisms of electrochemical hydrogenation of benzyl mercaptan were by breaking C–S bond to form H_2S and toluene.

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Desulfurization technologies are environmental processes readily used in refining and petrochemical. Hydrodesulfurization (HDS) is a mature technology which operates under a relatively severe reaction condition; hence it is an energy intensive process. Also, the economic feasibility of HDS is dependent on the supply of hydrogen. In view of reducing greenhouse gas emissions, tremendous efforts have been devoted to improve and optimize the HDS technology, as well as to explore novel desulfurization technologies [1–6].

Among the emerging desulfurization technologies, electrochemical hydrogenation desulfurization (EHDS) is a low cost, environmental friendly technology which is capable of achieving a high degree of automation.

Introduction

In electrochemical reduction desulfurization, sulfur compounds are electrochemically reduced to form H_2S on the

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cathode under mild reaction conditions, which can be easily separated from the reaction system. Desulfurization of fossil fuels by electrochemical reduction were reported for various reaction systems [7–19]. Shu et al. [8,9] investigated a desulfurization process via NaBO_2 electro-reduction with pulse voltage using a boron-doped diamond (BDD) thin film electrode. It was an indirect hydrogenation method in which H_2O (hydrogen source) and NaBO_2 (medium) were converted into NaBH_4 on BDD electrodes. The C–S bonds in organic sulfide were reduced to C–H bonds and S^{2-} by NaBH_4 on Ni^{2+} catalyst at the cathode region. The NaBH_4 was converted to NaBO_2 and involved in the following reduction desulfurization process.

Baez et al. [10–12] have inventions about desulfurization process of hydrocarbon feeds using electrolytic hydrogen. The EHDS process for removing sulfur from hydrocarbon feeds involved divided cell which separated by metallic membrane. The hydrogen source (H_2O) was fed and oxidized at the anode to provide protons to the cathode through the membrane. The protons reacted with hydrocarbon feed containing organic sulfide to form H_2S . Hence, a sulfur-free treated hydrocarbon was produced at the cathode. The reported desulfurization efficiency of thiophene in heptane was above 40% at 333 K and 24-h reaction time using palladium black metal mesh as cathode, platinum as anode and 0.1 mol/L NaOH electrolyte. This process has a wide range of reaction temperatures because of durable metallic membrane.

Greaney [13–18] designed a heavy oil electro-desulfurization process using a divided electrochemical cell which was separated by an ionic permeable membrane. The heavy oil and hydrogen were pressurized and heated at the cathode side of the electrochemical cell. The sulfur compounds in the heavy oil were reduced and formed H_2S . The H_2S can be fed directly into the anode side of the electrochemical cell to produce sulfur and hydrogen, or passed to an oxidation zone containing an aqueous solution of an oxidized metal salt. The desulfurization efficiency of dibenzothiophene (DBT) under 2 MPa H_2 in dimethyl sulfoxide (DMSO) solvent with tetrabutylammonium hexafluorophosphate (TBAPF_6) electrolyte was greater than 16% at 498 K, 4.5 V voltage and 3.5 h reaction time at 300 rpm stirring speed.

In this work, the proposed electrochemical coupling reactions of organic sulfur hydrogenation and water electrolysis were based on the learnings from previous studies on a benzene-water hydrogenation reaction system [20–22]. Thiophene and benzyl mercaptan were model organic sulfur compounds, which were used to demonstrate the reduction desulfurization reactions of organic sulfur on the C/Nafion electrodes. Protons produced in the anode region by electrolysis of water, transferred to the cathode region through a proton exchange membrane. Desulfurization of organic sulfur by reacting with active protons, occurred in the cathode region. The hydrogen sulfide generated was further converted to elemental sulfur by oxidation of high valence cations. The reaction mechanisms and kinetics of electrochemical reduction desulfurization were determined. The desulfurization efficiency and operating conditions of the coupling reactions were discussed.

Experimental

Materials

Polytetrafluoroethylene (PTFE) latex, 5% Nafion solution, and Nafion[®]117 membranes were obtained from DuPont Company. Analytical grade octane, thiophene, benzyl mercaptan were obtained from the Beijing Chemical Plant. Carbon cloth with 3 K vertical textures was used.

Preparation of C/Nafion electrodes

The C/Nafion electrodes were prepared by hot pressing treated carbon cloth and pretreated Nafion 117 membrane at 0.5 MPa for 10 min at 175 °C [21].

Electrolysis and performance indicator

The C/Nafion electrode was used the working electrode and Pt was the counter electrode. The anode and cathode were separated by C/Nafion electrode. The electrolyte acidity of anode was at a set concentration of H_2SO_4 , whereas organic sulfides solution (purified octane as solvent) was in the cathode chamber. The cell was held at a constant temperature in a water bath. The main reaction was organic sulfides hydrogenation on the cathode. The electrons produced during the water electrolysis from the external circuit reached the cathode, were used by hydrogenation reactions. Protons produced in anode region by electrolysis of water, transmitted into cathode region through proton exchange membrane. The schematic diagram of the electrochemical reduction desulfurization reaction system was shown in Fig. 1.

A CS350 electrochemistry test station was used to measure alternating current impedance (AC impedance). The data of

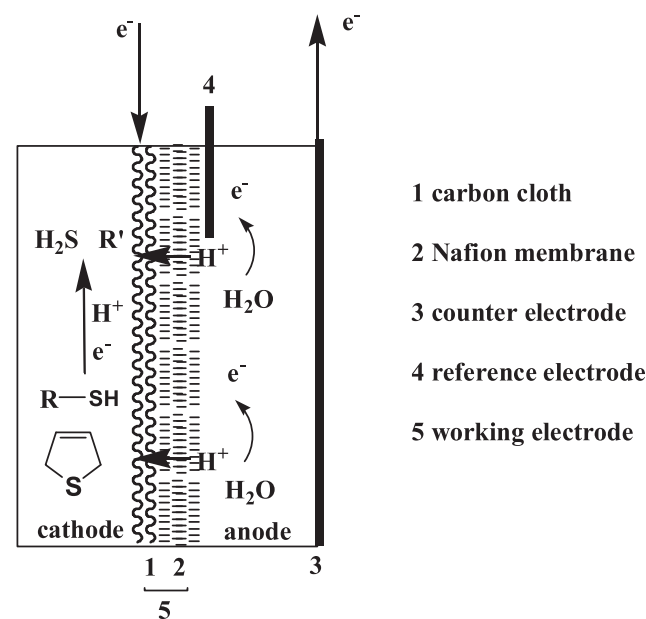


Fig. 1 – Schematic diagram of the electrolyte cell.

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