

Electrochemical hydrogenation of thiophene on SPE electrodes

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Abstract. Electrochemical reduction desulfurization is a promising technology for petroleum refining which is environmental friendly, low cost and able to achieve a high degree of automation. Electrochemical hydrogenation of thiophene was performed in a three-electrode system which SPE electrode was the working electrode. The electrochemical desulfurization was studied by cyclic voltammetry and bulk electrolysis with coulometry (BEC) techniques. The results of cyclic voltammetry showed that the electrochemical hydrogenation reduction reaction occurred at -0.4V. The BEC results showed that the currents generated from thiophene hydrogenation reactions increased with temperature. According to Arrhenius equation, activation energy of thiophene electrolysis was calculated and lower activation energy value indicated it was diffusion controlled reaction. From the products of electrolytic reactions, the mechanisms of electrochemical hydrogenation of thiophene were proposed, consisting of two pathways: opening ring followed by hydrogenation, and hydrogenation followed by ring opening.

1. Introduction

The sulfur emissions from combustion of fossil fuels are detrimental to environment and human health. In petroleum refining industry, desulfurization processes are commonly used to produce low sulfur transportation fuels, such as gasoline and diesel. Catalytic hydrodesulfurization (HDS) is a mature technology which operates under a relatively severe reaction condition; hence the process operating costs are high. As a result, tremendous efforts have been devoted to improve and optimize the conventional HDS technology, as well as to explore new desulfurization technologies for producing low sulfur gasoline and diesel.[1-6] Among the new desulfurization technologies, electrochemical desulfurization is a promising technology which is environmental friendly, low cost and able to achieve a high degree of automation.

There are two types of electrochemical desulfurization: electrochemical oxidation desulfurization and electrochemical reduction desulfurization. In electrochemical oxidation desulfurization, sulfur compounds are oxidized and transform to sulfoxides or sulfones. Due to their polarity changes, sulfoxides or sulfones can be removed by adsorption or extraction process. In electrochemical reduction desulfurization, sulfur compounds are electrochemically hydrogenated on the cathode under mild reaction conditions.[7-11] The reaction mechanisms of electrochemical reduction desulfurization needs further studies.



Organic sulfur compounds are common sulfur compounds in petroleum, among which thiophenic compounds are dominant. Thiophenes account for 90% and 80% of total sulfur compounds in gasoline and diesel, respectively. These compounds have relatively stable molecular structure and are refractory to desulfurization processes. In this paper, electrochemical hydrogenation reactions of thiophene on SPE electrode were investigated. Protons produced in the anode region of SPE electrode by electrolysis of water, transferred to the cathode region through a proton exchange membrane. Desulfurization of thiophene by reduction reactions occurs in the cathode region of the electrolytic tank. The hydrogen sulfide generated is further converted to elemental sulfur by oxidation of high valence cations.

2. Experimental

2.1. Materials

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

2.2. SPE Electrodes Preparation

SPE electrodes were prepared by hot pressing treated carbon cloth and pretreated Nafion 117 membrane.[12] SPE electrodes were hot pressed at 0.5 MPa for 10 min at 175 °C.

2.3. Electrolysis and Performance Indicator

The SPE electrode was the working electrode and Pt was the counter electrode. The anode and cathode were separated by SPE electrode. The electrolyte acidity of anode was 0.5 mol/L H₂SO₄ and thiophene solution (octane as solvent) was in the cathode chamber. The cell has a constant temperature by circulation constant temperature water bath. The main reaction was thiophene hydrogenation on the cathode. The electrons produced during the water electrolysis from the external circuit reached the cathode where they were used by hydrogenation reactions.

A CHI650A electrochemistry test station was used to measure the cyclic voltammograms and the current of the process with the bulk electrolysis coulometry (BEC) curve. In-situ cyclic voltammetry was conducted by cycling the potential at various scanning rates (300, 200, 150, 100, 75, 50, 30, 15, and 10 mV/s) between 1.2 and -1.0 V until a stable voltammogram was obtained. The potential (E) denotes the working electrode potential versus saturated calomel electrode (SCE) as a reference electrode.

The composition changes of thiophene electrolysis were analyzed by Agilent 7890 gas chromatography (GC-SCD) and Agilent 7890A 5975C gas chromatography-mass spectrometry (GC-MS).

3. Results and Discussion

Figure 1 shows the cyclic voltammetry curves of octane and thiophene-octane solution in the range of -1.0~1.2V. The results showed that there was no redox peak of octane, whereas there were an oxidation peak and a reduction peak of thiophene-octane solution system, which were redox couples. The electrochemical reduction reactions of thiophene at the SPE electrode occurred at -0.350V and reduction reaction products oxidized at 0.106V with the change of the scanning potential.

The peak potential and peak current at various cyclic voltammetry scanning rates from 10 to 300 mV/s are shown in Table 1. The reduction peak shifted to the negative potential and the oxidation peak of anode moved to the positive potential with increased scanning rate. The electron transfer rate increased with increased scanning rate. At a constant diffusion rate, the peak current exhibited a lag phenomenon because the concentration of substance though diffusion to the electrode cannot be provided in time. Hence, these two peaks moved away from the equilibrium potential. At the same time, the $I_p/(v_{1/2})$ values of the reduction peak and oxidation peak decreased with increased

scanning rate. The ratio of the oxidation peak current and reduction peak current was larger than 1, and increased with increased scanning rate. These were consistent with the mechanism of proceeding chemical reactions according the cyclic voltammetry criterion[13]

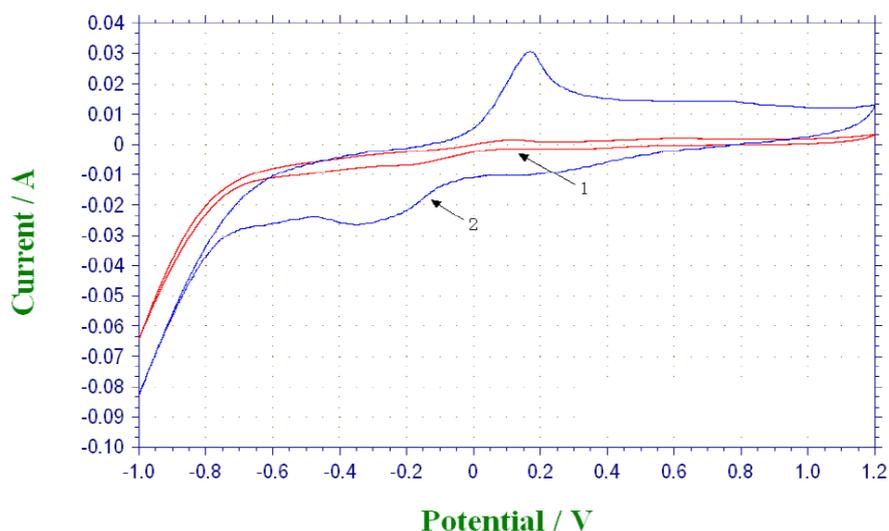


Figure 1. Cyclic voltammety curve on the SPE electrode, in octane (1) and thiophene solution (2).

Table 1. The relationship between potential and current of peak at different scanning rate.

ScanningRate ν (mV/s)	ReductionPotential (V)	Reduction I_p (mA)	Oxidation Potential (V)	Oxidation I_p (mA)
10	-0.079	-6.238	0.067	7.305
15	-0.085	-6.753	0.069	8.474
30	-0.101	-8.033	0.067	11.850
50	-0.132	-7.527	0.072	14.150
75	-0.143	-9.255	0.073	17.710
100	-0.156	-10.970	0.075	22.170
150	-0.198	-13.360	0.079	26.140
200	-0.239	-14.360	0.082	34.492
250	-0.246	-16.231	0.084	39.120
300	-0.350	-16.192	0.163	30.430

Thiophene reduction peak of electrochemical hydrogenation was near -0.400V by the cyclic voltammetry. In order to improve the reaction rate and avoid the hydrogen evolution reaction under the condition of high potential, the selected potential of the bulk electrolysis with coulometry (BEC) was set to -0.800V. Table 2 shows the electrolysis current as a function of reaction temperature. The current efficiency increased with reaction temperature.

According to the Arrhenius equation, the rate constant of electrochemistry reactions can be expressed as: $\ln i = -[E_a/R] [1/T] + \ln A$, where i is the reaction current, E_a is the activation energy, R is the gas constant, T is the reaction temperature. The value of $- [E_a/R]$ can be obtained from the slope of $\ln i$ versus $1/T$ plot. Figure 2 shows the plot of $\ln i$ versus $1/T$ for the thiophene hydrogenation. The reaction activation energy of thiophene electrolysis hydrogenation was 14.06 kJ/mol determined by linear regression. The positive activation energy indicated that the reaction rate increases with

temperature. A low activation energy value indicates the thiophene hydrogenation process is controlled by the diffusion step, not controlled by the electrochemical reaction.

Table 2.The relationship between the temperature and the electrolysis current under-0.800V.

$T(^{\circ}\text{C})$	$T(\text{K})$	$i (\text{A})$	$1/T$	$\ln(i)$
25	298.15	-0.010	3.354×10^{-3}	-4.605
35	308.15	-0.012	3.245×10^{-3}	-4.423
45	318.15	-0.014	3.143×10^{-3}	-4.255
55	328.15	-0.017	3.047×10^{-3}	-4.098
65	338.15	-0.019	2.957×10^{-3}	-3.948
75	348.15	-0.023	2.872×10^{-3}	-3.781

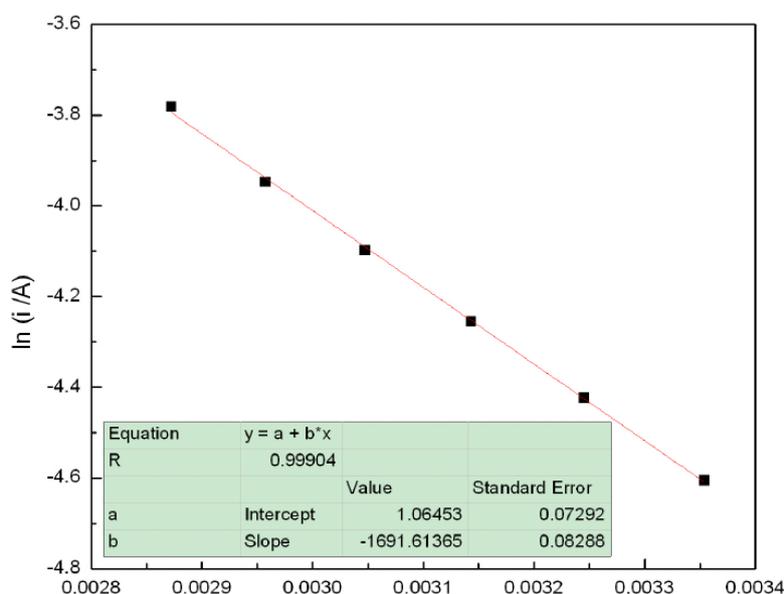


Figure 2.The relationship between $\ln(i/A)$ and $1/T$ at the potential of -0.800V.

No sulfur containing products were detected by gas chromatography in the thiophene solution after the reaction. An additional experiment was performed to determine the thiophene reaction products. Pure thiophene was subjected to constant potential electrolysis and the products were characterized by GC-MS. Sulfur compounds, such as 4,5-dihydrothiophene, 2-ethylhexylthiol, diethylsulfide, ethylethynylsulfide, butenylthiol, allylmethylsulfide, 2-butylthiophene, and thiophene-2-methanethiol, were found in the reaction product. In addition, some C_5 - C_7 hydrocarbons, such as normal pentane, 2-methylbutane, and normal heptanes were detected. Based on the composition of reaction products, the pathway of thiophene reduction-hydrogenation reactions on combined SPE electrode was proposed, as shown in Figure 3.

The composition of the reaction products suggested that electrochemical reduction reactions of thiophene on the combined SPE electrode exhibited two reaction pathways. One pathway was started from the formation of the cyclic sulfide by hydrogenation saturation of thiophene, the cyclic sulfide was converted to various unsaturated thiols and sulfides by ring cleavage reactions, which were further converted to saturate sulfides, thiols and/or hydrocarbons. Another pathway was direct transformation of thiophene to the sulfides by ring opening, which followed by hydrogenation. In the further

hydrogenation, the thiol was converted to various compounds by hydrogenation, isolation, and rearrangement reaction since it has unsaturated bond. At the same time, activated thiophene could react with unsaturated thiols and produced various thiophenic compounds with alkyl chains. These sulfur compounds could undergo further reactions, such as ring cleavage, hydrogenation, and dealkylation.

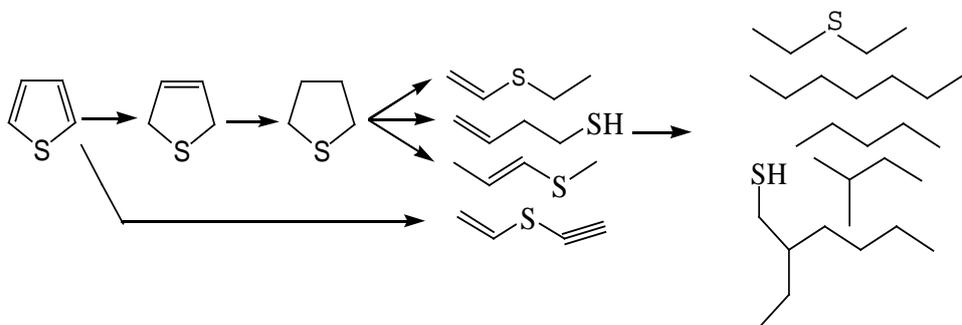


Figure 3.Reaction pathway of thiophene on the SPE electrode.

4. Conclusions

The electrochemical hydrogenation reactions of thiophene on SPE electrode were investigated using cyclic voltammetry and bulk electrolysis with coulometry (BEC) techniques. The results of cyclic voltammetry showed that the electrochemical hydrogenation reduction reaction occurred at about -0.4V. The BEC results showed that the currents generated from thiophene hydrogenation reactions increased with temperature. According to Arrhenius equation, activation potential of thiophene electrolysis was calculated and lower activation energy value indicated it was diffusion controlled reaction. From the products of electrolytic reactions, the mechanisms of electrochemical hydrogenation of thiophene on the combined SPE electrode were proposed, consisting of two pathways: opening ring followed by hydrogenation, and hydrogenation followed by ring opening. One pathway was started from the formation of the cyclic sulfide by hydrogenation saturation of thiophene, the cyclic sulfide was converted to various unsaturated thiols and sulfides by ring cleavage reactions, which were further converted to saturate sulfides, thiols and/or hydrocarbons. Another pathway was started from thiophene direct to the sulfide by ring opening, followed by hydrogenation.

References

- [1] ChenY, WangL, ZhangY, LiuT, LiuX, JiangZ and LiC, A New Multi-Metallic Bulk Catalyst with High Hydrodesulfurization Activity of 4, 6-Dmdbt Prepared Using Layered Hydroxide Salts as Structural Templates 2014*Applied Catalysis A: General***474** 69-77.
- [2] KimT, AliS A, AlhooshaniK, ParkJ-I, Al-YamiM, YoonS-H and MochidaI, Analysis and Deep Hydrodesulfurization Reactivity of Saudi Arabian Gas Oils 2013*Journal of Industrial and Engineering Chemistry***19(5)** 1577-1582.
- [3] VillasanaY, Ruscio-VanalestiF, PfaffC, MéndezF J, Luis-LuisM and BritoJ L, Atomic Ratio Effect on Catalytic Performance of Few-Based Carbides and Nitrides on Thiophene Hydrodesulfurization 2013*Fuel***110**259-267.
- [4] ZhangM, YangT, ZhaoR and LiuC, Effect of Solid-State Synthesized Alumina Properties on the Structure and Catalytic Performance of Nimo Catalyst in Hydrodesulfurization2013*Applied Catalysis A: General***468**327-333.
- [5] YinC-L, ZhaiX-P, ZhaoL-Y and LiuC-G, Mechanism of Hydrodesulfurization of Dibenzothiophenes on Unsupported Nimow Catalyst 2013*Journal of Fuel Chemistry and Technology***41(8)** 991-997.
- [6] ZuberC, HochenauerC and KienbergerT, Test of a Hydrodesulfurization Catalyst in a Biomass Tar Removal Process with Catalytic Steam Reforming2014 *Applied Catalysis B:*

- Environmental* **156** 62-71.
- [7] WangW, WangS, LiuH and WangZ, Desulfurization of Gasoline by a New Method of Electrochemical Catalytic Oxidation 2007 *Fuel* **86(17)** 2747-2753.
- [8] ZhaoW, ZhuH, ZongZ-M, XiaJ-H and WeiX-Y, Electrochemical Reduction of Pyrite in Aqueous NaCl Solution 2005 *Fuel* **84(2)** 235-238.
- [9] ArnanzaA, MarcosM-L, DelgadoS, González-VelascoJ and MorenoC, The Effect of Thiophene Ring Substitution Position on the Properties and Electrochemical Behaviour of Alkyne–Dicobaltcarbonylthiophene Complexes 2008 *Journal of Organometallic Chemistry* **693(23)** 3457-3470.
- [10] GreaneyM A, WangK, BielenbergJR and HissongDW, Electrodesulfurization of Heavy Oils Using a Divided Electrochemical Cell **2011** US Patents, patent number 7985332.
- [11] ChapuzetJ, LasiaA and LessardJ 1998 *Electrocatalytic Hydrogenation of Organic Compounds, Electrocatalysis* Wiley-VCH, New York pp 155-96.
- [12] HuangH, YuY and ChungK H, Seasonal Storage of Electricity by Hydrogen in Benzene–Water System 2012 *International Journal of Hydrogen Energy* **37(17)** 12798-12804.
- [13] LrfajB 2001 *Electrochemical Methods: Fundamentals and Applications* Wiley, New York pp 156-165.