An Integrated Process of Reductive Desulfurization by Sodium Borohydride and Its Electroreduction Regeneration in Ionic Liquid

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Abstract. In this study, a novel desulfurization method was developed by introducing ionic liquid (IL) into the integrated process of reductive desulfurization by NaBH4 and its regeneration via NaBO2 electroreduction, where ILs play a dual role of electrolyte and extracting agent. Under the conditions of -2.4 V forward pulse voltage, 0.6 V reverse pulse voltage, 0.6 s forward pulse time, 0.4 s reverse pulse time, 0.8 s turn-off time, 80 min electrolytic time, 4/1 IL/oil volume ratio, sulfur removal reached more than 95% for model fuel oil. Therefore, the novel integrated process of reductive desulfurization by NaBH4 and its electroreduction regeneration in IL is feasible and promising.

1. Introduction
Deep desulfurization of fuel oil has become a research hotspot because most of countries in the world have established strict laws and rules to regulate the sulfur content of fuel. Hydrodesulfurization (HDS) is the traditional industrial process for fuel oil desulfurization. However, HDS is carried out under severe operating conditions and is less effective for aromatic thiophenes. Thus, recently increasing attention is being given to some non-HDS alternative technologies such as extractive desulfurization [1], oxidative desulfurization [2], adsorptive desulfurization [3], biodesulfurization[4]. Sodium borohydride (NaBH4), a good reductant, is widely used in the desulfurization of organic sulfides. The desulfurization mechanism of NaBH4 is as follows [5]. Firstly, NaBH4 hydrolyzes to produce active hydrogen (H*) (NaBH4 + H2O → NaBO2 + H2). Then, the organic sulfides are desulfurized and transformed into their corresponding hydrocarbons in the presence of some metal salts (e.g. NiCl2, CoCl2) and H*. In addition, NaBH4 can be prepared by sodium metaborate (NaBO2) electroreduction (Cathode: BO2- + 6 H2O + 8 e- → BH4- + 8 OH-; Anode: 4 OH- - 4 e- → 2 H2O + O2↑) [6, 7]. NaBO2 exactly is the hydrolytic by-product of NaBH4. Therefore, desulfurization cost can drastically be reduced by integrating NaBO2 electroreduction for the preparation of NaBH4 with NaBH4 reduction for fuel oil desulfurization. However, BO2- is reduced to BH4- on the cathode, due to charge repulsion it is very difficult for the negatively charged BO2- to get close to the surface of cathode. So the yield of NaBH4 is very low when constant voltage is used for NaBO2 electroreduction, accordingly leading to low sulfur removal. Pulse voltage consists of a forward pulse (cathodic pulse) and a reverse pulse (anodic pulse). Reverse pulse voltage can play a role of attracting the negative charged BO2- to the surface of working electrode while forward pulse voltage can play a role of...
converting $\text{BO}_2^{-}$ on the surface of working electrode into $\text{BH}_4^{-}$ by electroreduction. Alternate reverse pulse voltage and forward pulse voltage are applied to the working electrode. Namely, the attraction of $\text{BO}_2^{-}$ to the surface of working electrode alternates with the electroreduction of $\text{BO}_2^{-}$ into $\text{BH}_4^{-}$ on the working electrode. Therefore, the yield of $\text{NaBH}_4$ will be improved enormously, accordingly improving sulfur removal.

In addition, hydrogen evolution reaction ($2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2\uparrow + 2\text{OH}^-$) and oxygen evolution reaction ($4\text{OH}^- - 4e^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2\uparrow$) may carry out in the process of pulse electrolysis, which can result in low current efficiency. Ionic liquid (IL) has been widely used as excellent electrolyte in various electrochemical processes owing to its wide electrochemical window. Furthermore, IL is also an excellent extracting agent for organic sulfides and has been widely used in the extractive desulfurization of fuel oil. Therefore, IL can play a dual role of electrolyte and extracting agent by introducing IL into the integrated process of reductive desulfurization by $\text{NaBH}_4$ and its regeneration via $\text{NaBO}_2$ electroreduction.

According to the above ideas, a novel desulfurization method was developed in this work. The desulfurization method consists of five steps. (1) The organic sulfides in the oil phase move to the IL phase by extraction. (2) $\text{NaBH}_4$ is prepared by $\text{NaBO}_2$ electroreduction ($\text{BO}_2^{-} + 6\text{H}_2\text{O} + 8e^- \rightarrow \text{BH}_4^{-} + 8\text{OH}^-$). (3) $\text{NaBH}_4$ hydrolyzes to produces active hydrogen ($\text{H}^*$) and the byproduct $\text{NaBO}_2$. (4) The organic sulfides are desulfurized and transformed into their corresponding hydrocarbons in the presence of nickel chloride and $\text{H}^*$. (5) The produced hydrocarbons move to the oil phase again.

2. Experimental section

2.1. Materials
Model fuel oil with sulfur contents of 500 ppmw was prepared by dissolving benzothiophene (BT) and 3-methylbenzothiophene (3-MBT) in n-octane. The IL $\text{N}_{122,102}[\text{TFSI}]$ was synthesized according to the previous references [8, 9]. BT (98%), 3-MBT (98%), n-octane (AR), $\text{NaBO}_2\cdot4\text{H}_2\text{O}$ (99%), nickel chloride hexahydrate ($\text{NiCl}_2\cdot6\text{H}_2\text{O}$, 98%) were supplied by Shanghai Aladdin Reagent Co. Ltd.

2.2. Desulfurization experiment
All desulfurization experiments were carried out in an electrolytic cell. The electrolytic cell was divided into a working electrode (WE) compartment and a counter electrode (CE) compartment by a cation exchange membrane. A glassy carbon electrode was used as the working electrode and a Pt wire was used as the counter electrode. A Ag/Ag$^+$ electrode was used as the reference electrode (RE). The Ag/Ag$^+$ electrode was prepared by immersing a silver wire in 0.1 mol/dm$^3$ $\text{AgSO}_3\text{CF}_3/\text{EMI}[\text{TFSI}]$ solution and was separated from the reaction system with an outer glass tube. The experimental procedure is as follows. First, a certain amounts of ILs and a mixture containing IL, $\text{NaBO}_2\cdot4\text{H}_2\text{O}$ and model fuel oil were added into the counter electrode compartment and the working electrode compartment, respectively. Then, the reaction mixture in the working electrode compartment was stirred and the electrochemical workstation was turned on in sequence. A moment later, $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ was added into the working electrode compartment slowly and the desulfurization reaction started immediately. After the desulfurization reaction, the mixture in the working electrode compartment rested for a while and was divided into an oil phase and an IL phase. The oil phase was used for the sulfur content analysis by gas chromatography (GC). The sulfur removal could be calculated by the equation (1).

$$\text{Sulfur removal (\%)} = \frac{S_0 - S_1}{S_0} \times 100\% \quad (1)$$

where $S_0$ is the sulfur content in the original fuel oil sample and $S_1$ is the sulfur content in the desulfurized fuel oil sample.
3. Results and Discussion

3.1. Effect of pulse parameters on sulfur removal

3.1.1 Forward pulse voltage. Forward pulse voltage plays a role of converting \( \text{BO}_2^- \) into \( \text{BH}_4^- \) by electroreduction. Based on the results of cyclic voltammetry analysis, the voltage range for electroreduction of \( \text{NaBO}_2 \) into \( \text{NaBH}_4 \) is between \(-1.8\) and \(-2.8\) V. Low forward pulse voltage can help to increase sulfur removal, but hydrogen evolution reaction may carry out when forward pulse voltage is too low. Figure 1(a) shows the effect of forward pulse voltage on sulfur removal. Sulfur removal initially increases with the reducing of forward pulse voltage, and then decreases. The maximum value of sulfur removal is obtained when forward pulse voltage is -2.4 V.

![Figure 1](image_url)

Figure 1 Effect of (a) forward pulse voltage, (b) reverse pulse voltage, (c) forward pulse time, (d) reverse pulse time, (e) turn-off time, (f) total electrolytic time on sulfur removal. Other conditions: 4/1 IL/oil volume ratio.
3.1.2 Reverse pulse voltage. Reverse pulse voltage plays a role of attracting $\text{BO}_2^-$ to the surface of working electrode. High reverse pulse voltage can help to attract $\text{BO}_2^-$ to the working electrode surface, but too high reverse pulse voltage may result in oxygen evolution reaction and conversion of $\text{BO}_2^-$ to borax [10]. Instead, too low reverse pulse voltage is not adequate to attract $\text{BO}_2^-$ to the surface of working electrode. As shown in Figure 1(b), sulfur removal initially increases with the increase of reverse pulse voltage, and then decreases. Sulfur removal reaches its maximum value while reverse pulse voltage is +0.6 V.

3.1.3 Forward pulse time. Increasing forward pulse time can help to increase the conversion rate of $\text{BO}_2^-$ into $\text{BH}_4^-$, accordingly increasing sulfur removal. However, when reverse pulse voltage and reverse pulse time are fixed the amount of $\text{BO}_2^-$ attracted to the surface of working electrode is limited. Therefore, further increase of forward pulse time makes no contribution to sulfur removal after all the $\text{BO}_2^-$ attracted to the surface of working electrode has been converted into $\text{BH}_4^-$. Figure 1(c) shows the effect of forward pulse time on sulfur removal. Sulfur removal initially increases with the increasing of forward pulse time when forward pulse time was less than 0.6 s, and then remains almost constant even though forward pulse time continued increasing.

3.1.4 Reverse pulse time. Increasing reverse pulse time can increase the amount of the $\text{BO}_2^-$ attracted to the surface of working electrode, which can increase the yield of $\text{BH}_4^-$, accordingly increasing sulfur removal. However, the amount of the $\text{BO}_2^-$ attracted to the surface of working electrode is limited for a certain surface of working electrode. Furthermore, when forward pulse voltage and forward pulse time are fixed the amount of conversion of $\text{BO}_2^-$ into $\text{BH}_4^-$ is also limited. Therefore, too long reverse pulse time also makes no contribution to sulfur removal. Figure 1(d) shows the effect of reverse pulse time on sulfur removal. Sulfur removal initially increases with the increasing of reverse pulse time when reverse pulse time was less than 0.4 s, and then remained almost constant even though reverse pulse time continued increasing.

3.1.5 Turn-off time. Turn-off time plays a role of providing adequate time for the hydrolysis of the NaBH$_4$ prepared by NaBO$_2$ electroreduction. Turn-off time is too short to give enough time for the hydrolysis of NaBH$_4$, which may result in the exhaustion of a portion of the NaBH$_4$ through electrooxidation at the stage of reverse pulse [11]. That means that a portion of the NaBH$_4$ prepared by NaBO$_2$ electroreduction does not work on fuel oil desulfurization. Instead, too long turn-off time makes no contribution to sulfur removal because the time required for the hydrolysis of NaBH$_4$ is fixed for a certain amount of NaBH$_4$ prepared by NaBO$_2$ electroreduction. Figure 1(e) shows the effect of turn-off time on sulfur removal. Sulfur removal initially increases with the increasing of turn-off time when turn-off time was less than 0.8 s, and then remains almost constant even though turn-off time continued increasing.

3.1.6 Total electrolytic time. Total electrolytic time is composed of total forward pulse time, total reverse pulse time and total turn-off time. Namely, total electrolytic time = (forward pulse time + reverse pulse time + turn-off time) × pulse numbers. Figure 1(f) shows the effect of total electrolytic time on sulfur removal. Sulfur removal initially increases with the increase of total electrolytic time when total electrolytic time was less than 80 min, and then remains almost constant even though total electrolytic time continues increasing. Consequently, 80 min was chosen as the optimum total electrolytic time in this work.

3.2. Effect of IL/oil volume ratio on sulfur removal
ILs play a dual role of electrolyte and extracting agent during the course of desulfurization. The increase of ILs can increase the extraction rate of organic sulfides, accordingly increasing sulfur removal. Figure 2 shows the effect of IL/oil volume ratio on sulfur removal. In addition, in order to confirm that reductive desulfurization with NaBH$_4$ plays a significant role during the course of
Desulfurization, the sulfur removal of the integrated desulfurization process was compared with that of the single extractive desulfurization process with the same ILs. As shown in Figure 2, the sulfur removal of the integrated desulfurization process was much higher than that of the single extraction desulfurization process within the investigated IL/oil volume ratio. The results indicate that the reductive desulfurization with NaBH₄ really plays a significant role during the course of desulfurization. In addition, for the integrated desulfurization process sulfur removal initially increases with the increasing of IL/oil volume ratio when IL/oil volume ratio was less than 4 and then remains almost constant even though IL/oil volume ratio continues increasing. Therefore, the IL/oil volume ratio of 4/1 is chosen in this work.

![Figure 2](image.png)

**Figure 2** Effect of IL/oil volume ratio on sulfur removal.

4. Conclusions

In this work, a novel desulfurization process based on the integrated process of reductive desulfurization by NaBH₄ and its regeneration via NaBO₂ electroreduction using IL as electrolyte was presented for fuel oil desulfurization. The factors that influenced sulfur removal were investigated. Under the conditions of -2.4 V forward pulse voltage, 0.6 V reverse pulse voltage, 0.6 s forward pulse time, 0.4 s reverse pulse time, 0.8 s turn-off time, 80 min electrolytic time, 4/1 IL/oil volume ratio, sulfur removal reached more than 95% for model fuel oil. This work will push forward the practical application of the desulfurization method with NaBH₄.

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References

[1] Chandran D., Khalid M., Walvekar R., et al. (2019) Deep eutectic solvents for extraction-desulfurization: A review. Journal of Molecular Liquids, 275: 312–322.
[2] Andevary H. H., Akbari A., Omidkhah M. (2019) High efficient and selective oxidative desulfurization of diesel fuel using dual-function [Omin]FeCl₄ as catalyst/extractant. Fuel Processing Technology, 185: 8–17.
[3] Li X. J., Song H., Chang Y. X. (2018) Study of isothermal equilibrium, kinetics and thermodynamics of adsorptive desulfurization on synthesized (CuYY)-Y-I-Y-III zeolite. China Petroleum Processing & Petrochemical Technology, 20 (2): 24–33.
[4] Chen S. Q., Zhao C. C., Liu Q. Y., et al. (2018) Thermophilic biodesulfurization and its application in oil desulfurization. Applied Microbiology and Biotechnology volume, 102: 9089–9103.
[5] Back T. G., Yang J. K., Krouse H. R. (1992) Desulfurization of benzo- and dibenzothiophenes with nickel boride. The Journal of Organic Chemistry, 57(7): 1986–1990.

[6] Steven A. (2002) Electroconversion cell. US Patent 6497973.

[7] Sanli A. E., Kayacan İ., Uysal B. Z., et al. (2010) Recovery of borohydride from metaborate solution using a silver catalyst for application of direct rechargable borohydride/peroxide fuel cells. Journal of Power Sources, 195 (9): 2604–2607.

[8] Sato T., Masuda G., Takagi K. (2004) Electrochemical properties of novel ionic liquids for electric double layer capacitor applications. Electrochimica Acta, 49 (21): 3603–3611.

[9] Sato T., Masuda G., Nozu R., et al. (2003) Ionic liquids, electrolyte salts for electrical storage devices, liquid electrolytes for electrical storage devices, electrical double-layer capacitors, and secondary batteries. CA Patent 02441981.

[10] Park E. H., Jeong S. U., Jung U. H., et al. (2007) Recycling of sodium metaborate to borax. International Journal of Hydrogen Energy, 32 (14): 2982–2987.

[11] Braesch G., Bonnefont A., Martin V., et al. (2018) Borohydride oxidation reaction mechanisms and poisoning effects on Au, Pt and Pd bulk electrodes: From model (low) to direct borohydride fuel cell operating (high) concentrations. Electrochimica Acta, 273: 483–494.