NRC Publications Archive
Archives des publications du CNRC

A review of electrochemical desulfurization technologies for fossil fuels
Lam, Vincent; Li, Guangchun; Song, Chaojie; Chen, Jinwen; Fairbridge, Craig; Hui, Rob; Zhang, Jiujun

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.
For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada   Conseil national de recherches Canada

Canada

Review

A review of electrochemical desulfurization technologies for fossil fuels

Vincent Lam [a], Guangchun Li [a], Chaojie Song [a,*], Jinwen Chen [b,**], Craig Fairbridge [b], Rob Hui [a], Jiujun Zhang [a]

[a] Institute for Fuel Cell Innovation, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver BC, Canada V6T 1W5
[b] CanmetENERGY, One Oil Patch Drive, Devon, AB, Canada T9G 1A8

ARTICLE INFO

ABSTRACT

Desulfurization is an important process for crude oil upgrading. Electrochemical desulfurization technologies have advantages over conventional hydrodesulfurization technologies in terms of low temperature and pressure operation with high product selectivity and therefore less energy consumption. In this paper the authors reviewed the research done in the past decades on electrochemical desulfurization for fossil fuels. The principles, electrochemical methods, electrochemical reactors, catalysts and electrolytes employed in the electrochemical desulfurization process were discussed; and future research work is recommended.

Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.

Contents

* Corresponding author. Tel.: +1 604 221 3000x5577; fax: +1 604 2213001.
** Corresponding author. Tel.: +1 780 987 8763.
  E-mail addresses: chaojie.song@nrc.gc.ca (C. Song), jinwen.chen@nrcan-rncan.gc.ca (J. Chen).

1. Introduction

As conventional oil reserves deplete, unconventional oil reserves including heavy oil, extra heavy oil, and oil sands and bitumen, which comprise of 70% of the world's total oil resources, are becoming more important [1,2]. With rising oil prices, the production of synthetic crude oil from unconventional resources such as oil sands is becoming increasingly economically viable [1]. However, these unconventional oils contain fairly large quantities of contaminants such as sulfur, nitrogen, nickel, and vanadium. For example, a sulfur content of 4.86 wt.% was reported for Athabasca oil sand bitumen [3]. Typical organic sulfur containing compounds in oil include thiophene, benzothiophene, dibenzothiophene, benzonaphthothiophene, dinaphthothiophene, mercaptans, and sulfides. In addition, oil contains inorganic sulfur such as elemental sulfur, and sulfides [4].

The combustion of high sulfur content fossil fuels can release harmful sulfur oxides into the air and therefore pose serious environmental problems. Thus, great efforts have been made to decrease the sulfur content in fossil fuels. Currently the widely used technology is hydrodesulfurization (HDS). HDS is a process in which crude oil is heated at high pressures and temperatures in the presence of hydrogen and catalysts. The resulting products are low sulfur oil and hydrogen sulfide gas that is removed in a post treatment step via the Claus process. However, HDS faces problems of high energy consumption, high cost of raw materials, and undesired by-product formation. In addition, while the goal is to obtain a low-sulfur fuel product, HDS can lead to a loss in octane (for gasoline) due to saturation of the olefins present in naphthas. Thus other desulfurization techniques with low cost and low energy consumption are needed.

Electrochemical desulfurization (ECDS) technology has been explored to remove sulfur by the electrochemical oxidation or reduction of sulfur compounds in fossil fuels [5–7]. This technology is able to remove sulfur at relatively low temperatures and pressures, which potentially makes the process much less energy intensive and more economical than conventional technologies. In ECDS, there is also a degree of freedom to control products by adjusting the applied potential. Promising results have been reported using this technique. However, the ECDS technology is still in its early development stage, and further research is needed to push this technology toward commercialization. With the intension to facilitate the research and development, we reviewed the progress of this technology, and discussed the principles and technology development for the electrochemical desulfurization of fossil fuels. As the organic compositions of coal, petroleum products, and bitumen are similar, a method for one can provide insight into methods for the others. In this review particular attention is paid to the desulfurization of petroleum feedstocks, including those derived from oil sands bitumen.

## 2. Principles of electrochemical desulfurization

2.1. Oxidation and reduction of organic sulfur compounds

Electrochemical desulfurization is based on the reduction and/or oxidation of sulfur-containing compounds in fossil fuels. The electrochemical cathodic reduction of organic sulfur compounds (expressed as R-SH) leads to the formation of H_2S, as shown in Eq. (1):

$$R - SH + 2H^+ + 2e^- = R - H + H_2S. \tag{1}$$
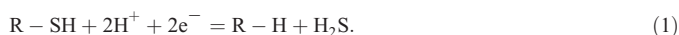
The resulting H_2S can be removed by a gas/liquid separation process.

The electrochemical anodic oxidation of organic sulfur compounds is expressed as Eq. (2):

$$R - SH + 4OH^- - 4e^- = RH + SO_2 + 2H_2O. \tag{2}$$
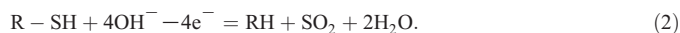
In Eq. (2), SO_2 represents RSH oxidation products, which might be O-containing RSH molecules (e.g. RSO_xH). The addition of oxygen to sulfur-containing compounds increases the polarity of the sulfur compounds so that they can be removed by extraction with polar solvents or by adsorption with polar adsorbents.

2.1.1. Reduction of sulfur compounds

Using sulfur model compounds such as thiophene and benzothiophene, the concept of electroreductive desulfurization of heavy hydrocarbons seems to be feasible [8–11]. Although electroreductive desulfurization enables easy separation of the resulting H_2S from the hydrocarbon feed, it has been found that the hydrocarbon feed may also polymerize, and sulfur oligomers may form and remain entrained in the polymerized hydrocarbon feed [12]. In addition, strong electrochemical reducing conditions can lead to contaminant deposition on the catalyst surface, severely deactivating the catalyst over time. In aqueous media under strong reducing potentials, hydrogen may evolve and clean the catalyst surface, although there is also a risk that the evolved hydrogen may cause problems for the catalyst's desulfurization efficiency. In their investigation of the electrochemical reaction of thiophenol derivatives on Pt, Vieira et al. [13] found that the derivatives required potentials much lower than the hydrogen adsorption/evolution potential on a Pt catalyst, resulting in much lower desulfurization efficiencies due to competition between the derivatives and hydrogen evolution.

2.1.2. Oxidation of sulfur compounds

Electrooxidative desulfurization has the advantage of not forming H_2S, a highly toxic gas. However like electroreductive techniques, electrooxidation can result in the formation of sulfur oligomers. In inventions that implemented electrooxidative desulfurization [14–19], sulfur was removed through physical separation of the formed sulfur
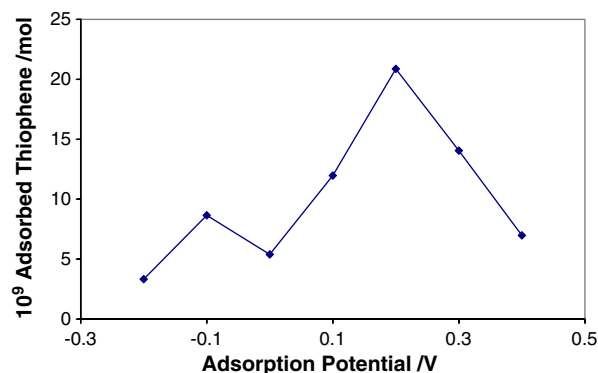

Fig. 1. The amount of thiophene adsorbed vs. the adsorption potential. Reproduced from J. Electroanal. Chem., 368 (1–2), M. Hourani, Desulfurization of thiophene by electrochemical perturbation, P. 141, copyright 1994, with permission from Elsevier.

oligomers. However, these sulfur oligomers may still poison the anode.

The mechanism for the oxidation of organic sulfur compounds such as thiophene and thiophenol derivatives on Pt electrodes has been studied [13,20]. The first step in the electrooxidation of thiophene and thiophenol derivatives is their chemical adsorption on the Pt electrode, with an optimum potential for maximum adsorption of thiophene on the electrode (Fig. 1). Analysis of the products revealed that thiophene was converted to less environmentally harmful inorganic compounds such as SO_4^{2-} and CO_2 [20].

2.1.3. Oxidation versus reduction

Electrochemical desulfurization can be carried out through either oxidation or reduction. The question is, which method is preferable for desulfurizing organic sulfur compounds? Hourani [20] found that the reaction of thiophene on Pt in acidic media occurred preferentially under reducing potentials in the hydrogen region, while oxidation was observed within the studied potential range only after the compound was reduced. Vieira et al. [13] also reported the same behavior for thiophenol derivatives on Pt. Sternberg et al. [12] reported that the desulfurization of dibenzothiophene from coal only occurred once the organic compound was partially hydrogenated. In another study conducted by Sternberg et al. [21], sulfur removal from a vitrain through reduction only occurred after the reduction of reactive aromatic hydrocarbons present in the vitrain, after which, sulfur was removed via hydrogenolysis. In the case of coal desulfurization, electrooxidation is preferred for the dissolution of the sulfur-containing inorganic phases in the coal matrix. The ferric ions produced as a result of pyrite dissolution can aid in the oxidation and desulfurization of the sulfur-containing organic phase in coal [22,23]. From the examples described, it can be construed that choosing oxidation or reduction for the electrochemical desulfurization of fossil fuels mainly depends on the properties of those fossil fuels.

2.2. Protonating agents

Studies have shown that the addition of protonating agents could facilitate the removal of sulfur and metal contaminants. For example, Ovalles et al. [24] found that, with the addition of methanol, both metal and sulfur removal was more efficient for petroporphyrin, Hamaca crude oil and residue (500 °C$^+$). It was found that for the residue (500 °C$^+$), 28% desulfurization could be achieved in the presence of methanol versus 18% in its absence [24]. In addition, the presence of methanol could facilitate the formation of sulfur compound radicals and then initiating polymerization, benefiting the sulfur removal. Electrolysis conditions such as potential and current density could also affect the efficiency. For example, a potential of −2.5 V was found to be optimal for both demetallization and desulfurization of the residue (500 °C$^+$). The final electric current density of 0.01 A cm^{-2} led to high desulfurization conversion, while a density of 0.02 A cm^{-2} resulted in high demetallization conversion.

Fairbridge et al. [8] also used methanol in their electrolyte solution for the hydrogenation of sulfur containing organic compounds. In a three electrode setup, they found that an electrolyte consisting of a mixture of methanol, water, and potassium hydroxide yielded the highest conversions of dibenzothiophene to biphenyl and phenylcyclohexane (28–33% on Raney nickel), and of nonyl-mercaptan to nonane (48–52% on Raney nickel). Replacing methanol with ethylene glycol in the potassium hydroxide electrolyte resulted in lower conversion of dibenzothiophene (20–26% on Raney nickel).

In addition to methanol, other materials could also be used as protonating agents. Selection of a protonating agent depends on the systems used. For example, in a lithium–ethylenediamine system, it was found that ethylenediamine (EDA) is an indispensable protonating agent. It was successfully demonstrated that EDA could effectively

remove sulfur during the electrochemical desulfurization of coal [21,25] and electrochemical desulfurization of kerogen from oil shale [9]. Lithium (Li) metal in EDA can reduce the content of sulfur, vanadium, and metalloporphyrins in Boscan asphaltenes [26]. Using Li-EDA, Markby et al. [25] removed approximately 62% of the sulfur in coal after 44 h of electrolysis over four separate experiments at 306 K using carbon electrodes. They also reported the enrichment of coal by addition of 44 hydrogen per 100 carbon atoms using Li-EDA. Sternberg et al. [21] reported the electroreduction of a vitrain in Li-EDA over two 30-hour electrolysis periods, after which 50% of the sulfur had been removed. They also reported a non-electrolytic reduction of dibenzothiophene in Li-EDA at 363 to 373 K. They proposed that the reaction of dibenzothiophene with Li could result in splitting of the carbon–sulfur bond. However, the formation of N-lithioethylenediamine might also occur, resulting in a decreased desulfurization efficiency. Another disadvantage of this method is that the complete separation of EDA from asphaltene is not possible, therefore high nitrogen and ash levels were observed in the treated samples [26].

2.3. Mediators

Mediators are used in the indirect electrochemical desulfurization of organic sulfur compounds. Lalvani [23] found that the addition of Fe to coal slurries during the electrolysis could increase the removal of sulfur from the organic portion of the coal and catalyze pyrite dissolution as well. Ferric ions could be produced via pyrite electrooxidation or iron electrooxidation, which then reacted with mercaptans to form disulfides through Eq. (3) [4],

$$2RSH + Fe^{3+} \rightarrow RSSR + Fe^{2+} + 2H^+ \tag{3}$$
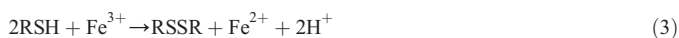
where the formed disulfides could be further oxidized to sulfate.

It was found that the ferric concentration could play an important role during desulfurization. If the Fe^{3+} concentration is too high, the adsorption of ferric sulfate on the coal's surface could occur, resulting in lower sulfur removal efficiency. Therefore, an optimum Fe^{3+} concentration should be determined experimentally in order to enhance coal desulfurization [22].

Ce^{4+} can be added to regenerate the Fe^{3+} via reaction (4) and also facilitate the desulfurization of coal as a mediator [7]. Lalvani et
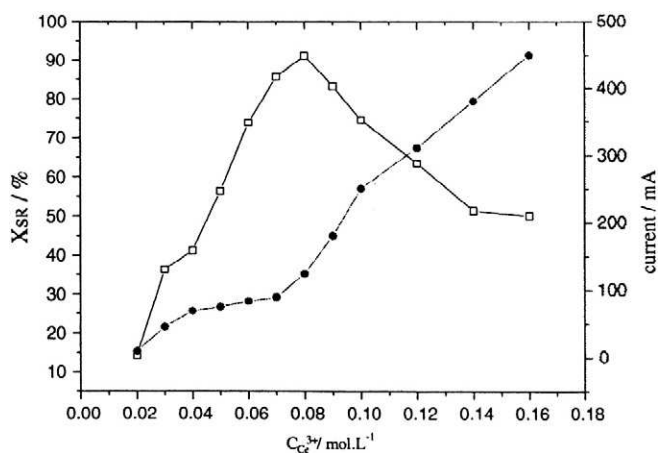

Fig. 2. Effect of Ce^{3+} on desulfurization ratio (X_{SR}).
Reprinted from Fuel, 86 (17–18), W. Wang, S. Wang, H. Liu, and Z. Wang, Desulfurization of gasoline by a new method of electrochemical catalytic oxidation, P. 2751, copyright 2007, with permission from Elsevier.

al. [22] investigated the effect of Ce^{4+} in the electrooxidation of coal in acidic media, and found an optimum Ce^{4+} concentration for desulfurization. They proposed a mechanism by which Ce^{4+} aided in the regeneration of Fe^{3+}:

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}. \qquad (4)$$

Wang et al. [7] reported significant desulfurization of gasoline using CeO_2/C catalysts and cerium nitrate electrolyte. They proposed a mediated desulfurization of gasoline via the following mechanism:

$$nCe^{4+} + [R-S] + 6H_2O \rightarrow nCe^{3+} + [R'] + (n-2)H^+ + SO_4^{2-} \qquad (5)$$
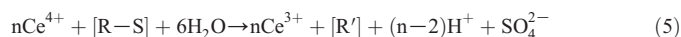
where R′ is the desulfurized product, and Ce^{4+} is the electrochemically regenerated species from the oxidation of Ce^{3+} at the anode. A positive correlation was observed between Ce^{3+} concentration and desulfurization up to a maximum value of approximately 90%. However further increases in Ce^{4+} concentration led to a decrease in desulfurization due to degradation of the gasoline (Fig. 2). The effect of Ce^{4+} on the electrooxidation of coal slurries was also investigated, and significant improvement of ash removal was found but no significant improvement in sulfur removal was observed [27].

Br^-, Cl^-, and I^- may also be used as mediators. Lalvani [23] studied their effect on desulfurization of coal in basic media, and found that the reaction rate initially declined with increasing mediator concentration but eventually increased upon further increases in mediator concentration (at the millimolar level). It was surmised that the initial addition of lower mediator concentrations might have lead to the formation of complexes with the Fe ions from pyrite electrooxidation. When the mediators' concentration was increased, a larger portion of free mediators might be available to mediate the desulfurization process.

3. Electrochemical methods

Several methods have been employed for electrochemical desulfurization, which can be generally grouped into two categories. The methods that facilitate electrochemical desulfurization by applying a fixed potential or drawing a fixed current can be categorized as static methods. Other methods where the applied potential changes over time, such as linear or square wave voltammetry can be categorized as dynamic methods. Bio-electrochemical desulfurization technique, which uses microorganisms such as bacteria to mitigate the sulfur removal in fossil fuels, is classified as an independent method.

3.1. Static methods

In static methods, electrochemical desulfurization is conducted at a fixed potential (potentiostatic) or a fixed current (galvanostatic). The advantage of the potentiostatic approach is that the applied oxidative or reductive potential can be controlled precisely, thus adding a degree of control over the desulfurization reaction mechanism and the extent of desulfurization. Choosing a suitable potential for electrolysis is a crucial step in potentiostatic methods, since the electrochemical desulfurization of fossil fuels shows potential dependence. Wapner et al. [28] observed this potential dependence in the desulfurization of coal. They found that higher potentials (1.6–2.0 V vs. SCE) facilitated the organic sulfur removal, and lower potentials (1.2–1.4 V vs. SCE) preferred for pyritic sulfur removal. In both cases, a total sulfur removal of 69% was achieved.

Galvanostatic methods allow for control over the reaction rate of the process, as the current is directly correlated to the reaction rate. However, there is less control over product selectivity as the electrode potential may change over time due to changes in kinetic and mass transport properties. Limitations in these properties are translated into increased cell overpotentials that equate to an increase in the overall cell potential. Exemplary works that have successfully

used this method to desulfurize organic compounds include the works of Ovalles et al. [24] and Yen et al. [9]. In their investigation, Ovalles et al. [24] made an interesting observation where higher metal contaminant removal and lower desulfurization for Hamaca residue (500 °C$^+$) was achieved at a current density of 0.02 A cm^{-2} versus a lower density of 0.01 A cm^{-2}. Yen et al. [9] desulfurized leached oil shale components by applying a constant current density and found that sulfur content could decrease significantly from 2.41% to 0.22% at a fixed current density of 50 mA cm^{-2}.

3.2. Dynamic methods

Dynamic methods offer the flexibility of controlling the applied potential or applied current. By changing the electrode potential over time, we can subject the feed to both oxidizing and reducing conditions, or subject the feed to varying degrees of electrooxidative/electroreductive conditions. Hourani [20] investigated the desulfurization of thiophene by electrochemical perturbation using square wave voltammetry on a Pt working electrode. It was found that thiophene adsorption on Pt competed with hydrogen adsorption starting at 0.2 V vs SHE (standard hydrogen electrode) in 0.5 M H_2SO_4 and electrooxidized independently in the Pt oxidation region starting at 0.5 V vs SHE. By applying a square wave voltammogram between the hydrogen evolution and oxygen evolution potentials (−0.2 to 1.3 V vs SHE), Hourani successfully electrooxidized thiophene to sulfate and carbon dioxide. Based on work of Gui et al. [29], the following electrodesulfurization reaction mechanism was proposed:

$$12H_2O + C_4H_4S \rightarrow SO_4^{2-} + 4CO_2 + 28H^+ + 26e^-. \qquad (6)$$

An optimal square wave frequency of 50 Hz was found under the employed experimental conditions [20]. It was surmised that higher frequencies could result in inadequate adsorption of thiophene on the electrode surface, and that lower frequencies could result in a smaller degree of desulfurization.

3.3. Bio-electrochemical desulfurization

Kim et al. [30,31] developed a novel electrochemical desulfurization method for petroleum products utilizing microorganisms. Using anaerobic bacteria, they were able to successfully desulfurize petroleum via the formation of H_2S. Bio-electrochemical desulfurization using anaerobic bacteria is an electrochemical reduction process, as electrons are needed for the sulfate-reducing bacteria to reduce organic sulfur compounds. Bacteria strains of desulfovibrio desulfuricans were found to be capable of degrading dibenzothiophene and desulfotomaculum nigrificans. Supplying electrons to the sulfate-reducing bacteria through the cathode of their electrochemical cell, Kim et al. were able to desulfurize Kuwait crude oil by 21% over 6 days at 303 K.

4. Reactors

Two types of electrochemical reactors are used for electrochemical desulfurization of fossil fuels: divided and undivided cells.

In a divided cell, a solid electrolyte membrane is used, which eliminates the need for a supporting liquid electrolyte in the hydrocarbon feed. The advantage over a liquid electrolyte system, is that additional processing steps required to separate the desulfurized products from the liquid electrolyte are not needed. However, the disadvantage is that the reactor design and operation can be limited by the membrane's properties. For instance, for Nafion® membranes to function effectively, a minimum humidity content is required, which is greatly affected by the temperature of the reactor. Depending on the nature of the feed's chemical environment, contaminants may also cause fouling or degradation of the membrane.

Undivided cells, where the anode and cathode are not separated by a membrane, and ionic conductivity is facilitated by a liquid electrolyte, are simpler reactors by design, but control over the desulfurization reaction can be limited. In these types of reactors, the feed is exposed to both reducing and oxidizing conditions. In some cases, the combination of an oxidizing and reducing environments may possibly lead to higher desulfurization conversion. In an example case, after electroreducing thiophene on platinum, Hourani [20] found that the reduced product can be further desulfurized through electrooxidation.

4.1. Divided cells

Fairbridge et al. [8] described a desulfurization process using a polymer electrolyte membrane system. The process involves electrocatalytic hydrogenation of the organic compound through electroreduction in the cathode compartment, proton production through water electrolysis in the anode compartment, and proton transfer from anode to cathode through the membrane as shown in Fig. 3. In the process, sulfur is freed from the organic compound through electroreduction and then combines with hydrogen to form hydrogen sulfide that can be easily removed. An advantage of this system is that it can operate at low temperatures and pressures relative to conventional HDS conditions. Their operating temperature was limited by the Nafion® membrane. Fairbridge at al. were able to convert 8% dibenzothiophene to biphenyl, phenylcyclohexane, and bicyclohexane using a cathode of Rh–Ru supported on carbon over 16 h. Using a catalyst of similar composition, a 100% conversion of octyl mercaptan to octane and di-n-octyldisulfide was achieved over 16 h.

Baez et al. [10]. patented an invention that is similar to the concept used by Fairbridge et al. [8]. The basis of this invention was such that the hydrocarbon feed was reduced at the cathode, which was separated from the anode by a membrane, while a hydrogen source was fed and oxidized at the anode to provide protons to the cathode to facilitate sulfur-hydrocarbon reduction. Separation of the freed sulfur from the hydrocarbon feed was enabled by the formation of H_2S. A metallic membrane was used to conduct protons, and a porous catalytic layer was added to the membrane to assist in the reduction of hydrocarbon feed. Over a 24-hour period at 333 K, a 40% desulfurization of thiophene in heptane was achieved. An advantage of this invention is that high temperatures could be used due to the use of a more durable metallic membrane. The recommended operating temperature was 298 to 573 K. No loss of membrane activity and decay of hydrogen efficiency during operation were observed by the inventors.
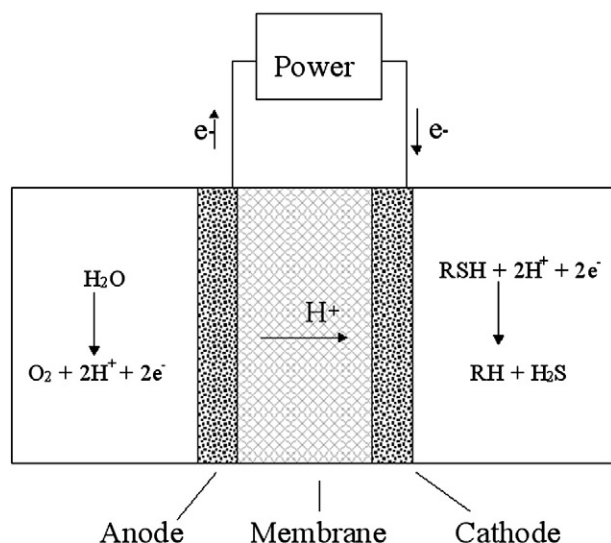
Greaney et al. [11] used a divided cell separated by an ionic-permeable membrane for the electrochemical desulfurization of 'hard' sulfur compounds. Heated and pressurized hydrocarbon feed was fed into the cathode compartment where it was electroreduced to form H_2S. The H_2S was then separated from the feed using a gas/liquid separation process, and recycled to the anode compartment where it was oxidized to produce protons. The protons then migrated through the membrane back to the cathode compartment. The principal reactions are as follows:

$$\text{Cathode} : RSH + 2H^+ + 2e^- \rightarrow RH + H_2S \tag{5}$$

$$\text{Anode} : H_2S \rightarrow 2H^+ + S + 2e^-. \tag{6}$$

Using this approach, a greater than 90% conversion of dibenzothiophene was achieved over 164 h. The desulfurization products included 2-phenyl benzenethiol, tetrahydro dibenzothiophene, as well as a species assumed to be 2-phenyl benzenethiol with two methyl groups attached.

Ahonen [14] also designed a cell consisting of two compartments separated by a membrane, wherein an oil–water emulsion was fed to either the anode or the cathode compartment with an alkali electrolyte in the other. In this way only oxidation or reduction of the oil occurred. The alkali electrolyte prevented the desulfurization products from polymerizing. In another configuration, the emulsion was fed through the cathode and anode or vice versa in succession in a divided cell. The treated product after passing through one compartment was oxidized or reduced with oxygen or hydrogen in between stages. In the latter suggested operation, after reduction/oxidation with hydrogen or oxygen, the emulsion was separated, and the oil was re-emulsified with clean water before entering the second stage.

4.2. Undivided cells

Over the years that have been numerous undivided cell systems implemented for electrochemical desulfurization. A list of these systems is shown in Table 1.

In undivided cells, various electrodes and electrolytes have been used with desulfurization accomplished by oxidation or reduction or both, as summarized in Table 1. For example, Bell et al. [32]

Fig. 3. Schematic representation of a divided cell for electrochemical desulfurization [8].

Table 1
Summary of electrochemical desulfurization using undivided cells.

Electrolysis conditions	Ionic media	Desulfurization efficiency	Ref.
Oxidation and reduction at 4 V, Pt electrodes	NaOH solution	91% for thiophene	[32]
Oxidation and reduction at 0.1 to 0.175 A, Pt electrodes	NaOH solution	25% for crude oil	[32]
Reduction at 50 mA cm^{-2} Al cathode, C anode	LiCl in ethylene diamine	94.2% for leached oil shale components	[9]
Oxidation and reduction at 2 to 15 A, Pt electrodes	NaOH solution	92% for heavy oil fraction	[14]
Oxidation at 1.2 to 2.7 V Pt, C, or stainless steel electrodes	Ionic liquid such as tetrabutyl ammonium hexafluorophosphate	73.5% for light cat naphtha	[16]
Reduction at −4.5 V stainless steel electrodes	Tetrabutyl ammonium hexafluorophosphate	16.5% for dibenzothiophene	[17]
Reduction at −4.5 V stainless steel electrodes	Tetrabutyl ammonium hexafluorophosphate	94% for dibenzothiophene	[18]
Reduction at −5 V stainless steel electrodes	Tetrabutyl ammonium hexafluorophosphate	12% for dibenzothiophene	[19]
Reduction at −2.7 V, Pb electrodes	LiClO$_4$ in THF	28% for Hamaca crude oil	[24]
Oxidation at 115 V, C electrodes	LiCl in ethylene-diamine	62% for coal	[27]

patented an oil purifying method in which hydrocarbon oil was mixed with an electrolyte and an ionizing organic solvent. The mixture was subjected to a potential ranging from 2 to 120 V, producing a current of at least 1 mA cm^{-2}. In this invention, both oxidation and reduction of sulfur compounds occurred as the electrochemical cell was not divided. A maximum of approximately 91% desulfurization was achieved in the given examples with a feed containing mineral oil, sodium hydroxide, water, and thiophene. Triton X-100 was also added in some of the examples to emulsify the oil and to reduce the bath viscosity and electrode fouling. They also found that the addition of Ca(OH)$_2$ was beneficial to forming insoluble sulfur compounds for ease of hydrocarbon feed separation.

Yen et al. [9] patented a method in which leached oil shale components were electrochemically hydrogenated and subsequently desulfurized. The invention focused on the upgrading of kerogen, which comprises of the majority of organic components in oil shale. In this invention, kerogen concentrate was mixed with an electrolyte solution, such as LiCl dissolved in EDA, and then was reduced for a minimum of 1 h at a minimum current density of 50 A m^{-2} at room temperature. A maximum of 94.2% sulfur could be removed.

Ahonen [14] developed an electrochemical desulfurization method to emulsify hydrocarbon fuel with an alkali electrolyte for desulfurization in an undivided cell. This invention was based on the fact that both reduced and oxidized forms of sulfide are acidic. Alkaline electrolyte was added to avoid the polymerization of organic sulfur compounds and to neutralize the acidic sulfur products. The electrochemical cell consisted of an undivided cell where the electrodes were chosen to minimize the evolution of hydrogen and oxygen. The electrodes were in the form of plates or a fluidized bed that would help prevent the separation of the emulsion. During the operation, the bath contents were heated and pressurized. In the examples given, 92% desulfurization was achieved for a heavy fuel oil fraction.

Shucker and Baird [15] patented an invention using an ionic liquid mixed with a polymerizable sulfur-containing hydrocarbon such as thiophene, alkylthiophene, benzothiophene, or alkylbenzothiophene. The aim of this invention is to produce sulfur oligomers from polymerizable hydrocarbons. After desulfurization via electrochemical oxidation, the sulfur oligomers remained in the ionic liquid phase due to the increased boiling point of the oxidation product, which was circulated in the system. The reactor was operated at temperatures from 273 to 473 K, with temperature dependant pressures, and at anodic potentials of 1 to 2.5 V vs Ag/AgCl at current densities of 1 to 10 mA cm^{-2}.

Using a similar concept, Schucker [16] patented a method in which a polymerizable hydrocarbon feed, specifically sulfur compounds in naphtha, was mixed with a solvent and an electrolyte before it was fed into an electrochemical reactor. Fig. 4 shows the schematic of the process. At pressures between 0 and 50 psig,
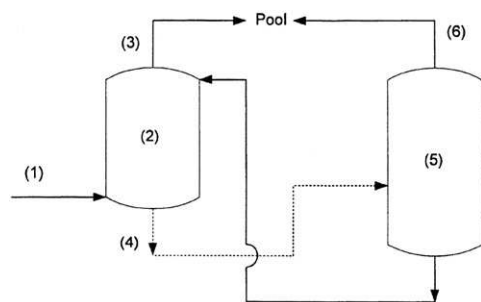

Fig. 4. Electrochemical desulfurization configuration. (1) the hydrocarbon feed, (2) the electrochemical reactor containing the ionic liquid, (3) the desulfurized product, (4) the ionic liquid containing sulfur oligomers and entrained hydrocarbons, (5) a distillation column, and (6) the entrained hydrocarbons [15].

temperatures between 298 and 423 K, and potentials from 1 V up to 2.5 V vs Ag/AgCl in the current density range of 1 to 10 mA cm^{-2}, a maximum of 73.5% desulfurization was achieved. In addition, a significant portion of the nitrogen content could also be removed from the hydrocarbon feed during the process.

Greaney et al. [17] developed a process using an undivided cell. In this process, dibenzothiophene, a 'hard' sulfur compound, was converted to mercaptans, which could be easily removed by either thermal decomposition, or caustic extraction. As the invention was specifically developed to treat heavy oils, the hydrocarbon feed would preferably have an API (American Petroleum Institute) gravity of less than 15. Ionic conductivity was provided either by the inherent conductivity of the hydrocarbon at high temperatures or by the addition of organic soluble salts such as 1-butyl-1-methylpyrrolidinium. They recommended the use of three dimensional electrodes such as carbon or metallic foams. In the examples given, a modest dibenzothiophene conversion of 16.5% was achieved over 3.5 h at a current of 1 A. They also devised another method for "hard" sulfur hydrocarbon and heavy oil in a preferably undivided electrochemical reactor [18]. In an example, they were able to achieve 94% conversion of dibenzothiophene at room temperature over 164 h using an applied voltage of 4.5 V, with Bu$_4$NPF$_6$ as a supporting electrolyte and stainless steel as the electrodes. For heavy oil desulfurization, they found that without a supporting electrolyte the preferred temperature and pressure ranges of the hydrocarbon feed and hydrogen were 449 to 533 K, and 300 to 500 psig, respectively, with an applied voltage of preferably 100 to 200 V and a preferred current density range of 100 to 500 mA cm^{-2}. In this case, up to 95% of sulfur was removed.

In another invention, Greaney et al. [19] used pressurized hydrogen in the electrochemical reactor. In a bath consisting of dibenzothiophene, tetrabutylammonium hexafluorophosphate, and dimethyl sulfoxide pressurized under a hydrogen atmosphere, they achieved a 16.5% conversion of dibenzothiophene under an applied potential of 4.5 V for 3.5 h using stainless steel electrodes.

5. Catalysts

5.1. Activity of catalysts

Choosing the right catalyst for electrochemical desulfurization is critical in determining the efficiency of the process, selectivity of the desired reaction mechanisms, and the longevity of the reactor. When choosing a catalyst, one must also consider its propensity to catalyze side reactions such as the evolution of hydrogen and/or oxygen. These side reactions are undesired as their occurrence consumes energy resulting in a decrease in the overall efficiency of the system. Usually highly active catalysts such as Pt have low overpotential toward the electrolysis of organic sulfur compounds, however, they also catalyze side reactions. Certain catalysts may also be prone to poisoning by constituents of the feed or by-products of the desulfurization reactions, which can result in kinetic limitations leading to higher operation voltages or higher costs and a decreased reactor lifetime in cases where the catalysts need to be replaced.

Low-active catalysts usually result in high overpotentials, low efficiency and a much longer processing time. Interestingly, it has been found that high oxygen evolution overpotentials can lead to the accumulation of free hydroxyl radicals on the electrode surface, benefiting the desulfurization in a basic media [27].

5.2. Catalyst materials

In the literature, both precious metal and non-precious metal based catalysts have been investigated for the electrochemical desulfurization of fossil fuels. The catalysts that have been investigated are summarized in Table 2. None of them has a clear advantage over the other. The catalysts are specific to the electrochemical desulfurization system utilized

Table 2
Typical catalysts used for desulfurization of fossil fuels.

Catalyst	Advantages and disadvantages	Desulfurization efficiency	Ref.
Pt	High activity, high cost, high O_2 and H_2 evolution, prone to poison	13% for Hamac residue	[24]
		100% for 1 mM thiophene in 0.5 M H_2SO_4	[20]
		91% for thiophene	[32]
		40% for coal	[5]
		60% for coal	[6]
Rh/Ru	High cost	8% for dibenzothiophene	[8]
Ir	High cost	100% for 1 mM PFT in 1 M H_2SO_4	[37]
Au	Low H_2 evolution, high cost, low activity	Minimal	[36]
Pb	Low O_2 evolution, low cost	28% for Hamac residue	[24]
PbO/C	Low O_2 evolution, low cost	77% for gasoline	[33]
Raney Ni	Low cost	14% for dibenzothiophene	[8]
CeO₂/C	Low cost	83% for gasoline	[7]

and to the chemical and electrochemical environments to which the catalyst is subjected. Of the patented inventions reviewed, many did not use precious metals in their electrodes, but rather suggested the use of cheaper catalysts or electrodes such as nickel, lead, or graphite. Because of catalyst poisoning and dissolution under highly corrosive environments and high applied potentials, it is desirable to use cheap and easily replaceable catalysts, especially when processing a large amount of material. For example, Greaney and co-workers [11,17–19] used stainless steel electrodes for all of the examples given in their patents. In addition, many inventions do not specifically require high catalytic activities, but simply the electrodes' anodic or cathodic function to remove or supply electrons. Therefore, precious metal catalysts were not needed. Ovalles et al. [24] compared the performance of Pb versus Pt cathodes for desulfurization and demetallization via electroreduction of Hamaca petroporphyrins, and found that both demetallization and desulfurization occurred preferentially on Pb by a factor of more than two. Demetallization and desulfurization on Pb were 38% and 28% respectively, compared to 16% and 13% for Pt, which was mainly due to Pt poisoning.

Fairbridge et al. [8] studied a number of catalysts including common HDS catalysts for the electroreduction of sulfur compounds. They found that Rh–Ru/C with an appropriate Rh:Ru ratio between 2 and 13 showed the highest activity toward hydrogenolysis of dibenzothiophene. Rh–Ru/C with the same Rh:Ru ratio was also found to be active for the conversion of octyl mercaptan. In addition, they also found that Raney nickel was catalytically active for the conversion of dibenzothiophene, nonyl mercaptans, as well as octyl nonyl sulfide, with conversion efficiency values of 14%, 24%, and 21%, respectively. However, the common HDS catalysts such as NiS_x, MoS_x, and Ni_2B did not show any catalytic activity, which was possibly due to the catalyst poisoning or limited mass transport of dibenzothiophene to the active catalyst sites.

Wang et al. [33] used β-PbO_2/C catalyst in their novel electrochemical fluidized bed reactor setup for the desulfurization of gasoline. Supported by the findings of Comninellis et al. [34], they suggested that desulfurization on β-PbO_2/C was related to accumulated free hydroxyl radicals on its surface. β-PbO_2/C exhibited a high resistance to oxygen evolution thus allowing free hydroxyl radicals to accumulate on its surface at high anodic potentials. Wilkinson [35] also studied the electrochemical desulfurization of oil and achieved 50% removal of sulfur from heavy sulfur crude oil, using lead electrodes.

Pt catalyst could be more active for the electrooxidative desulfurization of organic sulfur compounds only after these compounds had been electrochemically reduced [13,20]. Vieira et al. [13] studied three thiophenol model compounds: pentafluorothiophenol (PFT), mercaptohydroquinone (MHQ), and 2-mercaptobenzoic acid (MBA), and found that desulfurization conversion efficiencies for these

compounds were 100% (PFT), 50% (MHQ), and 15% (MBA) respectively due to their capacity to electro-reduction on the Pt surface. The electro-reduced product could then be electro-oxidized, removing sulfur. PFT was the most easily reducible compound followed by MHQ, and MBA. With the presence of contaminants, Ovalles et al. [24] found that higher desulfurization conversion was achieved on Pb than on Pt.

Another precious metal, Ir, performed similarly to Pt in electrochemical desulfurization. Soriaga and co-workers [36,37] studied 2,5-dihydroxy-thiophenol (DHT), 2,5-dihydroxy-4-methylbenzyl-mercaptan (DHMBM), and PFT. They found that without prior reduction of the compounds Ir was not active toward the electrochemical oxidation of PFT, even at potentials greater than the oxygen evolution potential region. Similar to that on Pt, PFT could only be oxidized on Ir once it has been reduced. It has been explained that the reduction of PFT on Ir surface results in the formation of an adsorbed sulfur layer that is readily oxidized [37]. The order of preference for reductive desulfurization on Ir is as follows: PFT > DHT > DHMBM. However, the sequence for oxidative desulfurization is the reverse, that is: DHMBM > DHT > PFT.

Au has also been explored as the catalyst for desulfurization, which was found to perform differently from Pt. Soriaga and co-workers [36] found that PFT could be directly oxidized on an Au electrode. The electrochemical desulfurization of PFT on Au was minimal in comparison to Pt due to Au's inability to chemisorb hydrogen atoms. The direct electrooxidation of PFT on Au outperformed Pt. The desulfurization of DHT on Au was an order of magnitude lower than on Pt. However, the oxidation of DHT on Au was comparable to that on Pt [36].

Degradation of catalysts during electrochemical desulfurization of fossil fuels is a serious issue. The catalyst activity can degrade significantly due to poisoning by contaminants and corrosion of the electrodes. To decrease the rate of catalyst degradation, catalyst materials, applied potentials, and chemical environments must be carefully chosen. The use of low-active catalysts could decrease the catalyst deactivation, since less active catalysts are less prone to poisoning. However, low-active catalysts are kinetically unfavorable, which may lead to longer processing times. The magnitude of the applied potentials should also be carefully chosen because high potentials may cause dissolution of metal catalysts. So far no research has been conducted particularly to address this issue. More attention should be paid in this area.

6. Electrolytes

In general, in electrolysis of fossil fuels, electrolytes are needed due to the low ionic conductivity of fossil fuels. In systems where ionic conductivity is required, a neutral electrolyte is preferred. For electroreductive desulfurization, acidic electrolyte media are used, while for electrooxidative desulfurization, basic electrolyte media are preferred; however acidic electrolyte can also be used, whose function might be different from that of a basic electrolyte. In some cases electrolyte may not be used, for example, when using very high applied potentials and/or very high temperatures. In this respect, Keller [38] recommended an applied potential ranging from 1000 to 25,000 $V.cm^{-1}$ for a pure hydrocarbon feed [38]. Greaney et al. [11,17–19] found that the inherent conductivity of heavy hydrocarbon feeds could increase exponentially with temperature, and suggested that at elevated temperatures, the ionic conductivity could be sufficient for electrochemical desulfurization, as shown in Fig. 5.

The conductivity of a hydrocarbon feed may change during the electrolysis. As sulfur containing compounds such as mercaptans tend to form acidic compounds when catalytically electrolyzed, the ionic conductivity of the hydrocarbon feed could be higher than expected.

In most cases, addition of electrolytes is required and has beneficial effects for the electrochemical desulfurization of fossil fuels. However, adding electrolytes to the hydrocarbon feedstream is
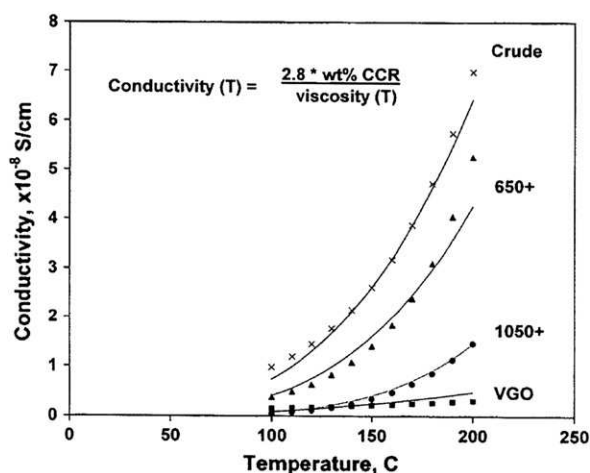
Fig. 5. Conductivity chart for various distillation fractions of petroleum crude [11,18].

problematic. Salts dissolved in the feed might be difficult to remove, which can cause problems due to undesired end product composition, post-processing steps, equipment fouling, as well as increased cost.

6.1. Basic electrolytes

High desulfurization conversion has been achieved under alkaline conditions using desulfurization mechanism that involved hydroxyl radicals [27,28]. Wang et al. [39] and Comninellis et al. [34] proposed that free hydroxyl radicals could oxidize organic sulfur to sulfone or sulfoxide. Interestingly, it has been observed that desulfurization of organic sulfur compounds in NaOH occurred even without an applied potential [40]. Wapner and Lalvani [28] observed that up to 56% sulfur removal from coal slurries in 1 M NaOH after 6 h under open circuit conditions, during which up to 42% of the organic sulfur content was removed. One disadvantage of this method is the formation of ash. Lalvani et al. [27] observed an increase in ash content when coal slurries were electrolyzed in alkaline media versus a reduction in ash content in acidic media. A later study found that low current densities led to an initial decrease in the ash content of coal, but further increases in the current density led to increased ash content [41].

6.2. Acidic electrolytes

Acidic electrolytes are usually used in electroreductive desulfurization because hydrogen is needed in the process. In electrooxidative desulfurization, the acidic electrolyte facilitates the formation of mediators that aid the desulfurization process. In the electrooxidation of coal slurries in acidic media, several mechanisms were observed including the oxidation of ferrous ion to ferric ion, and the oxidation of sulfide to elemental sulfur, and sulfate [5]. The ferric ion was found to be a major oxidation compound, oxidizing pyrite and thiophene. Lalvani et al. [5] were able to achieve 78% desulfurization of North Dakota lignite and 58% desulfurization of Illinois No. 6 bituminous coal via electrolysis in sulfuric acid using graphite and platinum electrodes respectively. Desulfurization of 48.3% was also achieved through electrooxidation in 9% HCl with Illinois No 6 coal. Further desulfurization of 61.7% was achieved with the addition of NaCl to the electrolyte [27]. They speculated that Cl$^-$ might have substituted for sulfur functionalities in coal, but this premise was not investigated further.

7. Summary and outlook

Electrochemical desulfurization technologies have proven potential for removing sulfur from fossil fuels. Two pathways by which sulfur can be electrochemically removed are electrooxidation and electroreduction. Electrooxidation leads to the addition of oxygen to organic sulfur compounds, and may result in polymerization; the product of which can easily be separated from the hydrocarbon feed through conventional separation processes such as distillation. Electroreduction generally removes sulfur via the formation of H$_2$S, which can be removed through a gas/liquid separation process. The effectiveness of either pathway is dependent on the nature of the fuel, the catalyst, the process setup, the reactor design, and the experimental conditions. Several approaches have been developed such as static and dynamic methods, and biological methods. Many different reactor configurations and designs have been proposed to carry out electrochemical desulfurization. Two primary configurations are divided and undivided cells. Divided cells may use a membrane as the electrolyte thus eliminating the need for a supporting electrolyte and therefore eliminating the additional separation processes that would otherwise be required to remove the electrolyte from the final product. Undivided cells may allow for a simpler reactor design and can lead to a combination of oxidative and reductive desulfurization that may result in higher desulfurization conversion.

It has been found that the addition of protonating agents such as methanol can significantly increase the electrochemical removal of sulfur. Mediators have also been found to enhance the desulfurization of organic sulfur compounds indirectly via chemical oxidation. Fe^{3+}, Ce^{4+}, I$^-$, Br$^-$, and Cl$^-$, have all been identified as effective mediators. An optimal mediator concentration is required to maximize desulfurization.

Typical HDS catalysts have been found not to be ideal for electrochemical desulfurization. For electroreduction, Raney nickel and Rh–Ru/C are catalytically active. Pb based anodes have demonstrated high catalytic activity toward desulfurization, and are less susceptible to poisoning than Pt. Moreover, Pb electrodes have been shown to be better than Pt for desulfurization. Au is catalytically active for the oxidation of thiophenol derivatives but has exhibited poor performance for electroreduction.

The presence of a supporting electrolyte is essential and has beneficial effects in many electrochemical desulfurization processes due to the low ionic conductivity of fossil fuels, especially at low temperatures. Electrolytes can be acidic or basic. Basic electrolytes lead to the addition of oxygen to organic sulfur compounds. Basic electrolytes can also avoid polymerization of organic sulfur compounds via nucleophilic attack by hydroxyl radicals. Therefore, a catalyst which can facilitate the formation of hydroxyl radicals and a system which can maximize the mass transfer of hydroxyl radicals to the hydrocarbon feed are definitely desirable. In basic electrolytes, desulfurization can occur even without an applied potential. At high temperatures, an electrolyte might not be needed because the inherent conductivity of some crude oils is high at elevated temperatures.

Although significant advancement has been made in the development of applicable electrochemical desulfurization technologies, further systematic research and development is needed to realize the true potential of such technologies. At the current status of the technology, neither desulfurization efficiency nor current efficiency for electrochemical desulfurization methods is attractive. Therefore, new catalysts are needed to achieve high selective activities for the electrochemical desulfurization of organic sulfur compounds. Studies on the catalyst deactivation will shed light on scientific understanding of catalytic mechanism and provide guidance for high active catalyst development. Thus research on this issue is needed. The principles and design of undivided electrochemical desulfurization process are similar to fuel cells. The concepts and catalysts development for fuel cell application may be employed in the ECDS process. Thus one research direction is to apply fuel cell catalysts to ECDS.

From the literature, it seems that catalysts containing Pb are promising in electrochemical desulfurization. Thus development of nanostructured Pb based electrocatalysts such as PtPb alloys might be another direction. However, Pb is toxic and is not environmentally friendly, developing/searching for other alloys for ECDS might be another research area. In addition, high temperature membranes are needed for divided cells, since high temperature operation can increase both desulfurization efficiency and current efficiency.

Acknowledgments

References

[1] U.S. Energy Information Administration, Petroleum, 2010.
[2] H. Alboudwarej, et al., Highlighting heavy oil, Oilfield Review 18 (Summer 2006) (retrieved on Feb. 25, 2011).
[3] J.W. Bunger, K.P. Thomas, S.M. Dorrence, Compound types and properties of Utah and Athabasca tar sand bitumens, Fuel 58 (1979) 183–195.
[4] H.J. Gluskoter, Inorganic Sulfur in Coal, 20, ACS, Philadelphia, 1975, p. 94.
[5] S. Lalvani, M. Pata, R.W. Coughlin, Sulphur removal from coal by electrolysis, Fuel 62 (1983) 427–437.
[6] W. Zhao, W. Xu, S. Zhong, Z. Zong, Desulfurization of coal by an electrochemical-reduction flotation technique, Journal of China University of Mining and Technology 18 (2008) 571–574.
[7] W. Wang, S. Wang, H. Liu, Z. Wang, Desulfurization of gasoline by a new method of electrochemical catalytic oxidation, Fuel 86 (2007) 2747.
[8] C. Fairbridge, E. Taylor, S. Petrovic, J. Lessard, J. Chapuzet, Electrocatalytic hydrogenation of organic sulphur compounds, NCUT Report 96-17 (CF), 1996.
[9] T.F. Yen, C. Wen, Electrolytic hydrogenation of leached oil shale components, U.S. Patent, 1977, 4043884.
[10] V.B. Baez, D.S.M., *Desulphurisation process of hydrocarbon feeds with electrolytic hydrogen*, U.S. Patent, 2007, 0108101 A1.
[11] M.A. Greaney, K. Wang, J.R. Bielenberg, D.W. Hissong, *Electrodesulfurization of heavy oils using a divided electrochemical cell*, WO, 2009, 082456 A1.
[12] H.W. Sternberg, C.L. Delle Donne, I. Wender, Similarity between the electrochemical elimination of sulphur from coal and from dibenzothiophene, Fuel 47 (1968) 219.
[13] K.L. Vieira, D.C. Zapien, M.P. Soriaga, A.T. Hubbard, K.P. Low, S.E. Anderson, Analysis of products from reactions of chemisorbed monolayers at smooth platinum electrodes: electrochemical hydrodesulfurization of thiophenol derivatives, Analytical Chemistry 58 (1986) 2964.
[14] H. Ahonen, *Method for Desulphurisation of liquid fuels and petrochemical feedstocks*, WO, 1993, 25636.
[15] R.C. Schucker, *Electrochemical oxidation of sulfur compounds in Naphtha*, U.S. Patent, 2001, 6274026 B1.
[16] R.C. Schucker, W.C. Baird, Jr., *Electrochemical oxidation of sulfur compounds in Naphtha using ionic liquids*, U.S. Patent, 2002, 6338788 B1.
[17] M.A. Greaney, K. Wang, F.C. Wang, *Electrochemical treatment of heavy oil feedstocks followed by caustic extraction or thermal treatment*, U.S. Patent, 2009, 0159503 A1.
[18] M.A. Greaney, C.A. Wright, J.M. McConnachie, H. Freund, K. Wang, *Electrodesulfurization of heavy oils*, U.S. Patent, 2009, 0159500 A1.
[19] M.A. Greaney, K. Wang, F.C. Wang, *Partial electrochemical hydrogenation of sulfur-containing feedstreams followed by sulfur removal*, WO, 2009, 082467.
[20] M. Hourani, Desulfurization of thiophene by electrochemical perturbation, Journal of Electroanalytical Chemistry 368 (1994) 139–142.
[21] H.W. Sternberg, C.L. Delle Donne, R.E. Markby, I. Wender, The electrochemical reduction of a low volatile bituminous coal: nature of the reduced material, Fuel 45 (1966) 469.
[22] S.B. Lalvani, C.B. Muchmore, K. Ramaswami, A low temperature technique for coal cleaning, Coal Science and Technology 9 (1985) 287.
[23] S.B. Lalvani, Desulphurisation of Coal Slurries by Electrolysis, NTIS, Springfield, VA, 1985 (DE85 018433).
[24] C. Ovalles, I. Rojas, S. Acevedo, G. Escobar, G. Jorge, L.B. Gutierrez, A. Rincon, B. Scharifker, Upgrading of Orinoco Belt crude oil and its fractions by an electrochemical system in the presence of protonating agents, Fuel Processing Technology 48 (1996) 159–172.
[25] R.E. Markby, H.W. Sternberg, I. Wender, Extensive reduction of coal by a new electrochemical method, Nature 199 (1963) 997.
[26] J.M. Sugihara, T. Okada, J.F. Branthaver, Reductive desulfuration on vanadium and metalloporphyrin contents of fractions from boscan asphaltenes, Journal of Chemical and Engineering Data 10 (1965) 190.
[27] S.B. Lalvani, S. Nand, R.W. Coughlin, Electrolytic pretreatment of Illinois No. 6 coal, Fuel Processing Technology 11 (1985) 25.
[28] P.G. Wapner, S.B. Lalvani, G. Awad, Organic sulphur removal from coal by electrolysis in alkaline media, Fuel Processing Technology 18 (1988) 25.
[29] J.Y. Gui, D.A. Stern, F. Lu, A.T. Hubbard, Surface chemistry of five-membered heteroaromatics at Pt(111) electrodes studied by EELS, LEED, Auger spectroscopy and electrochemistry: furan, pyrole, and thiophene, Journal of Electroanalytical Chemistry 305 (1991) 37.
[30] T.S. Kim, H.Y. Kim, B.H. Kim, Petroleum desulfurization by desulfovibrio desulfuricans M6 using electrochemically supplied reducing equivalent, Biotechnology Letters 12 (1990) 757.
[31] B.H. Kim, T.S. Kim, H.Y. Kim, *Bioelectrochemical desulphfurization of petroleum*, European Patent, EP 0323748 A1, 1989.
[32] C.W. Bell, J.K. Wittle, A.L. Speece, *Electrolytic oil purifying method*, U.S. Patent, 1975, 3915819.
[33] W. Wang, S. Wang, Y. Wang, H. Liu, Z. Wang, A new approach to deep desulfurization of gasoline by electrochemically catalytic oxidation and extraction, Fuel Processing Technology 88 (2007) 1002.
[34] C. Comninellis, A.D. Battisti, Electrocatalysis in anodic oxidation of organics with simultaneous oxygen evolution, Journal de Chimie Physique et de Physico-Chimie Biologique 93 (1996) 673.
[35] F.E. Wilkinson, *Improvements relating to the desulphurisation of oils of mineral origin*, U.K. Patent, 1953, 686529.
[36] B.G. Bravo, S.L. Michelhaugh, M.P. Soriaga, Reversible redox chemistry, hydrodesulfurization, and anodic oxidation of thiophenols: a comparison at platinum and gold electrodes, Journal of Electroanalytical Chemistry 241 (1988) 199.
[37] M.E. Bothwell, M.P. Soriaga, Reversible redox chemistry, hydrodesulfurization, and anodic oxidation of thiophenols chemisorbed at smooth polycrystalline iridium electrodes, Journal of Electroanalytical Chemistry 295 (1990) 123.
[38] H.F. Keller, *Removal of contaminants from hydrocarbon liquids*. U.S. Patent, 1974, 3857770.
[39] W. Wang, S. Wang, H. Liu, Z. Wang, Study on desulfurization of gasoline by electrochemical oxidation and extraction, China Petroleum Processing & Petrochemical Technology (2006) 47.
[40] S.B. Lalvani, P. Rajagopal, J.A. Koropchak, C. Chavez, B. Akash, C.B. Muchmore, Electrolytic pretreatment of coal for enhanced liquefaction, Fuel Processing Technology 31 (1992) 221.
[41] S.B. Lalvani, A. Weston, Coal cleaning in a semi-continuous flow reactor: galvanostatic studies, Fuel Processing Technology 21 (1989) 117.