

Iodide mediated electrolysis of acidic coke/coal suspension

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Received: 31 May 2007 / Revised: 12 February 2008 / Accepted: 14 February 2008 / Published online: 4 March 2008
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Abstract Hydrogen is among the emerging energy vectors that are being developed to replace nonrenewable hydrocarbon energy sources. The preferred method to produce hydrogen without generating greenhouse gases is the electrolysis of water using renewable energy. The reduction of energy during the water electrolysis process is a desirable goal regardless of the source of electric power. Similar to ferrous/ferric mediation, iodide can be used as a mediator in the electrolysis of an acidic suspension of coke or coal. The iodide ion is oxidized at a far lower anodic potential than the alternative oxygen evolution reaction. This reduces the cell electrolysis voltage and, consequently, reduces electricity use. The iodide consumed at the anode is continuously regenerated by chemical reaction with the coke/coal in suspension.

Keywords Catalytic chemical regeneration · Electrochemical gasification · Iodide mediator · Iodide/triiodide redox couple · Diffusion limiting current · Water electrolysis

1 Introduction

Total global output of primary energy increased at 2.2% annually from 1994 to 2004. The U.S. Department of Energy Information Administration suggests that overall

world energy consumption will rise by 60% from 1997 to 2020 [1]. About 80% of this energy demand will be fulfilled by carbon-based fuels (coal, natural gas and oil, including that from oil sands), which in turn will contribute to higher greenhouse gas (GHG) emissions.

As conventional petroleum fields are depleted, production from heavy oil and oil sands will increase. Today's oil sands processing technology generates more CO₂ than that produced during the exploration and production of conventional crude oil [2] (150 kg equivalent CO₂ (CO₂e) per barrel of synthetic crude versus 80 CO₂e per barrel for conventional light crude). Approximately 66% of these CO₂ emissions arise from upgrading steps where significant amounts of hydrogen are required, further contributing to greenhouse gas emissions from both upgraders and refineries.

The steam-methane reforming process is used extensively to produce hydrogen for the oil and gas industry. This process produces about 10 tonnes of carbon dioxide for each tonne of hydrogen. These reactions require high temperatures and pressures to produce hydrogen and carbon monoxide (reforming reaction); with a second step to convert carbon monoxide with water to hydrogen and carbon dioxide (water gas shift reaction). Developing hydrogen sources other than steam methane reforming could have a major impact on future clean fuel production and petrochemical industries. In the early 1970s, catalytic steam gasification of carbon was of interest and hydrogen was identified as the primary product [3]. Electrochemical gasification to produce hydrogen, utilizing the coke from petrochemical processing, is an alternative that is examined in this study.

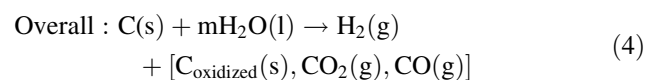
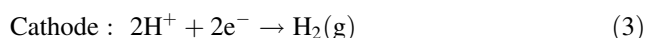
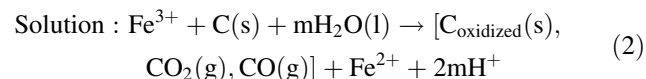
Electrolysis of water can directly produce hydrogen. The challenge, however, has been that the cost and the GHG emission from the electric power used in electrolysis

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has remained significant since the electric power used is generated normally by conventional methods. Electric power generated using renewable sources is still not widely available. It is desirable to make the electrolysis of water less energy demanding and more efficient regardless of the source of the electric power. Our work is focused in reducing the cell voltage for water electrolysis using a mediator.

Coughlin, Farooque [4–7] and others [8–29] have shown that hydrogen can be obtained by coal or coke slurry electrolysis, thereby using less energy than conventional water electrolysis. Some of the early studies concentrated on the oxidation products of the coal, peat, oil shale and bituminous materials to produce more valuable hydrocarbon materials [8–17, 20–23, 30–32]. Where the emphasis was on hydrogen generation, the electrolytic oxidations were conducted at low temperatures and in acidic media using ferrous ion as a mediator. The energy savings resulted from the substitution of the oxygen evolution reaction at the anode with the oxidation of the ferrous ion, which has significantly lower oxidation potential. This research showed that there was no depletion of ferrous ion because it was regenerated by the coke/coal in solution, as indicated below [4–22].



The mineral ion is oxidized electrochemically at the anode (Eq. 1) and regenerated in solution by chemical reaction (Eq. 2). Up to 90% current efficiency for hydrogen production, and cell voltages less than 1 V were observed [4–7, 20–23]. Simple analyses indicated that such coal-assisted water electrolysis might compete with conventional hydrogen production technologies [7]. However, the process does not exclude the undesirable CO₂ as one of the likely byproducts as indicated by Eqs. 2 and 4. The ferrous ion serves to shuttle electrons between the anode and the coal. The present work shows that iodide can be used as a mediator to the same effect as the ferrous ion.

Iodide/iodine is one of the first common choices for a redox couple for obtaining high efficiency in liquid electrolytes [33]. Ferrous ion is most conveniently studied in acidic or neutral solutions because of hydrolysis in the alkaline pH region. Air oxidation of the cation is also possible with ferrous ion. Both of these are not issues in terms of the stability of iodide solutions. Different

electrode materials are normally sought to get better energy efficiency (by reducing the overvoltage of the electron transfer) and longer service life. For instance, owing to the interaction of the iodide and triiodide with silver, significantly reduced oxidation potential shifts are observed on silver electrode over that on platinum working electrode [34–36]. The iodide/iodine change can be monitored conveniently using light absorption methods. The iodide/iodine couple is thus worth considering as an alternative to the well known ferrous/ferric couple to transfer charge from the electrode to the electrochemically inactive coal/coke slurry.

2 Experimental

Solutions were made using greater than 18.1 MΩ cm resistivity water, purified by reverse osmosis and deionization (Nanopure SystemsTM). Limiting current measurements were performed in non-coordinating electrolytes of hydrochloric acid (HCl) and potassium chloride (KCl) solutions. All chemicals were of analytical grade and all measurements were conducted on freshly prepared solutions.

The standard three-electrode cell set up was used in the electrochemical measurements. The working electrodes tested were platinum disc, glassy carbon disc (both from Pine Instruments) or graphite rods. A Pine Instruments rotating electrode system was used to control the fluid convection rate, which also kept the coke/coal in suspension. The coke was obtained from an oil sands upgrader and had a particle size less than 74 μm. This coke was dried at 110 °C to drive off superficially adsorbed oil. Luscar-Cardinal RiverTM coal sample pulverized to less than number 40 mesh size was used in the experiments.

The working electrodes were electrochemically cleaned by holding them at 2.0 V for 2 min, followed by 20 min of potential cycling at 0.1 V s⁻¹ scan rate between potentials of -0.3 V and 1.4 V. The electrochemical measurements were carried out using an EG&G 273A potentiostat/galvanostat and EG&G software. The electrolyte was first purged by bubbling inert gas through the solution and this was continued throughout the experiments. All measurements were conducted at room temperature.

The cation specific membrane Nafion 117TM (Dupont) was used to separate the two half cells of the H-cell, avoiding any physical mixing of the cell contents. All potentials were measured against the SCE reference electrode isolated inside the anode half cell by vicronTM frit. Flag or wire platinum counter electrodes were kept in the cathodic compartment. This compartment was filled with hydrochloric acid and potassium chloride solutions.

3 Results and discussion

Theoretically, water electrolysis requires 1.23 V. In practice, the cell voltage is higher. Figure 1 shows the cyclic voltammogram (CV) of a working platinum disc electrode in acidic solution between the hydrogen reduction and oxygen evolution potentials. It shows that even on platinum, where the hydrogen reduction over-voltage is the smallest, the difference in potential between the start of the oxygen evolution and hydrogen ion reduction at the same platinum electrode is 1.7 V. This potential does not include many of the polarization and resistive elements of cells containing separate anode and cathode electrodes. More details of the peaks are given in [37, 38]. Commercial hydrogen–oxygen cells require voltages up to 3 V [39].

Linear voltammograms (LV) in Figs. 2 and 3 reveal that there were no functional groups in the coke and coal that were electrochemically active in the potential range before oxygen evolution from water. Acidic solutions often provide better solubilizing media for different mediators and lower the cell potential, making lower pH the preferred experimental condition particularly for metal ion mediators. The coke and coal samples agglomerated due to their hydrophobicity. They also tended to stick at the electrode surface. Mixing was required to get a uniform slurry during experimentation. The coke and coal particles were kept in suspension by the rotation of the working electrodes or a rotating magnetic bar.

Cost-savings in the production of hydrogen from the electrolysis of coke/coal occurs when the anodic reaction is substituted by some other reaction that is more facile and less energy-consuming than oxygen production from water. The linear voltammograms in Fig. 2 compares the oxidation potentials of ferrous ion and oxygen evolution on a

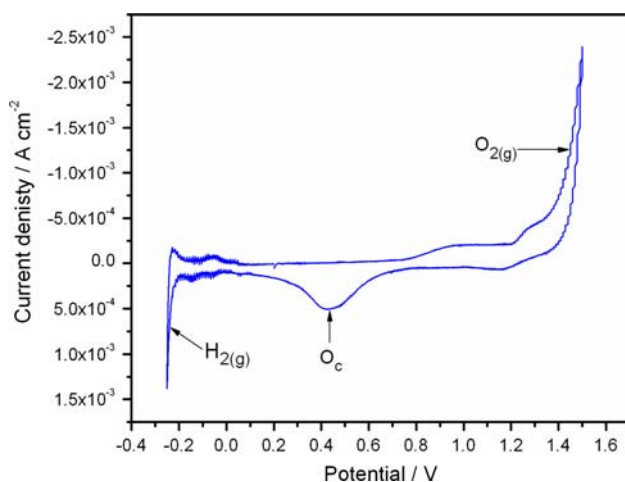


Fig. 1 Platinum disc electrode cyclic voltammogram in 0.9 M sulfuric acid solution at 1,000 rpm. The main peaks of $\text{H}_2(\text{g})$, and $\text{O}_2(\text{g})$ evolution and platinum oxide reduction are indicated

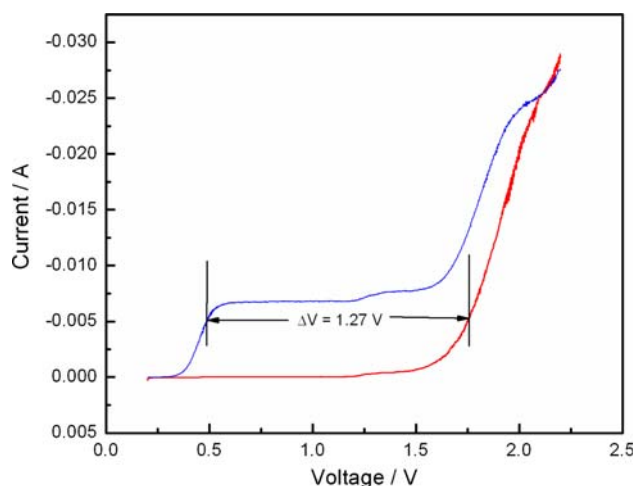


Fig. 2 Linear voltammograms of coke (4.4% by weight) in 0.9 M sulfuric acid supporting electrolyte with (blue curve) and without (red curve) 0.1 M FeSO_4

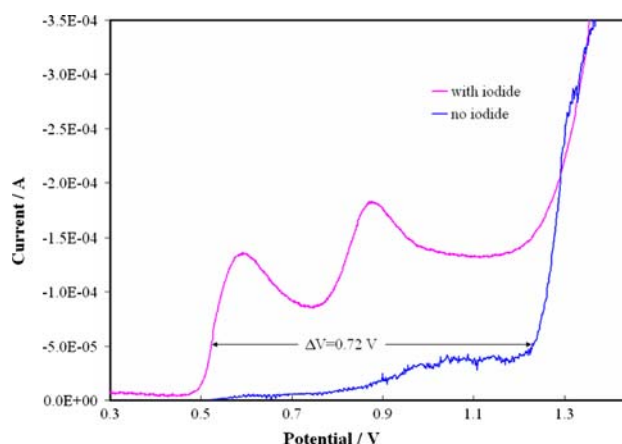
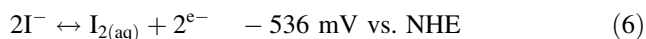
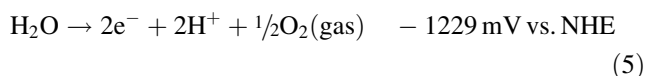


Fig. 3 Anodic linear potential scans on platinum disc of 0.25 M $\text{KCl}/0.5$ M HCl , coal slurry solution with and without 2.5 mM KI

platinum working electrode. The cathodic reaction under both conditions is the evolution of hydrogen. The results show that the oxidation of the ferrous ion and production of H_2 are more energetically favorable, as they occurred 1.27 V more cathodic than the alternate oxygen evolution reaction, at the experimental conditions. Because the over-voltage for oxygen evolution is larger than that of the reversible ferrous ion oxidation, this difference in potential would be larger at higher current densities, as can be seen by comparing the results in Figs. 2 and 3. A similar study conducted with and without the iodide ion (Fig. 3) gave a potential advantage of 0.72 V for the oxidation of iodide over the oxygen evolution process under our experimental conditions. The fact that the oxidation potential of iodide solution is around 0.5 V (vs. SCE) indicates that iodine is not likely to be a powerful oxidizing agent. However, from iodine's application in the well-known iodometric titration and other applications, its action is generally rapid [40].

The results show that the oxidation potentials of the iodide and the ferrous ion are very close. The resulting energy savings in the electrochemically-mediated splitting of water and generation of hydrogen are also comparable.

The primary advantage of conventional water electrolysis for the production of hydrogen when an iodide mediator is employed arises from reduction of the cell voltage by depolarization of the anode with the oxidation of iodide (Eq. 6), instead of oxygen evolution (Eq. 5).



where NHE is the Normal Hydrogen reference Electrode [38].

A system where both the oxidized and reduced forms of the mediator remain soluble improves the electrolysis process. Rapid electrochemical oxidation of the mediator at the electrode, and energetically favorable reverse chemical reduction reaction of the mediator, ensure continuous electron shuttling between the electrode and the reducing agent in solution. The oxidized form of the mediator should be sufficiently oxidizing to react with the coke, reverting back to its original soluble-reduced state. Below, we present experimental results showing that iodide satisfactorily meets these desired mediator conditions.

Figure 4a presents LV of the iodide solution at several convection rates. The convection dependence in the presence of coke, as monitored at the low and high convection rates, was similar to that shown in Fig. 4a. This indicates that the coke did not interfere in the electrochemical oxidation of iodide at the working electrode. A second oxidation-limiting current that was around 60% of the first peak was observed in the LV (Fig. 4a). After much study, the mechanism of the oxidation of iodide is in part still controversial [41–43]. The more widely accepted sequence of processes shown below could be used to explain the double oxidation limiting current plateau observed. The first plateau is for the heterogeneous oxidation reaction at the anode (Eq. 7), followed by homogeneous complexation reaction in solution (Eq. 8), and ending with another electrochemical reaction responsible for the second limiting current (Eq. 9).



The aqueous solubility of iodine is less than 1 mM [40] and the iodine concentration increases during the electrochemical process. Both a decrease in the iodide concentration as well as an increase in convection (i.e., increased

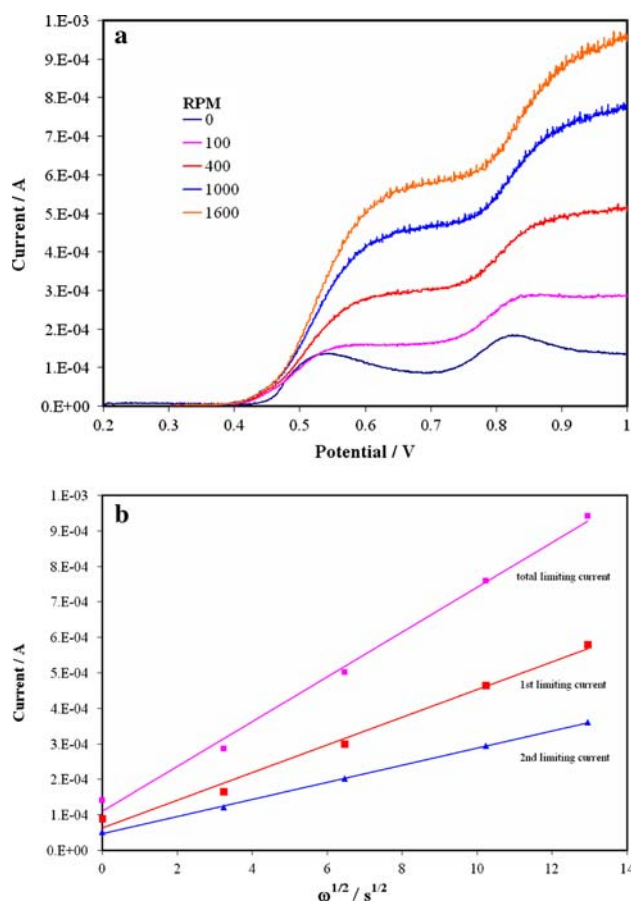


Fig. 4 (a) Linear potential scan of 2.5 mM KI/0.25 M KCl anode cell and 0.5 M HCl cathodic half cell at different rotation speeds of the glassy carbon disc working electrode. (b) Dependence of the limiting currents (total limiting current, first and second limiting current) on the square root of rotation speed (ω)

contact with the reductant) led to reduction in the second plateau, supporting the proposed complexation followed by an oxidation reaction mechanism. This hypothesis can be validated by having a strong homogenous reducing agent (thiosulfate is a very good candidate) that will remove the iodine as it is electrochemically generated, decreasing the probability of the reaction in Eq. 8. This possibility was outside the scope of this project and was not studied further.

Further, each limiting current was plotted against the rotation frequency. The first, second and overall limiting current dependencies all fitted the Levich line (Fig. 4b) in agreement with that expected for diffusion-limited electrochemical processes [38]. As the oxidation reaction rate increases, the reduction rate owing to the evolution of hydrogen gas increases at the same rate. One way the hydrogen evolution reaction rate can be increased is by increasing the complementary reaction of iodide ion oxidation at the anode. The increased rate of transport of

the iodide ion towards the electrode by convection, as shown in Fig. 4a and b, is one such alternative.

The dependence of the cyclic voltammetry of the mediator on scan rate was tested between 10 and 500 mV s^{-1} (Fig. 5). The peak current of a reversible system's linear sweep voltammogram is expressed by the following equation [38]:

$$i_p = 0.4463 \left(\frac{F^3}{RT} \right)^{1/2} n^{3/2} A D_0^{1/2} C_b v^{1/2} \quad (10)$$

where i_p is the peak current, F is the Faraday constant, R is the gas constant, n is the number of electrons exchanged, A is electrode area, D_0 is the diffusion coefficient, C_b is the bulk concentration, and v is the potential scan rate. The anodic peak current varies linearly with the square root of the scan rate (Fig. 5) indicating a reversible oxidation reaction in accordance with Eq. 10. The working electrode was a glassy carbon disc and shows that electrode materials, other than the well-behaved but costly noble metals, can be utilized for these types of electrochemical hydrogen generation. The rotation rate and scan rate dependences both show that the iodine electrochemical oxidation reaction is fast and reversible [41, 44, 45]. The capability of iodide as an electrochemical mediator in the production of hydrogen gas from the electrolysis of coke was established as follows.

The electron mediator activity of the iodide/iodine was tested and proven by conducting chronopotentiometric experiments in cells whose anode half cell contained measured volumes of iodide-coke mixture. The cathode half cell were filled with hydrochloric acid solutions. Constant anodic currents were applied to the anode so as to

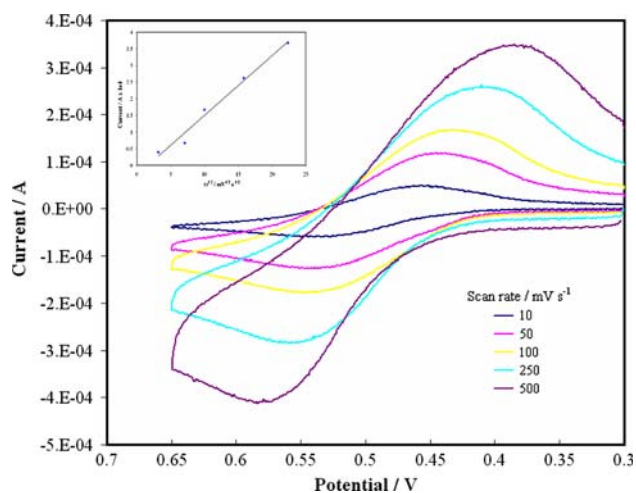


Fig. 5 Cyclic voltammograms of 2.5 mM KI/0.25 M KCl anode cell and 0.5 M HCl cathodic half cell for scan rates ranging from 10 mV s^{-1} to 500 mV s^{-1} (the working electrode was a glassy carbon disc). Inset—Peak current dependence of the iodide oxidation on scan rate

oxidize the iodide to iodine. Under this condition, the initial potential will be driven to a potential appropriate to oxidize the most readily oxidized species present (iodide in our experiments). As the concentration of the oxidizable species decreases the anode potential increases. During the chronopotentiometric experiments in which constant anodic currents were applied to the half-cell containing the iodide, the cell potentials remained practically steady at the initial potential over time, proving that there was no concentration polarization due to the depletion of the iodide. This could not have been possible without the regeneration of the iodide.

The charge passed is related to the amount of material that is electrolyzed according to Faraday's law.

$$Q = nFN \quad (11)$$

where, Q is the total charge passed (coulombs), n and F are as defined earlier, and N is the number of moles electrolyzed. Figure 6 compares LV before and after electrolysis in which 3 mA constant current was applied at the anode for 5,000 s to a 60 mL anolyte of 2.5×10^{-3} M KI, 6 g coke mixture and an equal volume hydrochloric acid cathode solution cell. The total charge passed was in excess of that necessary to exhaustively oxidize the iodide. If the iodide concentration had kept decreasing to levels insufficient to support the current that was forced through the cell, other oxidation (in our case, oxygen evolution) would occur leading to significant cell potential increases contrary to what was experimentally observed. Also, the limiting current values before and after electrolysis indicated that there was no change in the concentration of iodide. Thus,

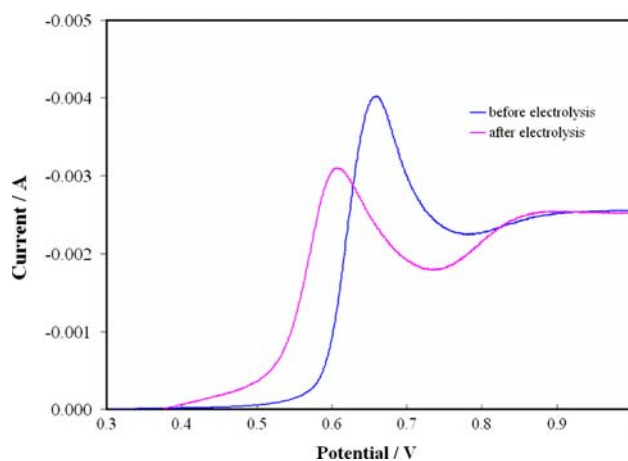


Fig. 6 Linear sweep voltammograms of 2.5 mM KI/0.25 M KCl, 1% by weight coke with graphite rod electrode anode half cell, and 0.5 M HCl cathode half cell, before oxidizing 60 mL of the anolyte (blue) and at the end after applying 3 mA constant current for 5,000 s (purple)

all of the electrochemically oxidized iodide was regenerated by chemical reaction in solution.

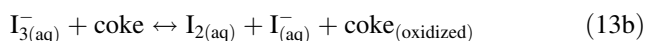
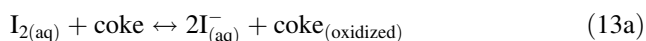
The electrochemically oxidized iodide could be regenerated by a chemical reaction in solution only. Electrochemical regeneration was out of the question, since proton conducting Nafion™ film was used to physically separate the contents of the anode and cathode compartments. Only oxidation occurred in the anode half cell that contained the mediator. The accompanying cathodic process in the half cell containing the counter electrode was hydrogen gas evolution. Since there was no other competing reducible substance, 100% Faradiac efficiency for hydrogen evolution was anticipated in such a cell setup. The difference in the peak (not the limiting current) of the LV in Fig. 6 indicates a change in the relative rates of the charge transfer kinetics and diffusion rate before and after electrolysis conditions [38, 46]. The coke also apparently facilitated the iodide oxidation as indicated by the cathodic potential shift (Fig. 6).

These results resemble those reported for the ferrous/ferric ion electrochemical mediation in acidified coke/coal slurry and are indicative of similar reaction mechanisms for both [4–22]. Halides in combination with oxide semiconductors have been tested for their potential to generate electric energy using photodriven regenerative electrochemical cells [47, 48]. The results in these studies were interpreted to involve mediation of charge transfer by one-electron oxidation of the halide [47, 49, 50]. Iodide/triiodide redox couples have specifically been used to shuttle charge between the sensitizer photoelectrode and counter electrode regenerative step [45, 47]. We envisage a similar reaction sequence in the electrochemical production of hydrogen using iodide as a mediator.

Anodic reaction



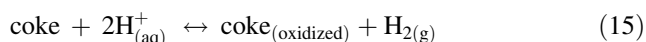
Catalytic reactions



Cathodic reaction



Net reaction



The net reaction is the oxidation of coke or coal (electrochemically inactive substances) and hydrogen gas production.

A three-stage process (Eqs. 12–15), involving a homogenous reaction in solution has been proposed for iodide/iodine. The equilibrium indicates that the likelihood of forming triiodide decreases concomitantly with the

iodine concentration. The effectiveness of the iodide catalysis is, therefore, highest at the start of electrolysis and over a short period before the iodine concentration builds up. To test this, a current sufficient to oxidize just 5% of the iodide was supplied. No decrease of the limiting current was observed. Also, there was no change in the second wave-limiting current during long periods of oxidation, which supports the statement that the iodide serves as a catalyst.

The current density the cell can support is one of the factors in the performance of the electrolytic cell. The well known ferrous/ferric mediator was used to measure the current density. Smaller electrolysis current density requires smaller applied potential. However, this also means that it will take longer to produce a given quantity of hydrogen and the cost of production could be higher. The electrolysis voltage was measured as a function of applied current in the presence of coke (Fig. 7). For the cell as constructed, the critical current density beyond which other energy-dissipating processes occur was 4.5 mA cm^{-2} of electrode. Below this current density, the change in potential is just due to $I \cdot R$ drop. For the cell, the Ohmic resistance during electrolysis was 383Ω as determined from the slope of the linear portion of Fig. 7. Since the amount of hydrogen gas is proportional to electric current density, the cell voltage is a good overall index to compare costs and energy use between mediators and alternative electrochemical systems.

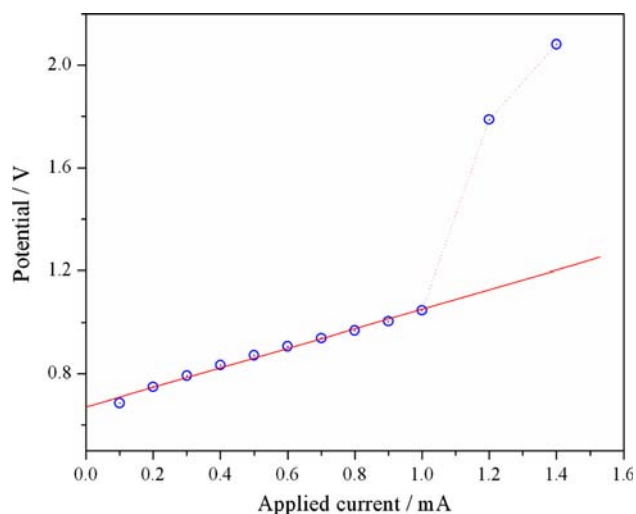


Fig. 7 Potential recorded as a function of applied oxidation current for a 5 mM FeSO_4 in 0.9 M sulphuric acid solution in the presence of coke at 2,000 rpm of the disc electrode. The linear portion of the curve shows the electrolysis current Ohmic drop

4 Conclusions

The concept of producing hydrogen at lower energy consumption (voltage) than water electrolysis was demonstrated, utilizing coal or coke slurry and iodide mediator in the anodic compartment. Iodide is oxidized at the anode at a far less anodic potential than that required for O₂ evolution in water. The mediator was regenerated by chemical reaction in solution with the coal/coke. That is, the iodine formed from the oxidation was sufficiently oxidizing that it was regenerated by reaction with coal/coke. Acidic solution and platinum flag were used in the cathode compartment where hydrogen was evolved, so that the reduction potential as well as the over-potential at the electrode, was minimized. The current efficiency for the evolution of hydrogen gas in the cathode compartment was 100%, since there was no competing or parasitic reaction in that half of the electrochemical cell.

The production and use of hydrogen in heavy oil upgrading is a major contributor to GHG emissions, and research into alternative methods for producing hydrogen continues. The work conducted in this project confirms that hydrogen can be obtained by iodide-mediated coal/coke slurry electrolysis, using less energy than conventional water electrolysis and, therefore, producing less greenhouse gas emissions.

Acknowledgements Partial funding for NCUT was provided by the Canadian Program for Energy Research and Development (PERD), the Alberta Research Council and the Alberta Energy Research Institute.

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