

75f Electrode Kinetics and Modeling of the Electro-Oxidation of Coal Slurries

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Introduction

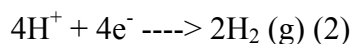
Hydrogen is expected to be a primary energy source in the 21st century for electricity generation, fuel and other applications. It is environmentally clean energy source since it generates no pollutants but produces water which can be recycled to make more hydrogen. Fossil fuels and water are the major sources for the manufacture of hydrogen. However, these processes are highly energy intensive consuming nearly twice the energy from these sources and not always environment-friendly.

Coal is an important traditional and cheapest source of hydrogen due to its diversity, availability, chemical stability and competitive price. In the conventional method of gasification of coal reported elsewhere [1], requires high temperature, and at the same time the process releases SO_x and NO_x which also requires the purification of the gases. In 1979 [2] a new method called electrochemical gasification of coal water slurry using platinum electrodes was carried out, which generated pure streams of CO₂ and hydrogen at anode and cathode respectively free of tar and sulfur compounds. The authors [2] have suggested the following reaction scheme taking place during the electro-oxidation of coal-water slurry.

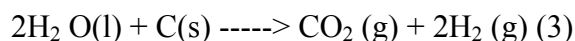
The anodic reaction is mainly carbon oxidation:



The cathodic reaction is hydrogen evolution:



The overall reaction is:



The above steps show the reactions without much in-depth explanation about their mechanism. Since the reactions involve four electrons transfer, which means the intermediate elementary steps have to be determined. Hence the actual mechanism is still unclear and is a matter yet to be explored.

Several authors [3,4] have proposed that the iron content in the coal is mainly catalyzing the reaction. Dhooze *et al.* [3] tried to elucidate the mechanisms associated with the electrolysis of coal that seems to be in agreement with the observations reported by Coughlin and Farooque [2]. But the authors did not explain that the coal particles have to be in contact with the anode for the electro-oxidation to take place. We are trying to propose a better explanation as to how the reaction of iron takes place at the electrode surface as well as on the coal particle surface.

Within this context, the objective of this work is to determine the reaction mechanism and give an explanation to the above uncertainty. Classical polarization on rotating disk electrode (RDE) will be performed to achieve the objective. The polarization curves will be modeled, and parameter estimation combined with modeling discrimination techniques will be used to elucidate the mechanism.

Experimental

The electro-oxidation of coal water slurries was studied using a Pt RDE. The electrochemical measurements were conducted at 40 °C in a glass cell containing aqueous solution of coal (size 74-105 μm) suspended in 1.0 M H_2SO_4 as electrolyte using Pt rotating disk electrode (0.5 mm diameter). The counter electrode was made of Pt-Ru, while SCE was used as the reference electrode. The measurements were done using a potentiostatic monitoring system from ARBIN Instruments. To study the effect of mass transfer, experiments were also carried out at different rpm of the electrode. The effect of the catalytic oxidation of iron has been tested by adding known quantities of iron sulfates in the solution. Pittsburgh seam No. 8 was used for the analysis.

Results and Discussion

Figure 1 shows the polarization performance of a coal water slurry solution (0.12 g/ml) containing 100 mM Fe^{2+} swept at 50 mV/s in acidic medium (1.0 M H_2SO_4) using Pt RDE at 40°C for different rpm. The curves indicate increase in limiting currents with increasing rpm and this happened even in baseline (1.0 M H_2SO_4) solution except that the limiting currents are negligible indicating almost no reaction. The maximum limiting current was close to 26.0 mA/cm² observed at a potential of approximately 0.6 V and 2100 rpm. We are speculating that the limiting currents observed could be mainly due to the oxidation of the coal in presence of iron. We have performed the experiments even in the absence of iron content to exactly compare and study the effect of iron content. We will use these results to diagnose the mechanism and to quantify kinetic parameters. Basically we will propose a hypothesis for the mechanism, predicting experimental behavior on the basis of the hypothesis, and comparing the predictions against the results. Further analysis and results will be presented.

References

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- [3] P. M. Dhooge, D. E. Stilwell and S. Park, *J. Electrochem. Soc.* **129**, 1719-1724 (1981)
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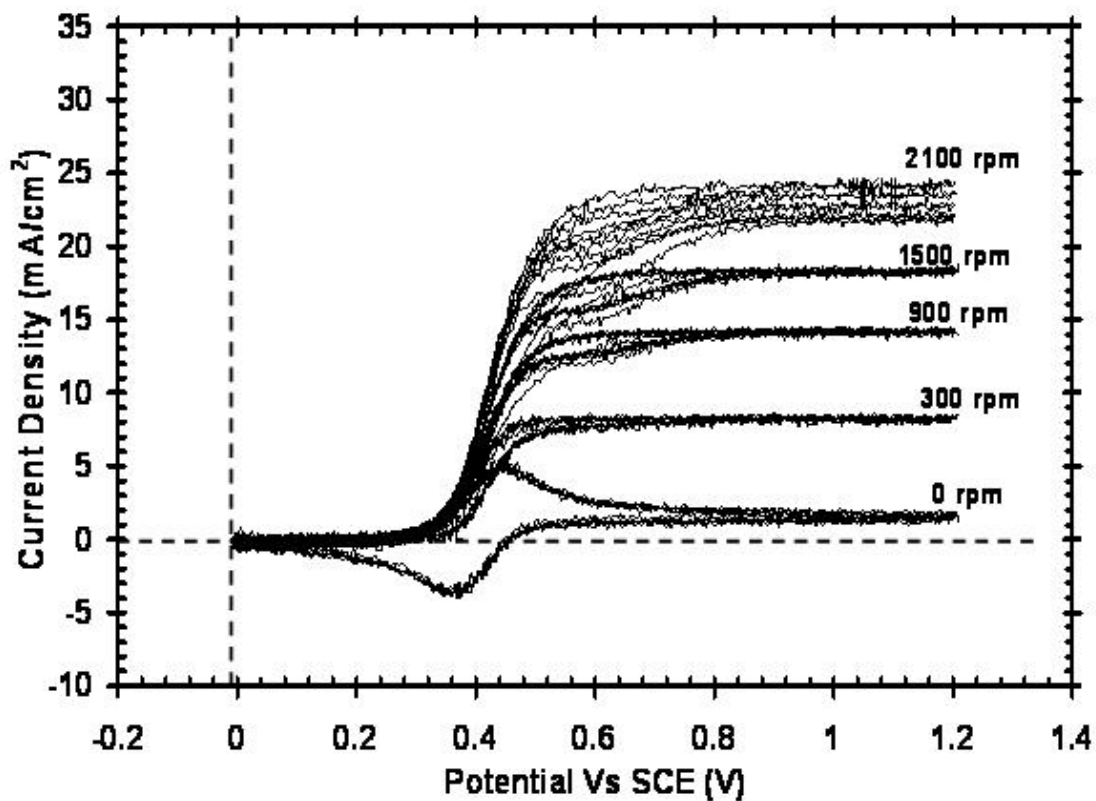


Figure 1. Polarization curves for Pt RDE at a scan rate of 50mV/s, coal concentration 0.12g/ml, 1 M H₂SO₄ and 100mM Fe (II) operating at 40°C.