JOURNAL OF APPLIED ELECTROCHEMISTRY 6 (1976) 279–282

SHORT COMMUNICATION

Recovery of electric power by hydrocarbon chlorination in a fuel cell containing molten salt electrolyte using a redox system as anolyte

S. YOSHIZAWA, Z. TAKEHARA, H. INOGUCHI

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto, Japan

Y. ITO

College of Liberal Arts and Science, Kyoto University, Kyoto, Japan

Received 1 May 1975

1. Introduction

Various hydrocarbon chlorides can be obtained by the use of a hydrocarbon–chlorine fuel cell, where the energy generated can be recovered simultaneously as electric power [1]. This paper describes the new type of cell using the redox system-containing anolyte. When we bubble the hydrocarbon gas (e.g. ethylene) into the redox system-containing anolyte, it reacts with the higher oxidized state ion (e.g. cupric chloride) to form the lower oxidized state ion (e.g. cuprous chloride), for example, according to the following.

$$C_2H_4 + 2CuCl_2 \rightarrow C_2H_4Cl_2 + 2CuCl. \quad (1)$$

The lower chloride is then anodically oxidized as follows:

$$2CuCl + 2Cl^- \rightarrow 2CuCl_2 + 2e^- \quad (2)$$

Thus the total anodic reaction is the chlorination of hydrocarbon and in this case, the three-dimensional gas–liquid reaction involved can lead to an acceleration of the overall anodic reaction.

2. Thermodynamic estimation

The E.M.F.s of ethylene–chlorine fuel cells have been calculated as a function of ethylene conversion efficiency and summarized in Table 1, where 1·2-dichloroethane is assumed to be the only product. It can be seen from Table 1 that more than 0·5 V might be expected by setting the conversion efficiency at about 50%.

Table 1. Conversion ratio and E.M.F.s of the ethylene–chlorine cell

Conversion ratio (%)	*E.M.F.* (V at 500°C)
80	0·52
60	0·55
50	0·57
30	0·58
10	0·62

3. Experimental methods

The cell assembly is shown in Fig. 1. $CuCl_2$ is produced at the graphite anode, which is then reduced to CuCl by ethylene gas fed through a carbon pipe. The chlorine electrodes are also carbon pipes, one of which (at right of Fig. 1) acts as the reference electrode and the other (at left of Fig. 1) as the counter electrode. The electrolyte of the cathodic compartment is the LiCl–KCl eutectic.

To examine the behaviour of the redox electrode separately, a lithium glass membrane (SiO_2 62 mol %, LiO_2 28 mol %, BaO 7 mol %, La_2O_3 3 mol %) is used as a separator. Only the lithium ion moves through this lithium glass, and the

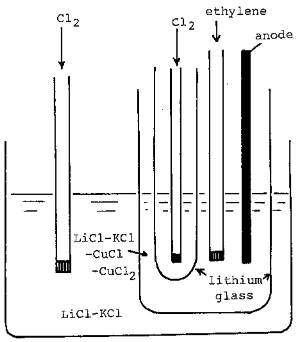

Fig. 1. Cell assembly.

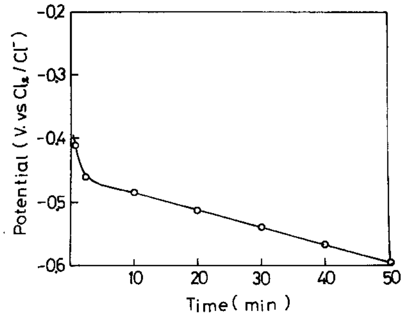

Fig. 2. Time-dependence of the anode potential decay. Total copper ion concentration = 1·5 mol dm^{-3}.

redox system does not migrate to the cathodic compartment. LiCl–KCl eutectic was dehydrated by bubbling hydrogen chloride gas and afterwards argon gas through it. $CuCl_2$ was used in the as-supplied form. All reagents were c.p. The purity of ethylene used was 99·0%. Measurements were carried out in a conventional way.

4. Anodic reaction of ethylene

4.1. *Anode potential*

The anode potential is given (non-rigorously) by the Nernst equation as follows, using concentration C and activity coefficient γ of Cu^{2+} and Cu^{+}.

$$E = E_1^0 + \frac{RT}{F}\ln C_{Cu^{2+}}/C_{Cu^{+}} \tag{3}$$

$$E_1^{0'} = E^0 + \frac{RT}{F}\ln \gamma_{Cu^{2+}}/\gamma_{Cu^{+}}$$

The value of E_1^0 can be obtained experimentally by setting the concentration ratio equal to 1 at different total copper ion concentrations. In our case, E_1^0 is −0·253, −0·250 and −0·235 V (versus Cl_2/Cl^-) at the total copper ion concentration of 1·0, 1·5 and 2·6 mol dm^{-3}, respectively.

4.2. *Reaction rate of ethylene with cupric chloride*

After polarizing the anode of Fig. 1 to a certain potential, the current was interrupted and the potential decay recorded (Fig. 2). From this the reaction rate constant k of ethylene with anodically produced $CuCl_2$ can be obtained as follows. The *total* ionic concentration of cuprous and cupric ion is constant during the potential decay.

$$C_{Cu^{+}} + C_{Cu^{2+}} = A. \tag{4}$$

Therefore Equation 3 can be rewritten as

$$E - E_1^0 = \frac{RT}{F}\ln\frac{C_{Cu^{2+}}}{A - C_{Cu^{2+}}}. \tag{5}$$

From Equation 5, the potential-time relation during potential decay is derived as follows, assuming a first order reaction mechanism for Reaction 1. If the partial pressure of ethylene is kept constant, the Cu^{2+} concentration change can be expressed simply as

$$-\frac{dC_{Cu^{2+}}}{dt} = kC_{Cu^{2+}} \tag{6}$$

integrating

$$\ln\frac{C_{Cu^{2+}}}{C_{Cu^{2+}}|_{t=0}} = -kt, \tag{7}$$

where, $C_{Cu^{2+}}|_{t=0}$ is the Cu^{2+} concentration just after the current interruption. From Equations 5 and 7, the following potential-time relation is finally obtained.

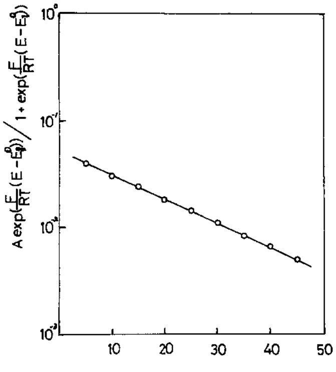

Fig. 3. Data plot according to Equation 8. A = 1·5 mol dm^{-3}.

$$\ln \frac{A\exp\left[\frac{F}{RT}(E-E_1^0)\right]}{1+\exp\left[\frac{F}{RT}(E-E_1^0)\right]} = -kt + \ln \frac{A\exp\left[\frac{F}{RT}(E_p-E_1^0)\right]}{1+\exp\left[\frac{F}{RT}(E_p-E_1^0)\right]}. \quad (8)$$

Here, E_p means the potential just after the current interruption. Fig. 3 shows the plot of the data shown in Fig. 2, according to Equation 8. A linear relation is observed, which supports the first order reaction mechanism postulated for Reaction 1.* From the slope, rate constants k were obtained as a function of the ethylene supply rate (Fig. 4). They change linearly with the gas supply rate, and by extrapolating this line to the zero supply rate, we can obtain the limiting k value of the order of 10^{-4} (s^{-1}), where the gas–liquid effective contact area is only the melt surface.

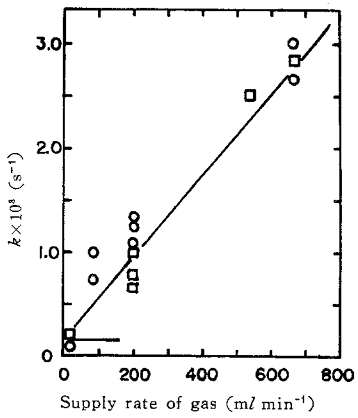

Fig. 4. Relation between the supply rate of ethylene gas and the rate constant k. Total copper ion concentration ○ 1·5 mol dm^{-3}; □ 2·6 mol dm^{-3}.

5. Cathodic reaction (positive electrode)

At a cathode, the following reaction is predominant.

$$Cl_2 + 2e^- \rightarrow 2Cl^-. \quad (9)$$

Polarization characteristics are shown in Fig. 5. Curve b shows the case before the porous carbon electrode is wetted by the electrolyte. Curve a shows the case after the electrode is wetted and contaminated with the redox system. If the cathode is directly exposed to the redox system, the reduction of Cu^{2+} migrating to the cathode from the anode takes place. This must be prevented by the use of a diaphragm or ion conducting membrane such as that of lithium glass† proposed above.

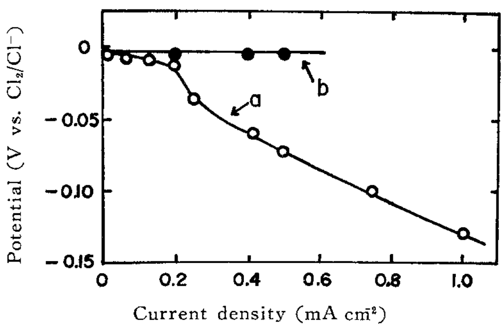

Fig. 5. Polarization curves for the chlorine cathode. (a) Wetted electrode; (b) non-wetted electrode.

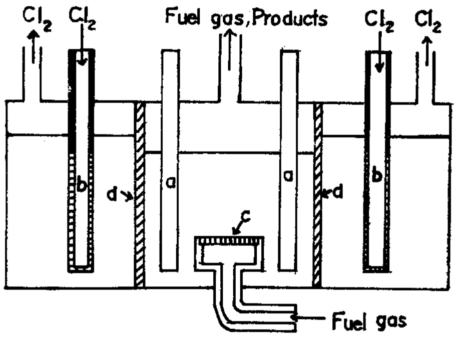

Fig. 6. Bubble gas column type cell. a–anode; b–cathode (porous electrode); c–porous plate; d–diaphragm or membrane.

6. Concluding remarks

The possibility of a high temperature ethylene–chlorine cell has been suggested, by which electric energy and various ethylene chlorides might be obtained at the same time. The use of this type of

---

* If one assumes a second order reaction, for example, no such clear-cut relation can be obtained.

† At the present time, the specific resistance of this membrane is rather high (~ 10^3 Ω cm). The production of low-resistant membranes is one of the interesting problems for the future.

cell might yield an efficiency of ethylene chlorination of 50% at a cell voltage of 0·5 V. By using a column-type cell (Fig. 6) or a packed column-type cell, scaling up of the ethylene–chlorine cell may be possible.

References

[1] S. Yoshizawa, Z. Takehara, Y. Ito, Y. Nakanishi, and Y. Koyama, *J. Appl. Electrochem.* 4 (1974) 81.