JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 143–146

Electrolytic recovery of chlorine from hydrogen chloride gas with fused molten salt electrolyte LiCl/KCl

Y. DING, J. WINNICK

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100, USA

Received 23 December 1994; revised 30 May 1995

A method of electrolytic recovery of chlorine from hydrogen chloride gas based on the fused molten salt LiCl/KCl is under development*. For the feasibility study, described here, a reticulated vitreous carbon (or porous carbon) cathode was immersed in a low-melting eutectic of LiCl/KCl. A graphite rod was used as the anode. Gaseous dilute hydrogen chloride, in a mixture with nitrogen, was reduced to elemental hydrogen and chloride at the cathode, and chlorine was produced at the anode. At stoichiometric current, current efficiency is greater than 90%. The removal efficiency is as high as 97%.

1. Introduction

The continued growth of byproduct HCl production has stimulated a number of proposals to recover chlorine values from HCl. A number of those involve oxidation of gaseous HCl with oxygen or air as in the classical Deacon process [1, 2]. The direct electrolysis of HCl has been discussed [3], with the Uhde cell [4] and de Nora cell designs [5] proposed. From a historical perspective the four main hydrogen/chlorine formation processes are [5]:

(i) Direct oxidation of hydrogen chloride by an inorganic oxidizing agent
(ii) Catalytic oxidation of gaseous hydrogen chloride (Kel–Chlor and Deacon processes)
(iii) Two-stage processes involving intermediate formation of a metal chloride from either its oxide or oxychloride and release of the chlorine by treatment with air or oxygen or by heating (e.g., the Cyanamid process [5]); and
(iv) Electrolysis of hydrogen chloride (Mobay direct electrolysis process, Denora cell and Uhde cell).

The direct oxidation method was abandoned due to extreme corrosion problems. In the Kel–Chlor method, the purity of the chlorine gas is a problem. As for the Deacon process, there is a problem of high energy cost. The third, two-stage processes, are inherently complex, being both equipment and labor intensive. The last, the electrolysis method, showed poor economics; it used aqueous HCl electrolyte causing a corrosion problem, and the chlorine was contaminated with water from electrolytic cell. Further, there is a problem of diaphragm (usually polyvinyl chloride) clogging and electrode deterioration due to crystal growth. Inorganic impurities that have a deposition potential more positive than that of hydrogen will plate on the electrodes and thus increase the hydrogen overvoltage.

A process is proposed here which yields purer chlorine, is inherently simple and has less serious corrosion problems than the normal direct electrolysis process. We modify the method suggested by Yoshizawa *et al.* [6] employing the LiCl/KCl eutectic molten salt as the electrolyte.

2. Theory

For the Mobay direct electrolysis process the cathode reaction is

$$H^+ + e^- = 1/2\,H_2 \qquad (1)$$

and the anode reaction is

$$Cl^- = 1/2\,Cl_2 + e^- \qquad (2)$$

The theoretical decomposition voltage for this process at room temperature is about 1.4 V (HCl concentration of about 1 M).

For the direct electrolysis of HCl, employing a eutectic molten chloride as the electrolyte, the cathode reaction is

$$HCl + e^- = Cl^- + 1/2\,H_2 \qquad (3)$$

and the anode reaction is

$$Cl^- = 1/2\,Cl_2 + e^- \qquad (4)$$

The theoretical decomposition voltage of HCl in this process at 400 °C is about 1 V which is less than that in the Mobay process. There will clearly be possible interference from water vapor present in the gas; the decomposition of water vapour occurs at nearly the same voltage.

3. Experimental details

The experimental electrolytic cell is shown in Fig. 1. The hydrogen chloride gas mixture is led through a graphite tube to a gas-diffusion, reticulated vitreous carbon cathode (80PPI) or porous carbon (40% porosity), which is immersed in the LiCl/KCl(41 mol %/ 59 mol %) at about 400 °C. The salts were labelled

---

* Patent pending (May 1995).

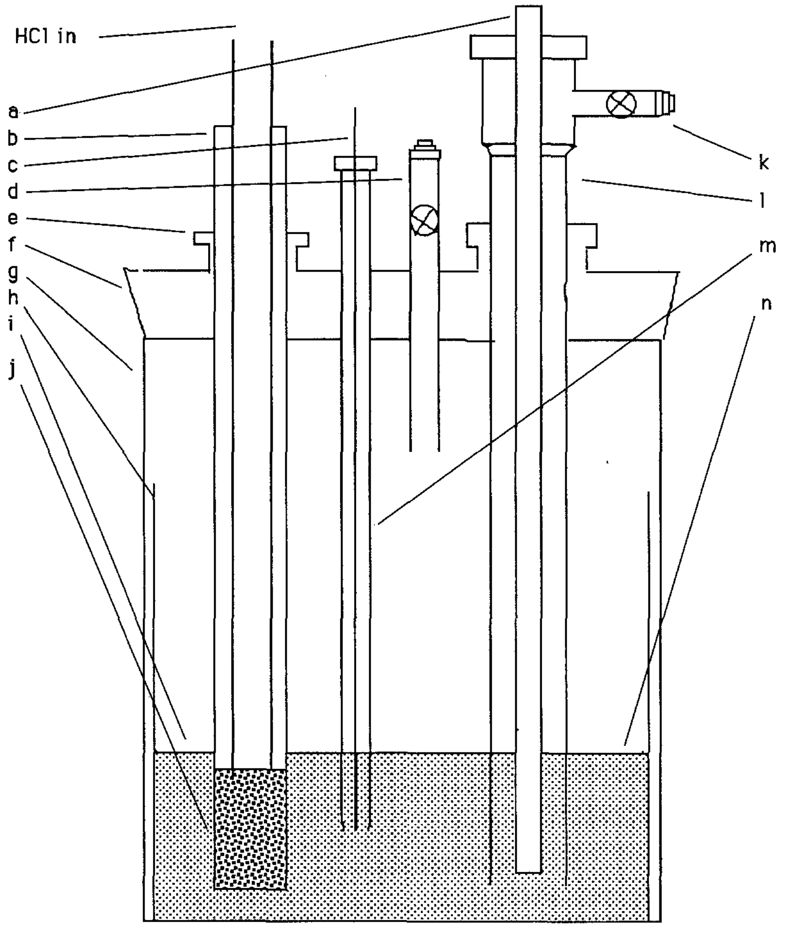

Fig. 1. Experimental cell. Key: (a) graphite anode, (b) graphite tube, (c) reference electrode, (d) gas exit, (e) ace-thread, (f) glass joint, (g) Pyrex glass container, (h) alumina crucible, (j) reticulated vitreous carbon, (k) chlorine exit, (l) Pyrex tube, (m) Pyrex protector and (n) eutectic molten salt.

99% pure (Aldrich Chemical Company, Inc.) and were not purified further. The anode is the graphite rod which is also immersed in the molten salt. The feed gas is the HCl/N_2 (0.98/99.2 vol %) mixture from Air Products and Chemicals, Inc. If not otherwise specified, the feed gas is always this composition. A Hewlett–Packard 6448B d.c. power supply and a Hewlett–Packard 6218c power supply were used throughout. A Simpson model 8010A digital multimeter was used to measure the voltage and an ultra-high sensitivity volt–ohm microammeter (Simpson 269, series 3) was used to measure the current. Total circuit resistance, not including the electrolyte, is less than 1 Ω.

The surface area of the solid graphite rod anode immersed in the melt is about 1 cm^2. The reference electrode, protected by the Pyrex tube, comprised a two phase $(\alpha + \beta)$ – LiAl (42 a/o) alloy prepared in our laboratory. An alumina reaction vessel was used as the eutectic melt container. A thick, porous carbon plate (or reticulated vitreous carbon circle plate) was attached to the bottom of the graphite tube and was employed as the cathode; this increases the contact time for the HCl gas with the cathode, as compared with the solid graphite tube. Before each experiment, HCl gas in nitrogen is bubbled through the eutectic melt to remove any traces of water [7].

The current efficiency, removal efficiency and polarization were determined. The effluent from the cathode was collected and analysed for remaining HCl. This captured hydrogen chloride was analysed using chemical titration with a model 94-17B chloride electrode from Orien Research Inc. and a AgCl/Ag reference electrode. The anodic production efficiency of chlorine and current efficiency were calculated and compared with the chlorine production using a bubble flow meter from Konntes. The flow rate of the feed mixture gas N_2/HCl and produced chlorine were measured with a bubble flow meter. The current efficiency from the residue hydrogen chloride analysis is compared with the data from the chlorine bubble flow meter as shown in Fig. 2. Without gas feed, there is no chlorine produced.

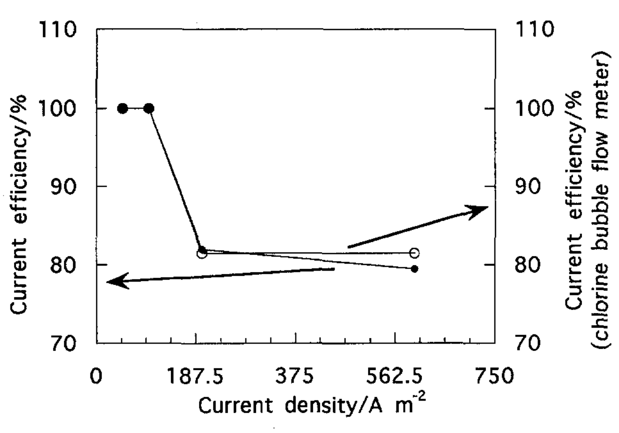

Fig. 2. Current efficiency at a feed gas flow rate of 2.58×10^{-3} $dm^3\,s^{-1}$ (HCl 0.98 mol %).

4. Results

The chlorine recovery efficiency from hydrogen chloride is calculated by dividing the decomposed hydrogen chloride, as deduced from the effluent concentration, by the amount supplied to the cathode. The current efficiency is calculated by dividing the decomposed hydrogen chloride by the theoretical charge: 1 F mol^{-1}.

Figure 3 shows the current efficiency and removal efficiency as a function of the current using porous carbon as the cathode, at one particular gas feed rate: 134.6 cm^3 min^{-1}. Total cell voltage as well as the conversion efficiency are shown in Fig. 4. The conversion efficiency increased with applied current; the current efficiency decreased with current. The conversion efficiency and the current efficiency as a function of the feed gas flow rate at constant current (88.5 mA) is shown in Fig. 5. The conversion efficiency decreases with the gas flow rate, as must be the case from stoichiometry. The conversion efficiency is about 92% at different gas feed rates near their stoichiometric current, as shown in Fig. 6.

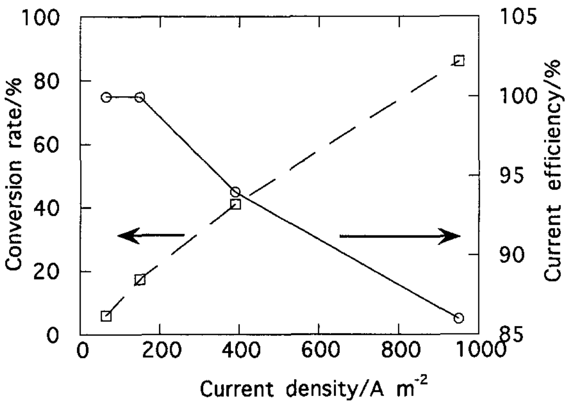

Fig. 3. Conversion efficiency and current efficiency against applied current at HCl/N_2 (HCl 0.98 mol %) flow rate of 2.24 × 10^{-3} dm^3 s^{-1}.

The cell resistance was measured using the current interruption technique. Without gas flow to the cathode, it measured about 8 Ω. However, it decreased significantly when HCl was fed and the cell was in operation. The cell resistance at a gas feed rate of 14 cm^3 min^{-1} and current of 56.5 mA is 2.9 Ω. This indicates a slight lack of ionic transport without the HCl source, as expected.

The current efficiency at several gas flow rates and HCl concentrations was measured as a function of current. The current efficiency was found to decrease with increasing applied current, due to transport-induced 'short circuiting', as detailed later.

When the porous carbon cathode was replaced with the reticulated vitreous carbon, the HCl removal efficiency at stoichiometric current increased to as high as

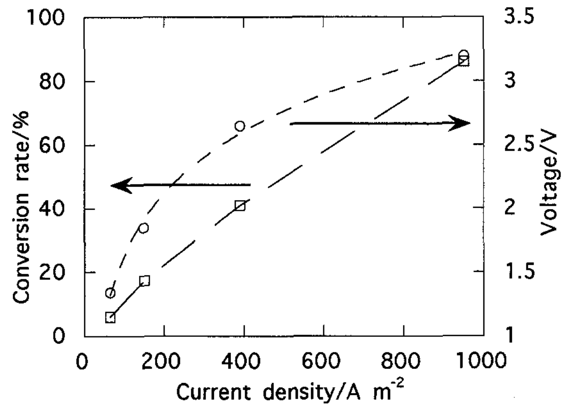

Fig. 4. Conversion efficiency and cell voltage against applied current at HCl/N_2 (HCl 0.98 mol %) flow rate of 2.24 × 10^{-3} dm^3 s^{-1}.

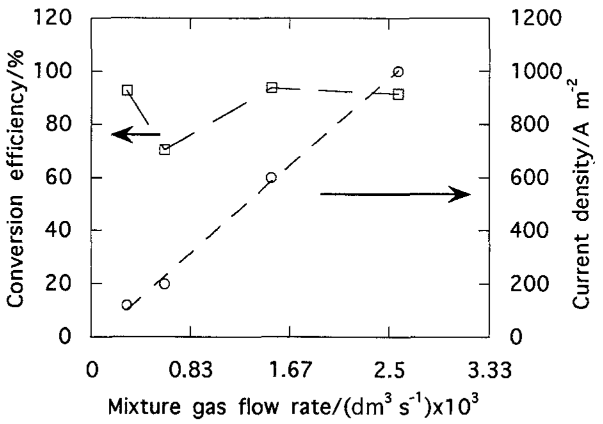

Fig. 6. Conversion efficiency against feed gas flow rate at stoichiometric current.

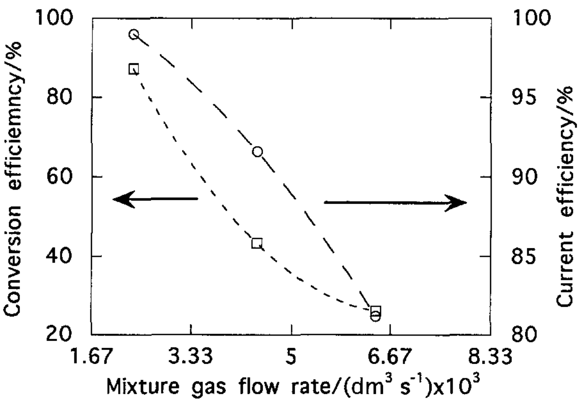

Fig. 5. Conversion efficiency and current efficiency against feed gas flow rate at 8.85 × 10^{-2} A current.

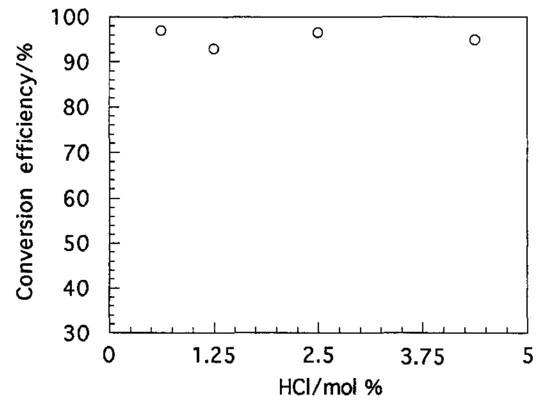

Fig. 7. Conversion efficiency against HCl concentration at 1.33 × 10^{-3} dm^3 s^{-1} gas flow rate.

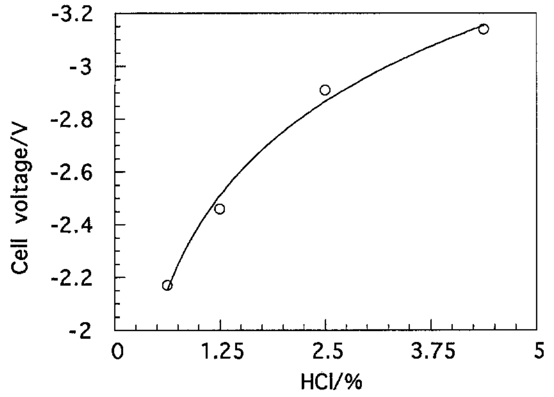

Fig. 8. Cell voltage against HCl concentration at constant gas flow rate of 1.33×10^{-3} dm^3 s^{-1} and stoichiometric current.

97%, as shown in Fig. 7. The cathode polarization decreased as compared with that using porous carbon as the cathode. Figure 8 shows the cell voltage as a function of the HCl concentration at its stoichiometric current. Figures 9 and 10 show the anode and cathode polarization as a function of current.

5. Discussion

These free-electrolyte tests show that high current densities can be maintained with a feed of dilute HCl gas, even with high removal rates. The required voltages are reasonable, considering the nonoptimized electrode structures. The morphology of the cathode has a significant effect on the chlorine recovery efficiency. When reticulated vitreous carbon was employed as the cathode, the chlorine recovery efficiency reached as high as 97% at the stoichiometric current, compared with that of about 90% using porous carbon and about 30% employing a pure graphite tube [10].

The current efficiency decreases with current while the recovery efficiency increases. However, the current efficiency decreases with HCl content at constant applied current, as does the recovery efficiency. The main factor that brings the current efficiency below 100%, in addition to some experimental error, is probably chemical recombination of some of the protons produced with chloride ions. This phenomenon would be lessened in a cell with immobilized, rather than free, electrolyte. Another, less important factor affecting the current efficiency, may be impurities in the eutectic melt; these may have contributed to unknown parasitic reactions, consuming a small amount of current. These would be diminished with purer melt components.

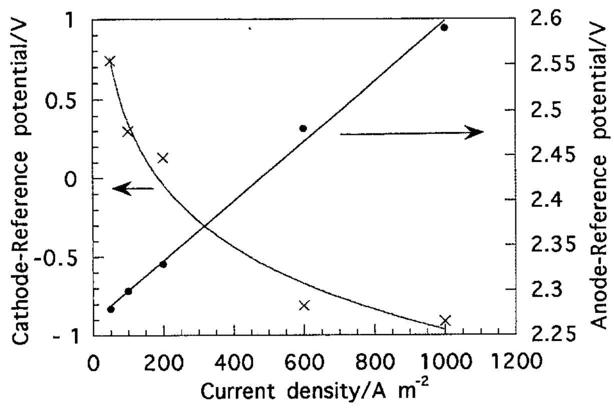

Fig. 9. Cathode (porous carbon) and anode polarization curves against current density at 2.58×10^{-3} dm^3 s^{-1} gas flow rate.

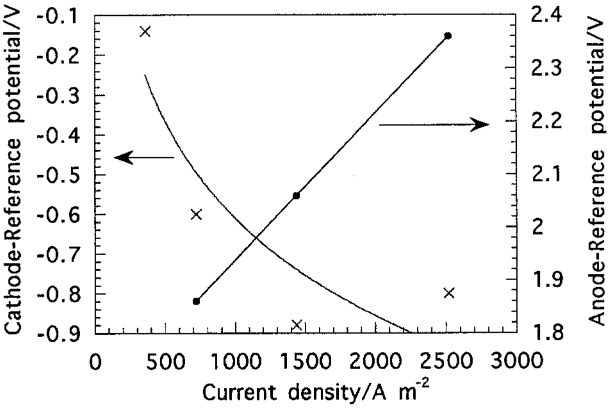

Fig. 10. Cathode (reticulated vitreous carbon) and anode polarization curves against stoichiometric current density at 1.33×10^{-3} dm^3 s^{-1} gas flow rate, with varying HCl concentrations.

6. Conclusion

The results show that a water-free HCl gas mixture can be treated for HCl removal with coincident recovery of chloride in a simple, one-step process. Although this study was carried out in free electrolyte, a commercial process would be designed using electrolyte retained in an inert matrix, perhaps made of silica. The electrodes would be flat, porous diffusion types arranged in a bipolar array, allowing for a high voltage, low current power supply.

Most of the overpotential exists at the cathode, as would be expected from the dilute nature of most of the gas mixtures. In a commercial array, the gas flow channels would be designed to minimize the power demand.

Acknowledgement

The authors are grateful for financial support received from the Argonne National Laboratory.

References

[1] H. Deacon, *US Patent 85 370* (1968).
[2] C. P. Roberts, *Chem. Eng. Prog.* **46** (1950) 457.
[3] H. G. Janson, *Chem. Ing. Tech.* **39** (1067) 729.
[4] P. Gallone and G. Hessner, *Electrochem. Technol.* **3** (1965) 321.
[5] J. S. Robinson, 'Chlorine Production Processes, Recent and Energy Saving Development', Noyes Data Corporation, Park Ridge (1981).
[6] S. Yoshizawa, Z. Takehara, Y. Ito and K. Oka, *J. Appl. Electrochem.* **1** (1971) 251.
[7] H. A. Laitinen, W. S. Ferguson and R. A. Osteryoung, *J. Electrochem. Soc.* **104** (1957) 516.
[8] A. M. Shams El Din, *Electrochim. Acta.* **4** (1961) 242.
[9] R. G. Anthong, B. J. Weilch and R. J. Steele, *Aust. J. Chem.* **21** (1968) 789.
[10] Y. Ding and J. Winnick, unpublished results.