

*An electrochemically regenerative hydrogen–chlorine energy storage system: electrode kinetics and cell performance**

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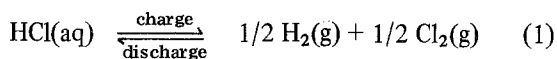
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The electrochemical oxidation and reduction of hydrogen and chlorine in hydrochloric acid has been investigated on graphite, ruthenized titanium and platinum electrodes. Both steady state and potentiostatic pulse methods were used. Cell studies were also carried out in cells with flow-by and flow-through chlorine electrodes. Results indicate that the electrode kinetics are fast and the electrolysis and fuel cell reactions can be carried out in the same cell with electric-to-electric efficiencies in excess of 75% at current densities of 300 mA cm⁻². Mass transfer limitations at the chlorine electrode during discharge can be eliminated by cell pressurization and the use of flow-through electrodes.

1. Introduction

The essential requirements of an energy storage system for electric utilities are: (a) high reliability; (b) low capital cost; (c) long life (more than 10 years); (d) high overall efficiency, over 70% electric-to-electric (ETE); and (e) high capacity (100 MW h).

The electrochemically regenerative hydrogen–chlorine cell:



shows good prospects for energy storage applications [1–3]. The economic impact and technical feasibility of implementing a hydrogen–chlorine energy storage system has been described previously [2, 3]. Also, the heat/mass balance [4] and the membrane characteristics related to the cell efficiency [5] of the hydrogen–chlorine system have been reported. This paper is concerned with the kinetics of the electrode reactions,

the performance characteristics of the regenerative cell and methods for achieving high electric-to-electric efficiency.

The hydrogen–chlorine electrolyzer has been studied and has been commercialized for a long time [6–11] because of the industrial interest in recovery of chlorine from waste hydrochloric acid. In contrast, there have been few studies of hydrogen–chlorine fuel cells [12–15] and these investigations were limited only to laboratory cells. Furthermore, these cells have only been operated below 100 mA cm⁻² and all the studies were limited to ambient pressure or lower.

The mechanism of hydrogen evolution has been studied for over a century [16, 17]. Many studies have been made in dilute hydrochloric acid (< 1.0 M). Hickling and Salt [18] carried out a comprehensive study of hydrogen evolution in HCl on various cathode materials in the current density range of 10⁻³ to 1 A cm⁻². It was found that Bi, Fe, Ni, W, Au and platinized Pt show Tafel behaviour while Hg, Cu, C, Cd, Sn, Al, Pt, Rh and Pb exhibit

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deviations from the Tafel plot. Later, Azzam and Bockris [19] studied hydrogen evolution at high current densities of greater than 1 A cm^{-2} on Hg, W, Ag, smooth Pt, Pd and Ni. For current density below 1 A cm^{-2} , smooth Pt exhibits the best catalytic activity for hydrogen evolution in 1–10 M HCl. Above 1 A cm^{-2} , the $E-i$ curves exhibited hysteresis on increasing and decreasing current densities.

An extensive review on the electrochemistry of chlorine was given by Mussini and Faita [20]. The chlorine evolution in dilute HCl is rather complex. Semchenko and Il'in [21] reported that the anodic by-products may be oxygen, ozone, hydrogen peroxide, chloric and perchloric acids, depending on the HCl concentration. Chlorine alone is liberated for HCl concentration of greater than 1.0 M, while decomposition of water increases with decreasing HCl concentration. At concentrations of less than 0.5 M, chloric acid appears first, followed by formation of perchloric acid. Chang and Wick [22] investigated chlorine evolution as well as chlorine reduction in HCl on Pt and Ir electrodes. The current-voltage behaviour for chlorine evolution is in accordance with the theory of Erdey-Gruž and Volmer while the chlorine reduction behaviour is not.

The ionization of chlorine and hydrogen in HCl has been studied by several laboratories [12, 14, 15]. In 1923, Foerster [12] constructed a hydrogen-chlorine cell stack consisting of three cells. The cell employed Acheson graphite electrodes (60 cm^2) and a 2 mm thick earthenware separator. He found that it was necessary to platinize the hydrogen electrode, whereas no electrocatalyst other than graphite was necessary for the chlorine electrode. A terminal voltage of 2.93 V at 0.2 A was obtained at room temperature with 2 M HCl as electrolyte. The flow rate of chlorine and hydrogen were 1.5 l h^{-1} and 12 l h^{-1} respectively. The hydrogen consumption under these conditions was only 2% and that of chlorine was 91%, because of its greater solubility. Yoshizawa *et al.* [14] in 1962 used carbon gas diffusion electrodes. They also found that a platinum electrocatalyst had to be used on the hydrogen electrode. They found that the overvoltage of both H_2 and Cl_2 electrodes is a minimum at HCl concentrations of 5.0 M to 8.0 M because of the increase in electrolyte conductivity. The energy efficiencies based on

ΔG and ΔH were evaluated as 51% and 41% at a current density of 40 mA cm^{-2} and 50° C . Bianchi [15] in 1965 used platinized graphite hydrogen electrodes and a percolating porous graphite chlorine electrode. The cell was able to deliver currents of about 50 mA cm^{-2} at 1.0 V and at 45° C with a power efficiency higher than 80%. The cell performance remained constant over a long period of time.

The present investigation involved half-cell studies on the anodic and cathodic processes on the hydrogen and chlorine electrode in HCl and studies of cell behaviour in cells with electrodes that were optimized for mass transport.

2. Experimental

2.1. Half-cell measurements

Half-cell measurements were carried out on the anodic and cathodic reactions on both the chlorine and hydrogen electrode. The electrode materials investigated were graphite, platinum and ruthenized titanium ($\text{RuO}_2/\text{TiO}_2$). The graphite was in the form of spectroscopic grade rods, the sheet platinum was supplied by Engelhard. The $\text{RuO}_2/\text{TiO}_2$ (1:4) electrodes were supplied as an experimental sample by the Hooker Plastics and Chemical Co. These were prepared by a technique that has been described previously [23]. Analytical reagent grade hydrochloric acid (37%) was obtained from Mallinckrodt Co. and was used without further purification. Doubly distilled water was used for preparing diluted hydrochloric acid. Hydrogen (99.95%) and chlorine (99.5%) were used without further purification.

The half-cell experiments were performed at atmospheric pressure and ambient temperature in a three-compartment glass cell. The voltage of the working electrode was controlled by a Princeton Applied Research (PAR) model 371 potentiostat. A PAR pulse generator (model 175) was used in the potentiostatic pulse measurements and a storage oscilloscope was used to record the transient behaviour. The details of the potentiostatic pulse measurement has been described previously [24].

2.2. Cell studies

Cell studies were carried out in cells with perfluori-

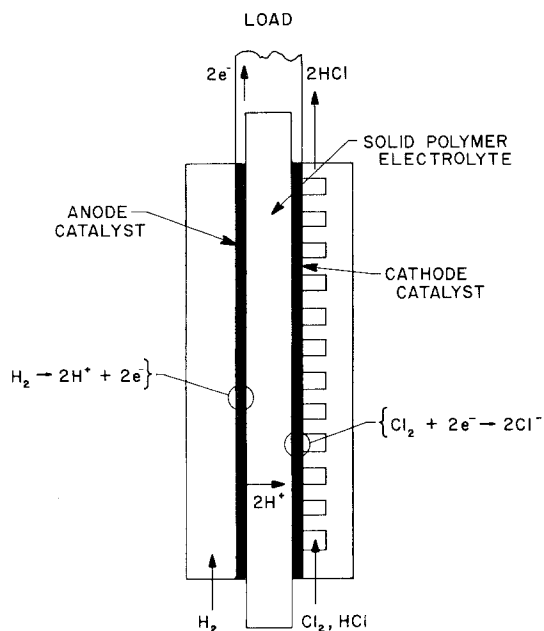


Fig. 1. Solid polymer electrolyte cell construction.

nated sulphonic acid (Nafion) membranes. Cell construction, as shown in Fig. 1, was based on the General Electric Company solid polymer electrolyte (SPE) fuel cell and the electrolyzer technology

that has been described in detail elsewhere [25]. The membrane electrode assembly consisted of platinumized hydrogen electrodes and ruthenized graphite chlorine electrodes that were bonded to opposite sides of the membrane. The membrane thickness was 0.025 cm and the square electrodes had an area of 46 cm². In some cells the chlorine electrode had in addition provisions for mass transfer enhancement during discharge. These consisted of platinumized niobium screens in abuttal with the ruthenized graphite electrode. Membrane support, current collection and cell enclosure was achieved by the use of a machined niobium housing.

During cell operation hydrochloric acid was circulated only through the chlorine electrode compartment. The hydrogen electrode compartment was free of electrolyte. On discharge the reactants were fed to the cell as hydrogen gas and as chlorine dissolved in hydrochloric acid.

3. Results and discussion

3.1. Open circuit of the hydrogen-chlorine cell

The hydrogen-chlorine cell differs from most

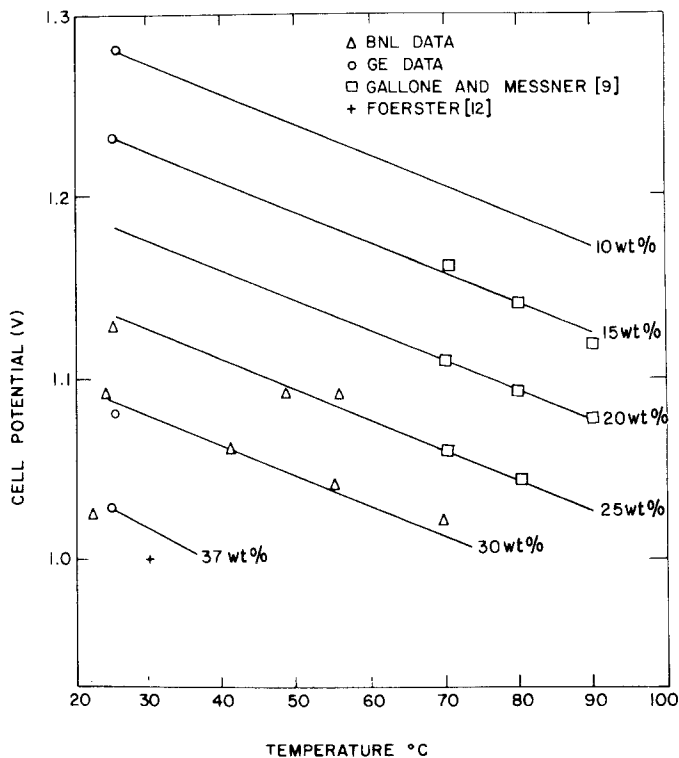


Fig. 2. Open circuit voltage of the hydrogen-chlorine cell as a function of temperature and HCl concentration.

batteries in that the open circuit voltage varies appreciably with temperature and depth of discharge. Fig. 2 shows the open circuit voltage as a function of HCl concentration and temperature, based on data from previous [9, 12] and present studies. The results can be fitted into an empirical equation [4]:

$$E_0 = 1.28 - 0.96(X - 0.1) - 0.0017(T - 25) + 4.3 \times 10^{-5}(273 + T)(\ln P_{H_2} + \ln a_{Cl_2}) \quad (2)$$

where E_0 is the open circuit cell voltage; X the weight fraction of HCl; T the temperature ($^{\circ}\text{C}$); P_{H_2} the partial pressure of hydrogen atmosphere and a_{Cl_2} the activity of Cl_2 in the electrolyte. Since the last term is negligibly small, Equation 2 becomes

$$E_0 = 1.28 - 0.96(X - 0.1) - 0.0017(T - 25) \quad (3)$$

The temperature variation of the open circuit voltage reflects the large negative entropy of formation of hydrochloric acid. This yields a $T\Delta S$ value of $8.77 \text{ kcal mol}^{-1}$ at room temperature. $T\Delta S$ is essentially invariant with the HCl concentration and corresponds to a thermoneutral voltage that is 0.38 V more positive than the open circuit voltage. Since the charging overvoltage is

only about 0.15 V , there is a cooling effect on charge and an additional heating effect on discharge.

3.2. Half-cell studies

3.2.1. The chlorine electrode. The current-potential behaviour for chlorine evolution and reduction on platinum, ruthenized titanium and spectroscopic grade graphite are shown in Figs. 3 and 4. Although the open circuit voltage decreases with increasing acid concentration, the overvoltage remains relatively constant. Both RuO_2 and platinum catalyze the chlorine electrode reaction. Platinum, however, corrodes at these potentials since the chlorine electrode potential is 0.27 V more positive than the $Pt/PtCl_4^-$ potential. In these half-cell measurements, the chlorine electrode was mass transfer limited on discharge.

A typical potential sweep for the RuO_2/TiO_2 electrode in 1 M HCl at 25°C is shown in Fig. 5. In contrast to the oxygen reaction, the chlorine electrode reaction is fast and highly reversible. The fast electrode kinetics of the reaction are evident from the results of the potentiostatic pulse measurements (Fig. 6).

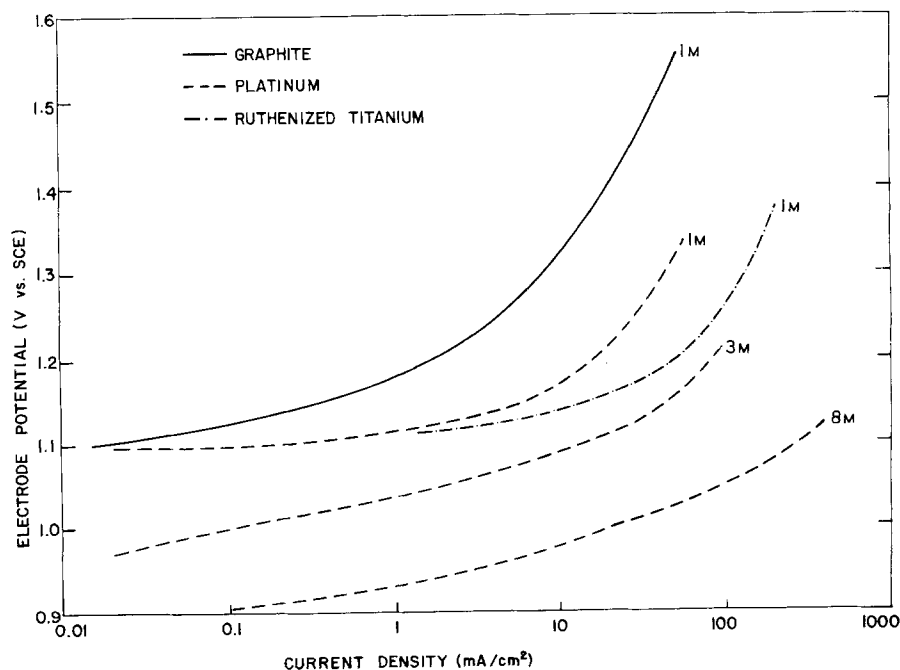


Fig. 3. Current-voltage behaviour during chlorine evolution as a function of HCl concentration and substrate; HCl concentrations are indicated on the figure.

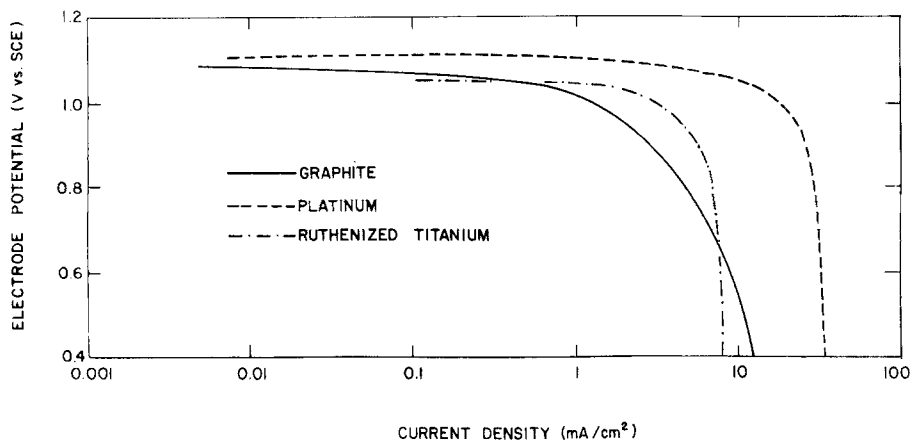


Fig. 4. Current-voltage behaviour during chlorine reduction on various substrates; 1.0 M HCl at 25°C.

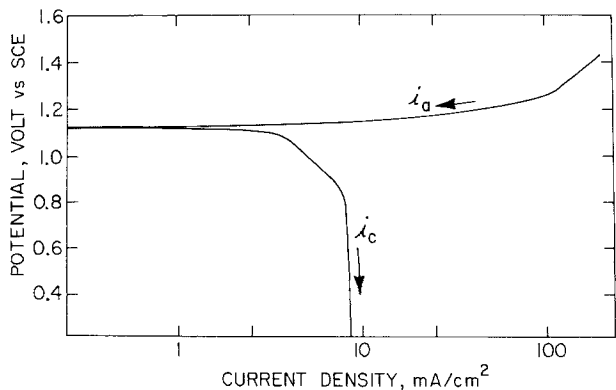


Fig. 5. Potential sweep of chlorine electrode reaction on $\text{RuO}_2/\text{TiO}_2$, 1.0 M HCl, 25°C. Sweep rate: 1 mV s^{-1} , i_c cathodic current, i_a anodic current.

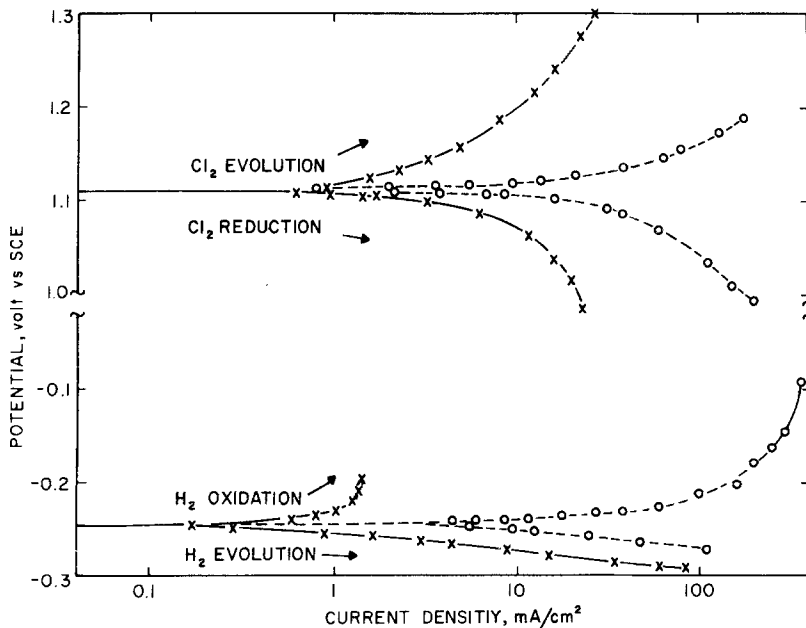


Fig. 6. Current-voltage behaviour for hydrogen and chlorine electrode reactions on smooth Pt by steady-state (X) and potentiostatic pulse (o) techniques; 1.0 M HCl, 25°C.

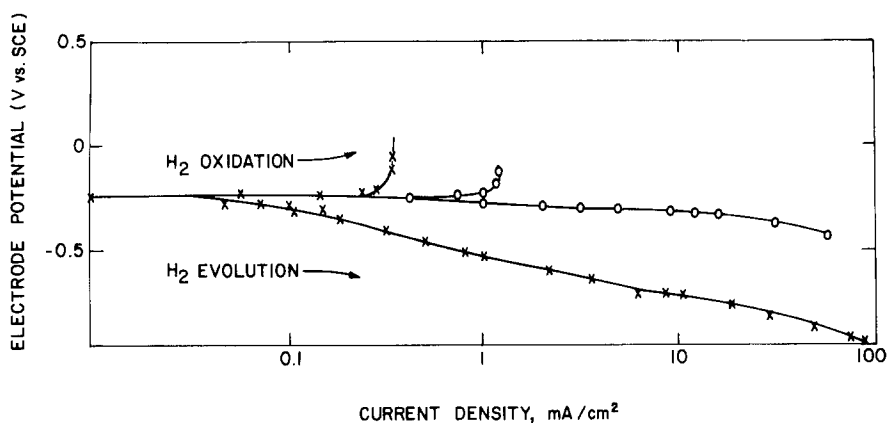


Fig. 7. Current–voltage behaviour during hydrogen evolution and hydrogen oxidation on smooth Pt (o) and graphite (x) electrodes; 1.0 M HCl at 25° C.

3.2.2. *The hydrogen electrode.* The hydrogen electrode current–potential behaviour on smooth platinum and graphite is shown in Fig. 7. No distinct linear Tafel region was observed. Platinum catalyzes the reaction. These results for hydrogen ionization and those found by the potentiostatic pulse measurements indicate that hydrogen oxidation is mass transfer limited.

3.3. Cell Studies

3.3.1. *Cells with flow-by chlorine electrodes.* The performance of cells with flow-by chlorine electrodes is shown in Fig. 8. It is evident that the cell kinetics are fast on charge. However, the cell was severely mass transfer limited on discharge. If one considers the limiting current (i_L) to be given by:

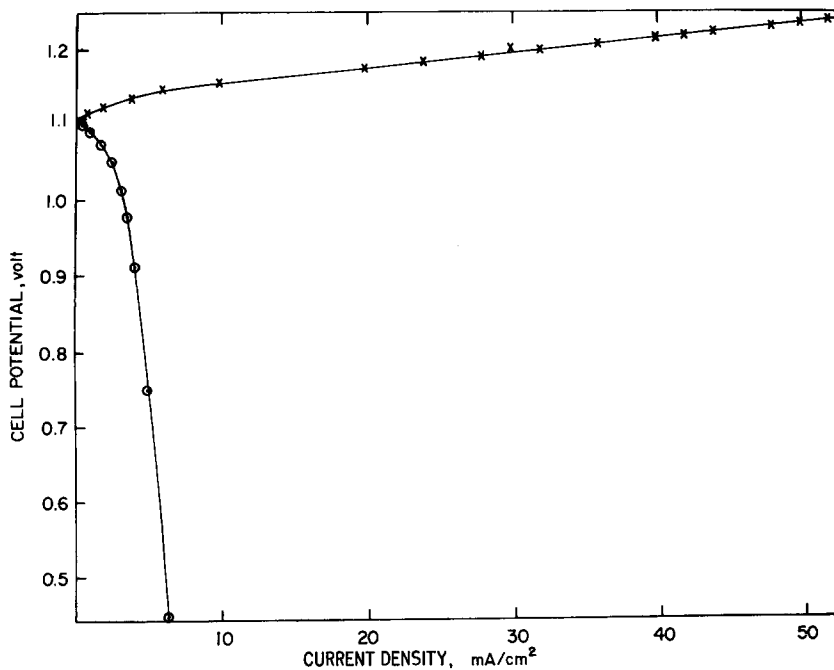


Fig. 8. Cell performance of flow-by electrode at 25° C, ambient pressure, flow rate 2 cm³ s⁻¹ and 25% HCl.

$$i_L = \frac{nFDC_0}{\delta}$$

where D is the diffusion coefficient, C_0 the solubility, n the number of electrons in the charge transfer reaction, δ the diffusion layer thickness and F the Faraday constant, then for $D = 1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [26], $C_0 = 0.062 \text{ mol l}^{-1}$ [9, 15, 27] and $i_L = 7 \times 10^{-3} \text{ A cm}^{-2}$, δ is 0.03 cm. With no forced convection, $\delta = 0.05$ cm. Improvement in discharge performance requires an increase in C_0 or an improvement in mass transfer characteristics of the cell. This was confirmed by the increase in chlorine electrode performance with increased chlorine pressure (Fig. 9) and by the effect of flow rate on cell polarization (Figs. 10 and 11). The limiting current density (i_L) electrolyte flow rate (V), relationship for the flow-by electrode is:

$$i_L = AV^{0.86}$$

where A is a constant. The velocity exponent indicates that flow in the cell was turbulent. All these results indicate that in a practical cell design every effort should be made to increase the chlorine solubility by pressurization and to enhance mass transfer.

3.3.2. Cells with flow-through chlorine electrodes.

The performance of cells with flow-through electrodes is shown in Figs. 12 and 13. The voltage-current behaviour, in contrast to that shown in Fig. 9, is linear over the entire current density range (0–300 mA cm^{-2}). The chlorine pressure has a marked effect on the discharge performance because of the increase in chlorine solubility. On charge the reactant (HCl) is concentrated ($> 1.4 \text{ M}$) so there are no mass transfer limitations. The decrease in charge polarization with temperature (Fig. 13) is due mainly to the decrease in membrane resistance with increasing temperature [5]. The effect of temperature on the discharge performance is rather complicated. Besides decreasing the membrane resistance, increasing the temperature decreases the chlorine solubility and increases the diffusivity, hence, the different dependence of the polarization behaviour with temperature on discharge.

It is instructive to compare the flow-through electrode cell performance with literature values [9, 11, 12, 15] and the results of the pulse experiments. Reported performance for various hydrogen-chlorine cells are shown in Figs. 14 and 15. The performance of the flow-through cells at 25° C and at one atmosphere pressure is shown.

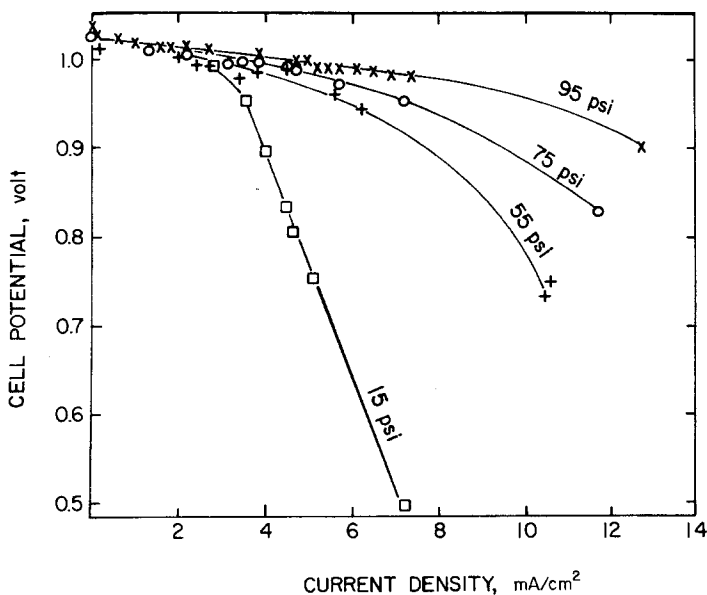


Fig. 9. Cell discharge performance for various chlorine pressures at 25° C, in 37% HCl with flow rate $2 \text{ cm}^3 \text{ s}^{-1}$.

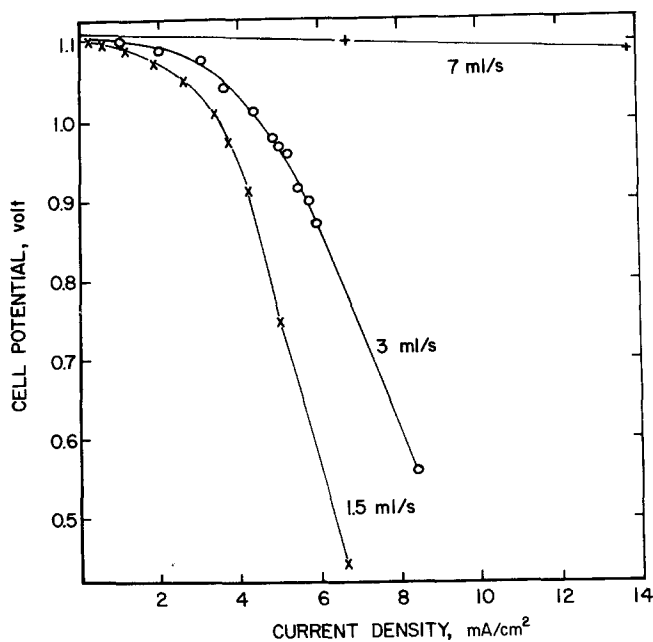


Fig. 10. Cell discharge performance for various electrolyte flow rates at 25° C and ambient pressure. Electrolyte concentration is 25% HCl.

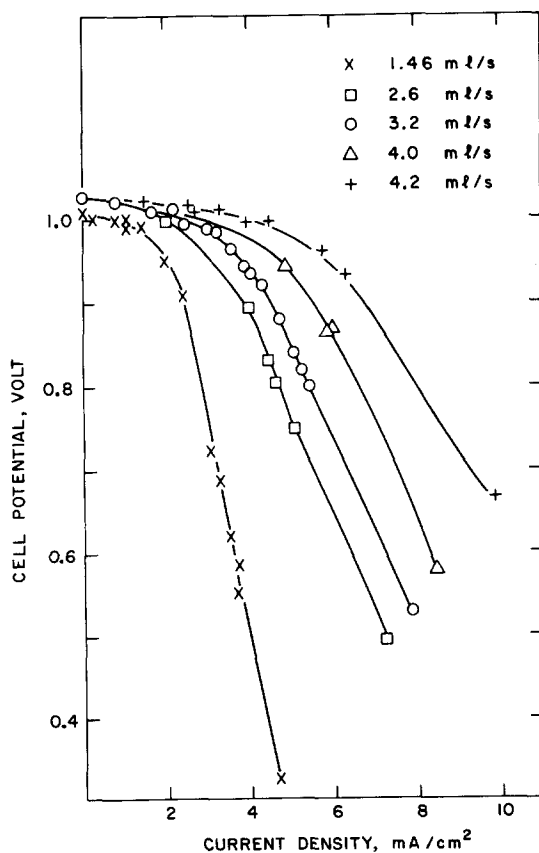


Fig. 11. Cell discharge performance for various electrolyte flow rates at 25° C and ambient pressure. Electrolyte concentration is 37% HCl.

When the resistance component in the membrane is subtracted from these results the polarization curves closely approach those determined from the pulse experiments. In the flow-through electrode cells, cell performance is determined by the electrode activation kinetics and the resistivity of the membrane.

3.4. Cell efficiency

Table 1 shows the dependence of the electric-to-electric efficiency on current density and temperature. The dependence of cell efficiency on power density, at 80° C and a pressure of 5 atmospheres, is shown in Fig. 16. Electric-to-electric efficiencies for other electrochemical couples [28–31] as a function of power density are shown for comparison. The high power density performance for the hydrogen-chlorine system is due to the fast electrode kinetics of the system and the high conductivity of the Nafion membrane in the hydrochloric acid medium.

3.5. Parasitic reactions

The occurrence of parasitic reactions is often a performance and life limiting factor in many battery systems. Fortunately, in the case of the

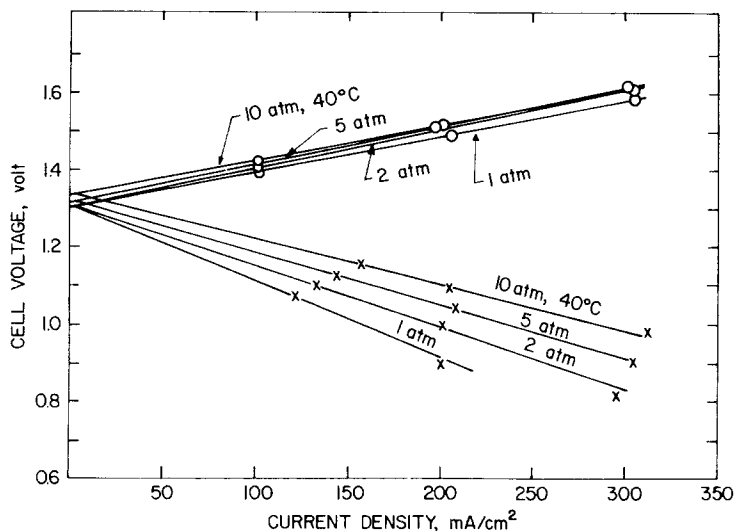
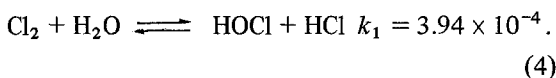
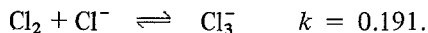


Fig. 12. Cell performance at various chlorine pressures, 25° C except as noted, flow rate 8 cm³ s⁻¹; 10% HCl.

hydrogen-chlorine system, there are no side reactions. Operation with acid concentrations in excess of 1.4 M inhibits oxygen evolution. The chlorine electrode on charge yields either Cl₂ or Cl₃⁻. This is evident when one considers the equilibria involved. Chlorine hydrolysis to hypochlorous acid is governed by the following equilibria at 25° C [32]:



Since the pH in the cell is less than zero, formation of hypochlorous acid is not a factor. Chlorine, however, can complex with chloride ions [26, 32, 33].



For this reason the chlorine solubility in the electrolyte increases with HCl concentration. This is advantageous since it enhances mass transfer to the chlorine electrode during discharge. Formation of ClO₂ is not a factor since the reversible potential for the Cl₂/ClO₂ reaction is more than 0.3 V positive to the Cl⁻/Cl₂ potential in these acid concentrations [34].

4. Summary

The electrode kinetics of the hydrogen-chlorine cell are fast. The electrolysis and fuel cell reaction

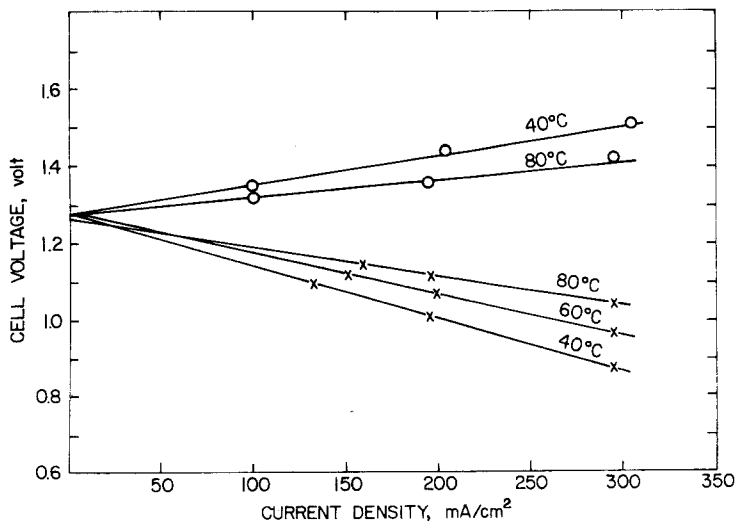


Fig. 13. Cell performance at various temperatures: 5 atm chlorine pressure, flow rate 8 cm³ s⁻¹; 10% HCl.

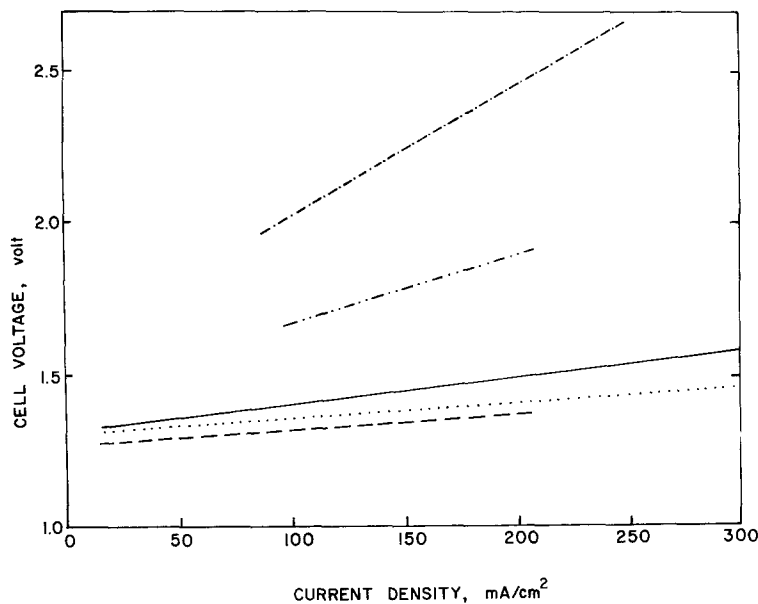


Fig. 14. Comparison of hydrogen-chlorine electrolyzer performance. (---) Gallone and Messner [9]; (-·-) Berndt *et al.* [11]; (-) present study, (···) after subtraction of resistance component; (- -) pulse result.

Table 1. Electric-to-electric efficiency (ETE) of hydrogen-chlorine cell (10% HCl, 5 atm chlorine pressure)

Current density (mA cm ⁻²)	ETE at 40° C (%)	ETE at 80° C (%)
50	92	95
100	85	90
200	71	81
300	58	75

can be carried out in the same cell with electric-to-electric efficiencies in excess of 75%. Mass transfer limitations at the chlorine electrode during discharge can be eliminated by cell pressurization and the use of flow-through electrodes.

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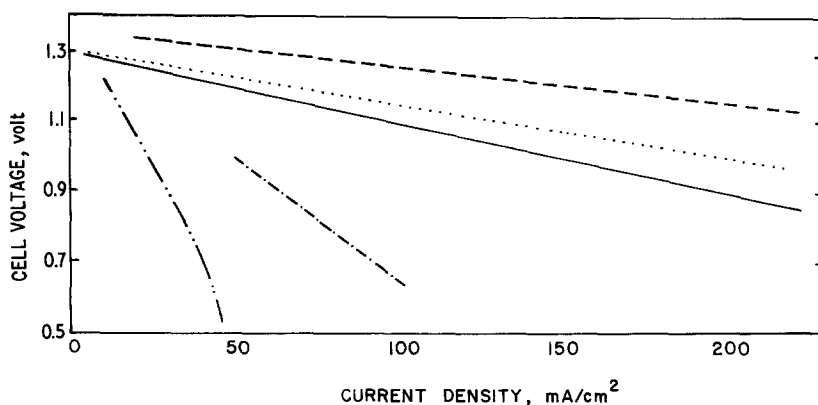


Fig. 15. Comparison of the discharge performance of hydrogen-chlorine cell. (-·-) Foerster [12]; (---) Bianchi [15]; (-) present study; (···) after subtraction of resistance component; (- -) pulse result.

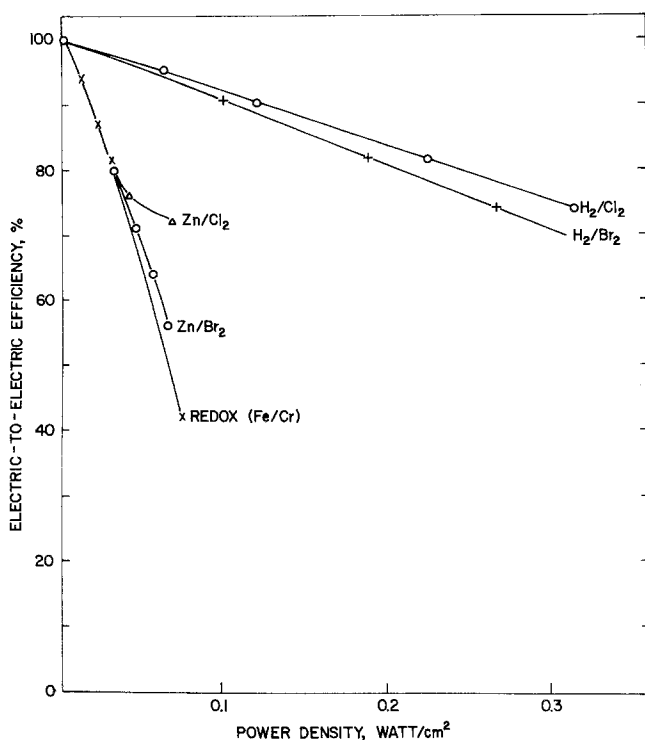


Fig. 16. Comparison of cell efficiency of various batteries.

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