Journal of Applied Electrochemistry **33**: 9–13, 2003.

H_2/Cl_2 fuel cell for co-generation of electricity and HCl

M. THOMASSEN*, B. BØRRESEN, G. HAGEN and R. TUNOLD
Department of Materials Technology, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
*(*author for correspondence, e-mail: magnus.thomassen@nt.ntnu.no)*

Received 1 May 2002; accepted in revised form 14 October 2002

Key words: Cl_2 reduction, co-production, fuel cell

Abstract

A H_2/Cl_2 fuel cell system with an aqueous electrolyte and gas diffusion electrodes has been investigated and the effects of electrolyte concentration and temperature on the open circuit voltage (OCV) and cell performance have been evaluated. Furthermore, the kinetics and long-term stability of Pt as electrocatalyst have been studied under various conditions. In addition, the long-term stability of Rh electrocatalyst has been evaluated. The OCV obtained showed that the Cl_2 reduction is more reversible than O_2 reduction. The ohmic drop was determining the cell performance at high current densities. An output power of about 0.5 W cm^{-2} was achieved with this system.

1. Introduction

Fuel cells are in general used as generators of electric energy, either for mobile or stationary applications. The fuel may either be pure hydrogen or a hydrogen rich compound like hydrocarbons or ammonia. As an oxidant oxygen is normally used, either pure or more commonly from air.

In a H_2/Cl_2 fuel cell, oxygen is substituted by chlorine as the oxidizing agent. Hence, the product from this cell is not water, but hydrogen chloride. This product is of more value than water and consequently the H_2/Cl_2 fuel cell is as much a chemical reactor as an electric generator and the competitiveness of such units is dependent on both the prices of electricity, chlorine and HCl.

Although comparatively less popular than H_2/O_2 fuel cells, early reports on H_2/Cl_2 fuel cells from the 1920s are available [1, 2]. Catalysts such as Pt [3–5], Pt–Ir alloy [7], RuO_2 [3, 6] or $Pb_2Ru_2O_7$ [4], have been evaluated for Cl_2 reduction.

The use of H_2/Cl_2 fuel cells for industrial applications has been proposed for plants having an excess of hydrogen and chlorine readily available. The chlorine–alkaline industry has a potential for energy savings with the use of H_2/Cl_2 fuel cells [8]. The use of H_2/Cl_2 fuel cells in industries where chlorine is produced as a byproduct, for example, in magnesium and sodium electrolysis, can also be beneficial.

H_2/Cl_2 fuel cells have also been suggested as an alternative to H_2/O_2 fuel cells in space applications [4], and as regenerative systems for storage of electric energy [3, 6, 9, 10].

2. Experimental details

The experimental fuel cell consisted of a housing made of PEEK (polyetheretherketone) and current collectors made of nonporous graphite. The active surface area of the electrodes was 2.2 cm^2. A separator made of PEEK separated the electrodes, which made it possible to vary the interpolar distance by using separators with various thicknesses. A schematic illustration of the cell is given in Figure 1.

The electrolyte with various concentrations of HCl was made from 37 wt % aqueous HCl (p.a. Merck), and pumped from a temperature-controlled reservoir through the cell housing and the separator by a Masterflex® pump via insulated viton (iso-versinic) tubes.

The single electrode potentials were studied in a cell with a similar design as the experimental fuel cell, but with a longer interelectrode distance. One of the gas diffusion electrodes was substituted with a platinum foil and a Ag/AgCl reference electrode was positioned in close vicinity of the remaining gas diffusion electrode. The magnitude of the ohmic drop between the gas diffusion electrode and the reference electrode was determined by electrochemical impedance spectroscopy (EIS) and the measured electrode potentials were *iR* compensated.

Commercially available 20% Pt on carbon (Pt/C), 0.5 mg cm^{-2} Pt gas diffusion electrodes (STD/DS/V2/ELAT and STD/SS/V2/ELAT) and 30% Rh on carbon (Rh/C), 1.0 mg cm^{-2} were obtained from E-TEK Inc. The gases, hydrogen (5.0 AGA) and chlorine (2.7 Gerling Holtz), were fed to the cell without any kind

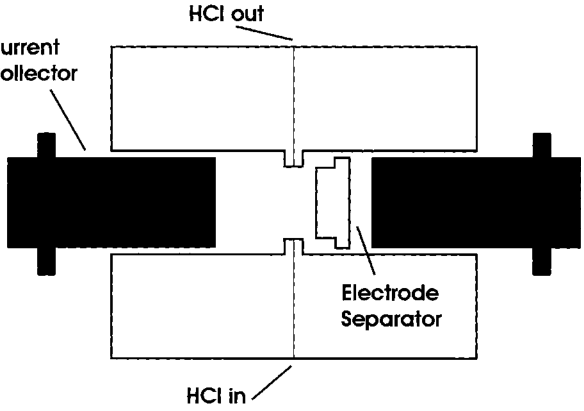

Fig. 1. Schematic illustration of experimental cell.

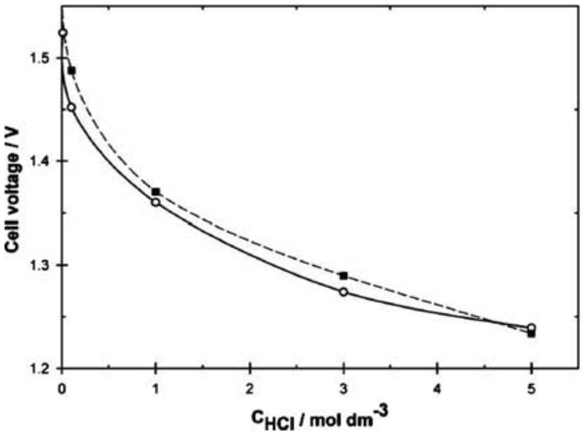

Fig. 2. Open circuit voltage against HCl concentration at 20 °C. (—) Experimental values; (- - -) theoretical values, calculated with data from [11].

of preheating or humidification and exited the cell through a water column to create a small overpressure inside the cell (~10 cm H_2O). The cathode exit gas was then led through a KOH solution to remove excess chlorine. The H_2 gas was controlled by a flow controller and the Cl_2 gas flow was regulated manually. Both gases had a flow rate of approx. 5 mL s^{-1}. The cell potential was controlled by a potentiostat (Autolab PGStat 20) connected to a 20 A current booster (BSTR 10A + Extension module), both from Eco Chemie. Polarization curves were obtained by a data acquisition unit (HP 34970A) connected to the current collectors to minimise the error from resistance in connectors and cables.

Means of preventing Cl_2 and H_2 recombination was deemed unnecessary for the present investigations due to the high OCV attained and the low solubility of H_2 in the electrolyte. For an industrial reactor this issue has to be addressed.

3. Results and discussion

3.1. *Effect of electrolyte concentration*

The open circuit voltage as a function of HCl concentration at 20 °C for a hydrochloric acid fuel cell (HCAFC) and theoretical (calculated) values are presented in Figure 2. Activity coefficients for HCl solutions are taken from [11]. As can be observed from the Figure, the measured and calculated values for the open circuit voltage are almost identical for HCl concentrations from 5 to 0.1 mol dm^{-3}, as apposed to H_2/O_2 fuel cells where the OCP is close to 1.0 V compared with the thermodynamically expected value of 1.23 V.

The low OCP of ordinary H_2/O_2 PEM fuel cells is caused by the poor kinetics of the oxygen reduction reaction (ORR), resulting in a mixed potential at open circuit [12], [13]. The mixed potential originates from the ORR, which may yield both water and hydrogen peroxide, and a parasitic anodic component of several possible origins, typically oxidation of traces of hydrogen in the cathode compartment. The absence of such a discrepancy between the thermodynamical and actual OCP of the HCAFC strongly indicates that the chlorine reduction reaction (CRR) has much better kinetics than the ORR (higher exchange current density), and thus govern the electrode potential. The high OCV of the HCAFC facilitates both high energy efficiency and power density in a fuel cell system.

Steady state polarization curves at 20 °C as a function of HCl concentration are presented in Figure 3. A comparison of the achieved power density at a given potential as a function of the electrolyte concentration show that the polarization curves does not have a linear variation with HCl concentration. The performance of the HCAFC increases with the electrolyte concentration from 0.01 to 3 M HCl. A further increase of the concentration to 5 M has an insignificant effect. The decrease in the slope of the polarization curves with increasing concentration at current densities above 0.4–0.6 A cm^{-2} indicates that higher electrolyte conductivity in the concentrated electrolytes (3 and 5 M), and thus a lower *iR* drop, is the primary cause for the observed performance increase. HCl has its highest conductivity in the 5–6 M concentration range [11]. One of the reasons for the nonlinear dependence of concentration on conductivity is that coulombic forces between the ions in the high concentration solutions retard the ion migration. This concentration effect is also reported by Shibli and Noel [7].

3.2. *Effect of temperature*

The effects of operating temperature on the overall fuel cell performance, as well as on the individual electrode reactions are shown in Figure 4(a) and (b). An increase in temperature leads to a decrease in electrode potential for both electrode processes and the overall operating cell voltage increases with temperature at all current densities over 250 mA cm^{-2}.

The polarization curves of H_2 oxidation and Cl_2 reduction are only affected to a small degree by the increase of temperature from 20 to 50 °C (Figure 4(b)).

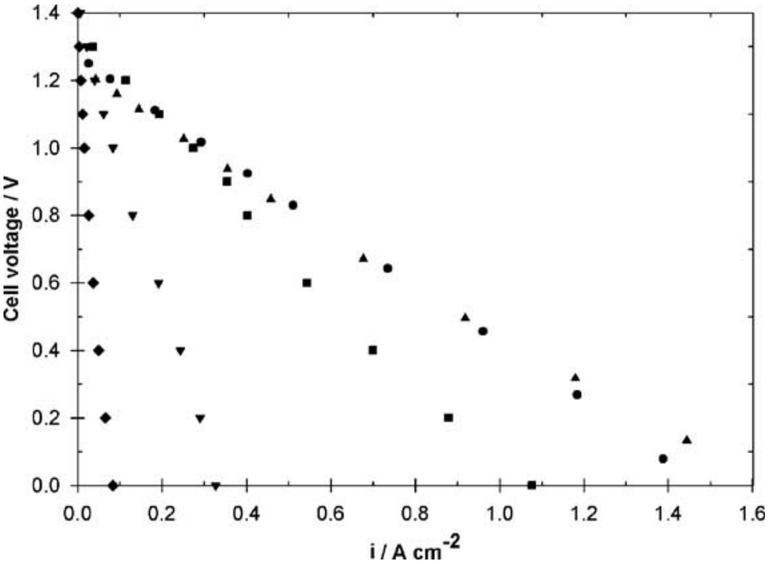

Fig. 3. Effect of HCl concentration on HCAFC performance at 20 °C. Key: (◆) 0.01, (▼) 0.1, (■) 1, (●) 3 and (▲) 5 M.

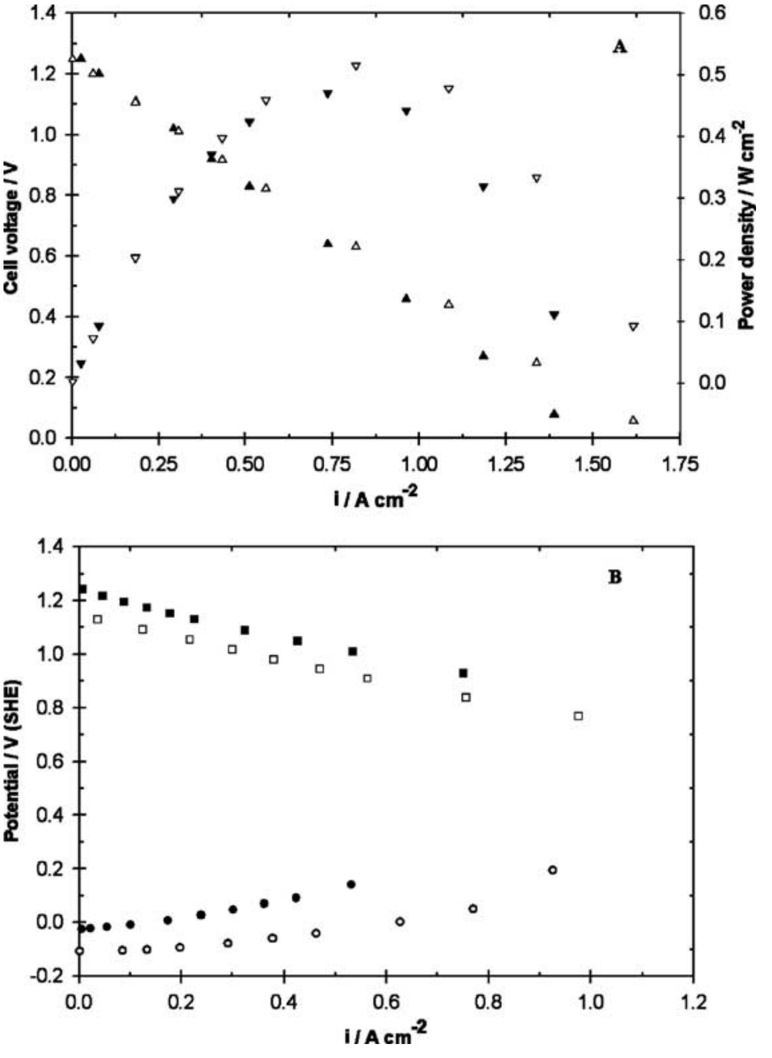

Fig. 4. Effects of temperature on the overall fuel cell performance and the individual electrode polarization curves, 3 M HCl as electrolyte. Key: (a) (▲) cell voltage 20 °C, (△) cell voltage 50 °C, (▼) power density 20 °C, (▽) power density 50 °C; (b) (●) H_2 oxidation 20 °C, (○) H_2 oxidation 50 °C, (■) Cl_2 reduction 20 °C, (□) Cl_2 reduction 50 °C.

The chlorine curve is only shifted in the direction of a more negative potential, the shape of the curve is unaffected. The hydrogen curve is also shifted to a more negative potential, but in addition, the overvoltage at a given current density decreases somewhat. The shifts to more negative potentials have a small effect on the open circuit potential of the cell, as can be seen from Figure 4(a). At current densities above 500 mA cm^{-2} the difference between the cell voltage at 20 and 50 °C is much higher than can be attributed to the improved hydrogen oxidation kinetics. This suggests that the main factor for the increased fuel cell performance with temperature is the increase of electrolyte conductivity and not enhanced electrode kinetics.

Operation of the fuel cell at higher temperatures might have lead to a further improvement of the fuel cell performance, but at temperatures above 50 °C, the corrosion of the cathode catalyst had reached a rate too high to attain stable polarization curves. This is explained in more detail in Section 3.4. In addition, the reduced viscosity of the electrolyte resulted in a drastic increase of electrolyte leakage through the gas diffusion electrodes and into the gas channels. The combination of these two effects made it impossible with the present cell design to achieve reproducible conditions at temperatures above 50 °C.

3.3. *Effect of pressure*

The effect of a small overpressure on the H_2-gas side is shown in Figure 5. The cell voltage was held at a constant value of 500 mV and at the points A and B a valve in the H_2-gas outlet was partially closed, creating a small overpressure in the anode compartment. The value of the overpressure was not recorded, due to lack of appropriate instrumentation, but was estimated to about 100 mm H_2O. Ten minutes after the valve was closed for the second time a stable current about 20% higher than the current with the valve open were established. Opening the valve reduced the current back to its original level. A similar test was made on the cathode, but no change in current density was observed with the addition of a small Cl_2 overpressure.

A pressure increase leads to higher activities of the reactants and decrease the mass transport limitations of the system, but the overpressure applied was not high enough to explain the 20% current increase if only reactant activity and mass transport are considered. The electrode reactions taking place in systems where the reactants are in the gas phase can either proceed through a direct adsorption on the catalytic surface with a subsequent electrochemical reaction or through a process where the reactant is first dissolved in the electrolyte. Depending on the relevant mechanism, a wetting/flooding of the electrode structure may significantly alter the performance. The hydrogen oxidation reaction is highly dependent on the three-phase boundary due to the extremely low solubility of hydrogen in the electrolyte, which effectively limits the reaction to proceed from gas phase reactants.

The solubility of chlorine is about 100 times higher than the solubility of hydrogen and the chlorine reduction reaction can with a high probability be described by the following sequence:

$$Cl_{2(g)} \rightarrow Cl_{2(aq)} \rightarrow 2Cl_{(ads)} + 2\,e^- \rightarrow 2\,Cl^-_{(aq)}$$

This renders the CRR virtually independent of the three-phase boundary.

In this system, the balance between the gas, electrolyte and catalyst phase inside the gas diffusion electrode is extremely sensitive to changes in temperature and gas pressure due to the low viscosity of the electrolyte. Thus, a possible explanation for the current increase with a small H_2 overpressure and no increase with a small Cl_2 overpressure is a displacement of the three-phase boundary inside the gas diffusion electrode to a more beneficial position and consequently, an increase of the active electrode surface for hydrogen oxidation.

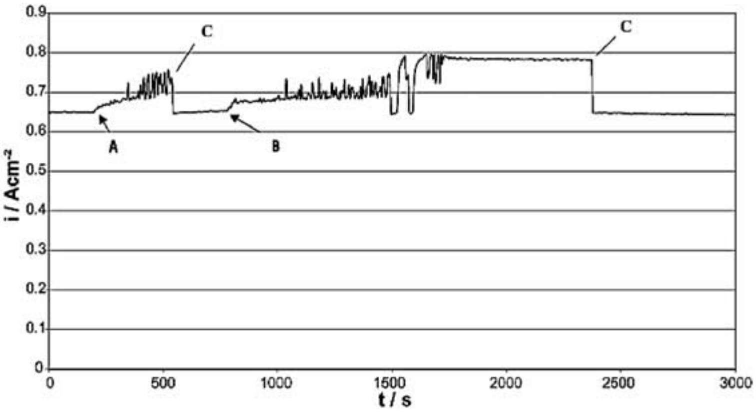

Fig. 5. Effect of anode gas pressure. Cell voltage 500 mV. The gas pressure was increased at (A) and (B) and decreased at (C).

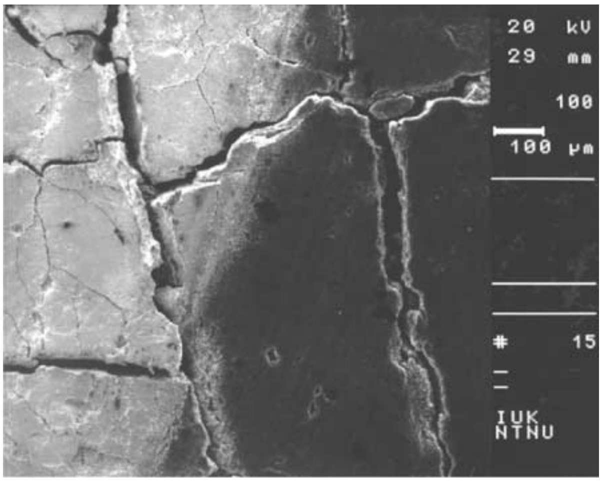

Fig. 6. SEM photo of fuel cell anode of a HCAFC. The white region on the left has been in contact with the electrolyte and a precipitated layer of Pt has formed.

3.4. *Fuel cell performance*

A long-term stability test was performed for the fuel cell with 1 M HCl as electrolyte, 25 °C operating temperature and a 300 mA cm^{-2} discharge current. A relatively rapid decrease in fuel cell performance was observed. After 120 h the cell voltage had dropped from 1.05 to 0.6 V. A visual inspection of the anode after the long-term test revealed a metallic coating on the area exposed to the electrolyte that is believed to be caused by a dissolution/precipitation of Pt. Figure 6 shows a SEM photo of the electrode, the white region on the left has been in contact with the electrolyte and a layer of Pt has been formed. It is well known that platinum is insoluble in hydrochloric acid, but in presence of chlorine it dissolves, forming chloroplatinic acid (H_2PtCl_6). A sample of the electrolyte was tested for Pt with inductive coupled argon plasma atomic emission spectroscopy (ICP), which showed a significant concentration of Pt in the electrolyte. These observations indicate that Pt is not stable as a cathode material within the operating conditions of the HCAFC and thus dissolves into the electrolyte and precipitates on the anode by the H_2 present on the electrode. A long-term stability test was also conducted with Rh as chlorine reduction catalyst. The preliminary results showed that Rh has a lower initial activity towards chlorine reduction, but a lower rate of corrosion than Pt in the system environment.

4. Conclusions

The performance of the HCAFC system investigated shows a strong dependence on electrolyte concentration. The optimum conditions for the system investigated are 50 °C and 3 M HCl, which gave a performance of 0.51 W cm^{-2} at 0.5 V.

Pt an Rh electrocatalysts are not stable in the system environment. Long-term stability tests showed a decrease in performance of 45% in 120 h. Rh was found to have a lower initial activity towards chlorine reduction but showed a higher long-term stability. Chlorine reduction is considerably more reversible than O_2 reduction, leading to an open circuit voltage close to the thermodynamic value.

Acknowledgements

The authors would like to acknowledge Norsk Hydro for financial support and Dr Emory S. De Castro at E-Tek for supplying the Rh-containing gas diffusion electrodes.

References

1. F. Foorster, *Z. Elektrochem.* **29** (1923) 64.
2. A. Schmid, *Helv. Chim. Acta* **7** (1924) 370.
3. R.S. Yeo, J. McBreen, A.C.C. Tseung and S. Srinivasan, *J. Appl. Electrochem.* **10** (1980) 393.
4. E.B. Anderson, E.J. Taylor, G. Wilemski and A. Gelb, *J. Power Sources* **47** (1994) 321.
5. A. Gelb, *US Patent 5 041 197* (1991).
6. D.L. Maricle, *US Patent 4 128 701* (1978).
7. S.M.A. Shibli and M. Noel, *Int. J. Hydrogen Energy* **18** (1993) 141.
8. E. Anderson, E.J. Taylor, N.R.K. Vilambi and A. Gelb, *Separation Science and Technology* **25** (1990) 1537.
9. D-T. Chin, R.S. Yeo, J. McBreen and S. Srinivasan, *J. Electrochem. Soc.* **126** (1979) 713.
10. E. Gileadi, S. Srinivasan, F.J. Salzano, C. Braun, A. Beaufrere, S. Gottesfeld, L.J. Nuttall and A.B Laconti, *J. Power Sources* **2** (1977) 191.
11. V.M.M. Lobo, 'Physical Science Data 41A: Handbook of Electrolyte Solutions' (Elsevier, New York, 1989).
12. A. Damjanovic, *in* O.J. Murphy, S. Srinivasan and B.E. Conway (Eds), 'Electrochemistry in Transition, From the 20th to the 21st Century' (Plenum, New York, 1992), pp. 107–126.
13. S. Gottesfeld and T.A. Zawodzinski, *in* R.C Alkire, 'Advances in Electrochemical Science and Engineering' Vol. 5 (Wiley, Weinheim, 1997), pp. 197–301.