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A DESIGN FOR ZINC-CHLORINE BATTERIES

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Summary

An alternative design for a zinc-chlorine electrical energy storage system is described. It is proposed that operation under higher than normal pressures may be advantageous. It is shown that suitable pressures can be built up in the cell during charging. Measurements of the vapour pressure of chlorine over chlorine hydrate are reported and it is shown that chlorine hydrate at usual room temperatures is capable of providing the flow rates required for optimum current. A schematic design is suggested for pressure operated Zn/Cl_2 cells. Safetly considerations are briefly discussed.

1. Introduction

In recent years, the zinc-chlorine battery has received considerable attention as a possible candidate for electric vehicles and particularly for utility load-levelling or peak-shaving applications [1 - 3]. The system is attractive because it is conceptually simple and appears to require mainly inexpensive materials for fabrication. The overall cell reaction is

$$Zn(s) + Cl_2(aq) \rightleftharpoons ZnCl_2(aq) .$$
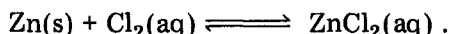
Several prototype batteries have been built and are described in detail in the literature [1 - 3]. The basic components of these systems consist of a zinc electrode plated on a dense graphite substrate, while porous graphite serves as the chlorine electrode. During charge, a concentrated (2 or 3M) solution of $ZnCl_2$ is electrolyzed between these electrodes. Metallic zinc is, therefore, plated on to the dense graphite (negative) electrode while chlorine is evolved from the porous graphite (positive) electrode. The evolved chlorine is dissolved in water and the mixture cooled to form the crystalline solid, chlorine hydrate, $Cl_2 \cdot xH_2O$. During discharge, the hydrate store is warmed to release chlorine which is mixed with a dilute (0.5M) solution of zinc chloride and allowed to flow through the porous electrode where each atom loses one electron to form the chloride (Cl^-) ion. At the same time, the deposited zinc passes into the solution as the zinc (Zn^{2+}) ion and the original concentration of zinc chloride in the electrolyte is restored.

   Since the formation of chlorine hydrate under normal conditions occurs below 9.6 °C the hydrate store requires a refrigeration system. Moreover, it has been shown [2, 3] that in order to obtain better utilisation of chlorine during discharge and to avoid polarisation during charging, it is necessary to circulate the electrolyte through the battery during both operations. Two or more pumps have, therefore, been used in the batteries reported in ref. 1. The operation of a refrigeration system and pumps and the warming of the hydrate store represent a power consumption and consequently a reduction in the overall system efficiency. In addition, the complexity of the system is greatly increased. This, in turn, increases the initial as well as the system maintenance costs. Elimination of the refrigerator, the heating, and the pumps, or any one of these, would, therefore, have obvious advantages. In the present report, we suggest that the zinc–chlorine system would require very much reduced refrigeration and pumping if operated at elevated pressures. But the build up of pressure normally requires motors and compressors, which again represent a loss to the overall system efficiency. However, any electrolysis which produces a gas at one of the electrodes is capable of developing extremely high pressures [6], if the cell is sealed. This pressure, in a closed cell, is the consequence of electrolysis and therefore represents no loss in efficiency. If this electrochemically generated pressure is used to replace the refrigeration and pumping requirements in zinc–chlorine systems, the overall system will be simpler and there will be a saving of external energy input. Moreover, the electrolysing current is not affected by this increase of pressure since the ionic mobilities are virtually independent of pressure [4]. Since the zinc–chlorine system has to be sealed extremely well in any case due to the toxic nature of chlorine, it would appear that there are unlikely to be any major difficulties in modifying the zinc–chlorine cell to operate at higher than normal pressure. This pressure would then result in the easier formation of chlorine hydrate and, when suitably channeled, would relieve the load on the circulating pumps to a very large extent. It will, therefore, probably be simpler in design with fewer moving parts than those constructed so far.

   In the present paper we shall examine the possibility of pressure operated zinc–chlorine systems, describe some experimental results, and suggest a schematic design for a battery operating at elevated pressures.

2. Electrochemical compression of gases

   If n moles of an ideal gas are liberated in a sealed electrolytic cell when a current i is passed through it for a time t, then

$$n = it(e/m) \tag{1}$$

where e is the electrochemical equivalent of the gas and m, the molecular weight. Now, if the cell has a free volume V, the mechanical energy of the generated gas would be given, as usual by

$$PV = nRT = itRT(e/m) \tag{2}$$

where P is the gas pressure, T the cell temperature and R the universal gas constant. If the electrolysis took place at a voltage v, the electrical energy which would be required to produce this gas pressure is the product vit. Hence, the rate at which the product PV increases with the supply of electrical energy is given by

$$r = \frac{PV}{vit} = \frac{RT}{v}\,(e/m)\,. \tag{3}$$

For most electrolytes, this rate is of the order of 1 l atm/W h. This figure is low compared with conventional electromechanical compressors which produce about 10 l atm/W h. However, since our system is a battery, the input electrical energy is ultimately recovered and the PV energy (in principle) is produced free of cost, since the pressure is generated as a consequence of the charging current and does not represent an overhead on it.

The formation of chlorine hydrate at elevated pressures

Chlorine hydrate is a clathrate-type, ice-like compound formed with water near its freezing point. Its formula is usually written as $Cl_2 \cdot xH_2O$ where x ranges from 6 to 8. The heat of formation of the hydrate at normal pressure is estimated to be 18.6 kcal/mole [1]. The density is reported in the same source as 1.23 g/ml for $Cl_2 \cdot 8H_2O$ and 1.29 g/ml for $Cl_2 \cdot 6H_2O$. In order to design a zinc–chlorine system operating at near normal temperatures, the relationship between the vapour pressure of chlorine over chlorine hydrate to the temperature at which the hydrate exists must be known. This data has been reported in ref. 1 for the lower range of temperatures, about $-10\,°C$ to $+20\,°C$. In our work we have carried out experiments to determine the vapour pressure–temperature curves in the higher temperature ranges between 10 and 30 °C.

The experimental arrangement consisted of a glass hydrate-forming chamber with a Perspex cover which was clamped into place with aluminium gaskets and Teflon covered O-rings. Three epoxy coated metal tubes were screwed into the Perspex cover and Teflon tubes were attached to these to form the gas inlet, outlet, and pressure monitoring vents. To start the experiment, the chamber was filled with the appropriate liquid (water or zinc chloride solution) and sealed. Chlorine was then bubbled through this and the chamber cooled externally until hydrate formation took place. After a large amount of hydrate had been formed, the inlet and outlet vents were closed and the chamber warmed to the desired temperature in a water-bath, which resulted in a rise in pressure within the chamber due to hydrate decomposition. When no further rise in pressure was noted over a one-hour period at a given temperature, this final pressure was taken to be the vapour pressure of chlorine over chlorine hydrate for that temperature. In this way, vapour pressures were measured in the temperature range from 0 to 25 °C for the hydrate formed in pure water, a 20% solution, and a 40% solution of zinc chlo-
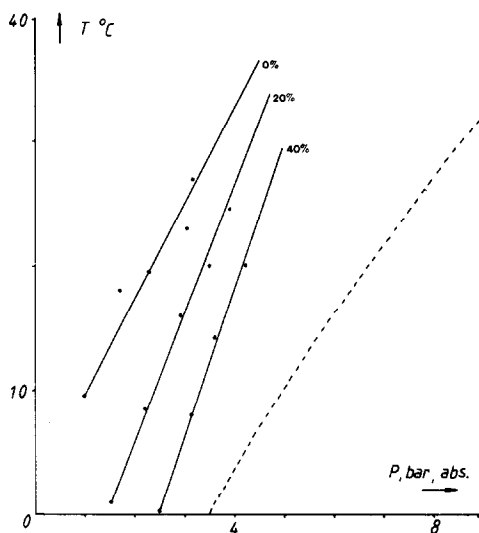
Fig. 1. The vapour pressure of chlorine over chlorine hydrate formed in water and an aqueous solution of zinc chloride. The dotted curve shows the vapour pressure of liquid chlorine.

ride in water, respectively. Unfortunately, due to defects in the apparatus we were unable to carry out tests above 25 °C. The results are shown in Fig. 1, where the vapour pressure curve for chlorine over liquid chlorine is also included for purposes of comparison.

It is clear from Fig. 1 that the lowest pressures required for the formation of chlorine hydrate at any temperature are obtained if this formation takes place in pure water. For instance, at 25 °C, the vapour pressure is observed as 2 atmospheres (gauge), although actual formation at 25 °C would require a pressure somewhat higher than this. Alternatively, if the hydrate is formed at a constant pressure, the solution will have to be cooled to a somewhat lower temperature than indicated by Fig. 1. This supercooling requirement has also been reported in ref. 1. Moreover, our results agree with the conclusion reported there that if the solution is cooled at constant pressure the supercooling is greater than if the solution is pressurized at constant temperature. This is a point in favour of the pressurized hydrate forming cell. In general, Fig. 1 seems to indicate that a system capable of withstanding a gauge pressure of 5 atm should be able to form chlorine hydrate at any ambient temperature up to 40 °C. Of course, the heat of formation would need to be removed continuously from the system, but this can be achieved by air, or water circulation, or, perhaps, with a simple cooling fin arrangement. In our experiment, we observed an immediate and rapid formation of the hydrate in water at 19 °C and 1.5 atm (gauge) when the forming chamber was cooled with ordinary tap water at 19 °C (the room temperature was 22 °C). It is concluded that the operating point of the hydrate store can be easily raised from

below 9.6 to over 20 °C with little change in the sealing of the system. Moreover, the decomposition of the hydrate during discharge in a pressurized system requires no heating, but only a lowering of the pressure. Once again, this is a process which produces, rather than consumes energy since the released gas can be utilised for pumping purposes later.

4. Flow rate requirements for porous graphite electrodes

In the batteries described in the literature [1 - 3], one or more pumps are used to transport the electrolyte through the porous graphite electrodes during discharge. Since, from the previous section it is evident that a chlorine hydrate store at room temperature will deliver chlorine at gauge pressures between 1 and 3 atm approx., it would be advantageous to use this pressure to produce the required electrolyte flow.

The flow rates reported in the literature [1] are quite low, approximately 2 ml min^{-1} cm^{-2} of electrode area, and are achievable by a small static head. It was therefore decided to construct a cell to determine the optimum flow rate. The cell consisted of a dense graphite, s.g. 1.79 g/cm^3 (Diabon OS2, EK82, supplied by Sigri Elektrographit GmbH, Postfach 1160, D-8901, Meitingen, G.D.R.) electrode, and a positive chlorine electrode of porous graphite (0.25 g/cm^3) supplied by the same firm. The PG-60 graphite electrodes referred to in the EPRI [1] report were, unfortunately, not available. A circular hole of 6.4 cm dia. was machined into a 10 × 10 × 5 cm block of the dense material. The inner wall of this hole served as the negative (zinc) electrode. A tube of porous graphite of dimensions 5.4 cm o. d., 2.2 cm i.d. and 5 cm long was inserted into the centre of the dense graphite block and the ends of the block were sealed with two Plexiglas covers with suitable inlet and outlet vents for the electrolyte. The porous graphite formed the positive (chlorine) electrode.

A diagram of the cell is shown in Fig. 2. All sealing was done with a two-component epoxy resin (UHU plus, schnell-fest) which seemed to suffer little damage from exposure to chlorine. The electrodes were activated by the electrochemical method developed by EPRI [1], which also served to produce a coating of zinc on the inner surface of the dense graphite electrode. After activation, the electrodes were flow rinsed with water.

To start an experiment, chlorine from a cylinder was used to form hydrate in water contained in the chamber described in Section 3. The outlet from this chamber was led into a 0.5M solution of zinc chloride where the chlorine under pressure dissolved in the liquid, and then forced the solution into the cell through the porous electrode. The outlet from the cell led to a measuring cylinder where the flow rate was controlled by controlling the diameter of the PVC tube feeding the chlorinated electrolyte to the cell. For each flow rate, the short circuit current delivered by the cell was determined by extrapolation of the currents measured on various loads (1 - 5 ohms) and the results for different flow rates are plotted on Fig. 3. The Figure shows
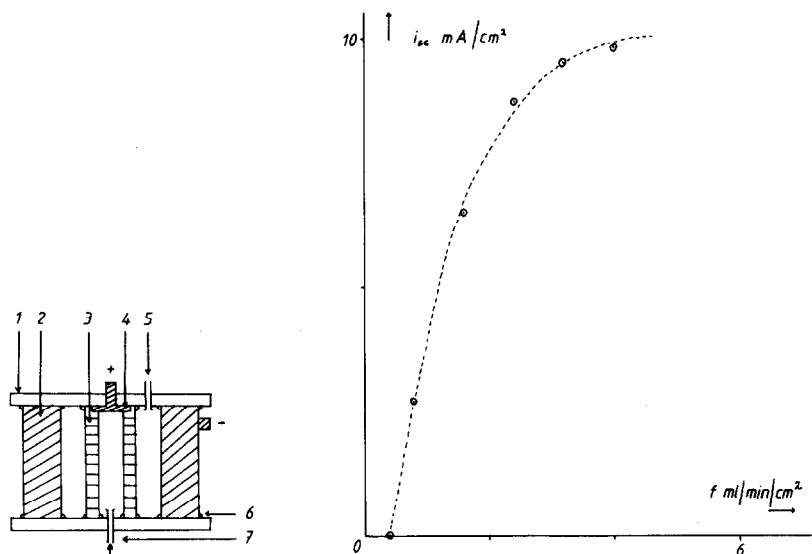
Fig. 2. The cell used for measuring optimum flow rates of chlorinated electrolyte during discharge (vertical cross-section). 1, Plexiglas cover; 2, dense graphite; 3, porous graphite; 4, dense graphite contact; 5, outlet tube; 6, epoxy seal; 7, inlet tube.

Fig. 3. The short circuit current in the cell of Fig. 2 as a function of chlorinated electrolyte flow rate(f).

that a maximum current of about 10 mA/cm² is obtained for a flow rate of about 4 ml min⁻¹ cm⁻². This value is too low for most practical applications, especially when compared with the figure of about 50 mA/cm² reported for "PG-60" porous graphite at a flow rate of 2 ml min⁻¹ cm⁻² [1]. However, it shows that the pumping requirements for optimum currents can be met by chlorine at about 1.5 atm gauge pressure. In fact, flow rates very much higher than the required 4 ml min⁻¹ cm⁻² are quite easily achievable. The low current density obtained by us is probably caused by the excessive porosity (over 70%) of the graphite electrode used.

This experiment, and the previous one, therefore demonstrate that the production and decomposition of chlorine hydrate are possible at room temperature and can be effectively used to pump electrolyte through the discharge cell. This, in addition to the fact that the required pressures can be easily generated in the cell during charging, supports our original suggestion that a zinc–chlorine battery can be made to operate entirely without external refrigeration and pumping.

5. Schematic design for a pressure operated cell

Figure 4 shows a possible design for a zinc–chlorine battery controlled by gas pressure. The design is purely schematic and should be considered only
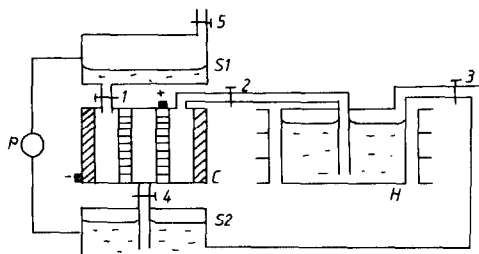
Fig. 4. Schematic design for a pressure operated Zn/Cl$_2$ cell. 1 - 5, Valves; S1, S2, electrolyte chambers; H, storage chamber for hydrate; C, cell; P, auxiliary pump.

TABLE 1

The operating sequence for the valves in Fig. 4

Step no.	Step function	Valves					Connections
		1	2	3	4	5	
1	charging	o	o	c	o	c	charger connected
2	clearing	o	c	c	o	c	open circuit
3	standby	c	c	c	c	c	open circuit
4	filling and discharging	o	c	o	o	o	load connected

o = open, c = closed.

as a block diagram and a basis for a more sophisticated design. The operation sequence of the cell is shown in Table 1, and is briefly described below (the steps refer to Fig. 4):

Step 1. Valves 1, 2 and 4 are open causing electrolyte to flow from S1 to S2 through the cell while chlorine enters chambers S1 and H, causing hydrate formation in H. The resulting pressure drop in H will attract most of the chlorine to this chamber.

Step 2. Valves 1 and 4 are open causing electrolyte to drain out of S1 and C into S2.

Step 3. All valves are closed and the battery remains in the charged condition.

Step 4. Valves 1, 3, 4 and 5 are open allowing chlorine from H to enter S2 where it pushes the electrolyte up through the cell into S1. Any chlorine in S1 is expelled into an absorber through valve 5 and is lost to the system. Any electrolyte remaining in S2 after the hydrate store H is exhausted is pumped by the auxiliary pump P to S1 and the cycle is restarted.

The design in Fig. 4 is intended only to show that the problem of the pressure operated zinc–chlorine cell is really one of chemical engineering and not of electrochemistry [5]. Much further work will be required to produce a practical battery.

6. Safety considerations

Zinc–chlorine batteries are usually condemned from an environmental point of view due to the toxic nature of chlorine. This fear is usually overly emphasised. Efficient design can minimize the chances of any chlorine spill as has been amply demonstrated in the EPRI, USA, report [1]. We suggest in this connection that it may be advantageous to encase any zinc–chlorine battery in a thin, hollow shell containing concentrated ammonia solution in water. This would render any rupture in the battery case highly visible as a white cloud of ammonium chloride. A large amount of the escaping chlorine would also be absorbed in the process.

Hydrogen evolution at the zinc electrode can represent an explosion hazard in the system. Hydrogen evolution also alters the pH of the electrolyte. However, both problems can be solved by following the EPRI [1] plan of installing a hydrogen–chlorine reactor in the gas line. The reactor consists essentially of an ultraviolet source which causes a slow recombination of the evolved hydrogen with chlorine, the resultant HCl being returned to the electrolyte.

7. Conclusion

The formation of chlorine hydrate has been shown to take place at temperatures up to 25 °C at pressures in the range 1 - 5 atm. Further work will be undertaken to investigate the formation of chlorine hydrate at temperatures up to 40 °C.

It has been shown that a zinc–chlorine battery operated by internally generated gas pressure is possible.

Such a battery will be simpler and require fewer moving parts than current designs of the battery.

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