

Short communication

Investigation of the charge/discharge characteristics of aqueous zinc–ferric chloride batteries

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Abstract

In a Zn–FeCl₃ battery, zinc granules were used as the anode and ammonium chloride as the electrolyte in both the anode and cathode zones, with ferric chloride as the active cathode substance and carbon felt as an inert cathode. A PE-01 homogeneous membrane was used as the membrane between the anode and cathode zones, with 100 ml of solution in both the anode and cathode zones. The charge/discharge characteristic of the battery was investigated for various concentrations of ferric chloride and ammonium chloride. At present, there are still some difficulties in using this zinc–ferric chloride battery as a rechargeable battery because zinc cannot be electrodeposited very well. However, it can possibly be used as a fuel cell and the operating lifetime of the fuel cell is very long. The actual energy density of a Zn–FeCl₃ fuel cells is approximately equal to the actual energy density of a Pb–PbO₂ battery. When a mixed solution of 2 M ferric chloride and 2 M ammonium chloride was used in the cathode zone with 4–5 M ammonium chloride in the anode zone, a better discharge characteristic was obtained, with a discharge time of approximately 14–15 h at 5 Ω. The most remarkable advantages for Zn–FeCl₃ fuel cell are that both zinc and ferric chloride are very cheap and environmentally friendly, with flat discharge voltage characteristics.

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1. Introduction

Zinc–chlorine, zinc–bromine, iron–chromium, iron–ferric/ferrous chloride and zinc–ferro/ferricyanide batteries have been extensively investigated [1–5], but no investigations of zinc–ferric chloride batteries have been reported, although the electromotive force of such a battery is not small (1.534 V) and both zinc and ferric chloride are very cheap and environmentally compatible. Thus, in the present investigation, ferric chloride and zinc were used as the active cathode and anode materials, respectively. Ammonium chloride was used as the electrolyte in both the anode and cathode zones. Carbon felt was used as an inert cathode, with a PE-01 homogeneous membrane as the membrane between the anode and cathode zones. The charge/discharge characteristic of the battery was measured for various concentrations of ferric chloride and ammonium chloride.

2. Experimental

The analytical grade reagents and electrode materials used were ammonium chloride, ferric chloride (FeCl₃·6H₂O), 99.99% zinc pieces (thickness of 0.15–0.25 mm) and carbon felt (thickness of 3 mm).

The charge/discharge characteristics were investigated using NEWARE charge/discharge equipment. Tafel and cyclic voltammetry plots were measured using a CHI potentiostat.

The electrolytic cell was made of organic glass. The total volume of the cell was 5 cm × 5 cm × 10 cm, which was divided into two equal parts of 5 cm × 5 cm × 5 cm by a membrane.

The solution volume in both the anode and cathode zones was 100 ml. The width of the zinc granules and the carbon felt electrode was 4.5 cm. The electrodes were immersed in solution to approximately 4 cm. The zinc electrode was formed by the superposition of more than one zinc granule, each of which was polished and washed with deionized water before the experiments. The solutions were prepared using deionized water.

The battery was charged/discharged at a constant resistance of 5 Ω and at room temperature.

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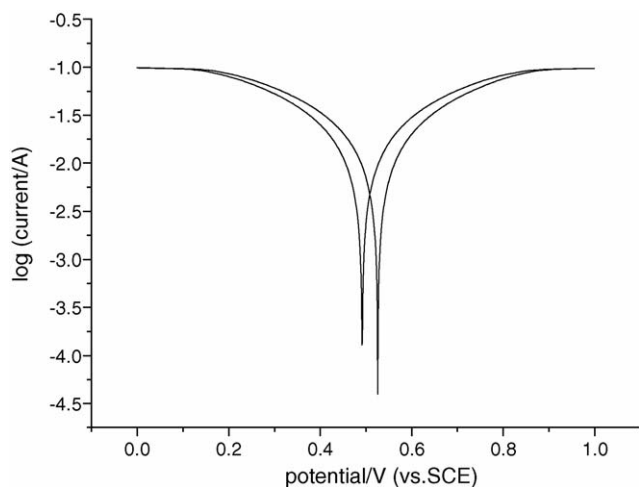


Fig. 1. Tafel plot for $\text{Fe}^{3+}/\text{Fe}^{2+}$ on a carbon felt electrode in a mixed solution of 2 M ferric chloride and 2 M ammonium chloride: initial E , 0 V; final E , 1 V; segment, 2; scan rate, 0.01 V s^{-1} .

3. Results and discussion

3.1. Tafel and cyclic voltammetry plots

Tafel and cyclic voltammetry plots for $\text{Fe}^{3+}/\text{Fe}^{2+}$ on the carbon felt electrode in a mixed solution of 2 M ferric chloride and 2 M ammonium chloride are shown in Figs. 1 and 2, respectively. Platinum with a large surface area was used as the counter electrode and 1 cm^2 carbon felt as the working electrode, with the back of the carbon felt electrode exposed to the solution for both Figs. 1 and 2.

Fig. 1 shows two equilibrium potentials close with each other, with the mean close to the standard electrode potential of a $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode, 0.771 V (versus NHE). Fig. 2 shows that the scan currents in both positive and negative directions are almost equal. This means that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ reversibility on a carbon felt electrode is very good. It is interesting that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ cur-

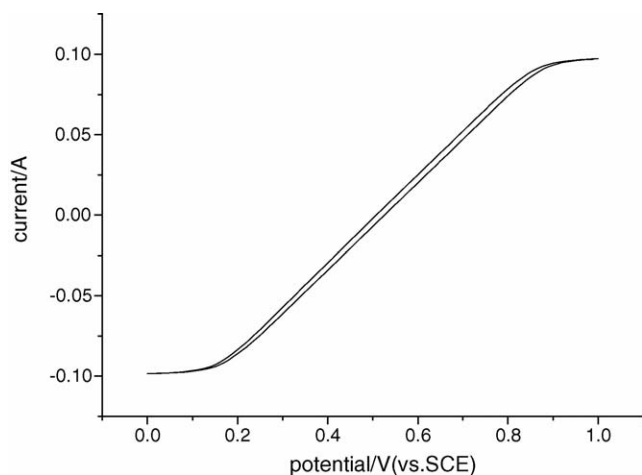


Fig. 2. Cyclic voltammetry plot for $\text{Fe}^{3+}/\text{Fe}^{2+}$ on a carbon felt electrode in a mixed solution of 2 M ferric chloride and 2 M ammonium chloride: initial E , 1 V; high E , 1 V; low E , 0 V; segment, 2; scan rate, 0.1 V s^{-1} .

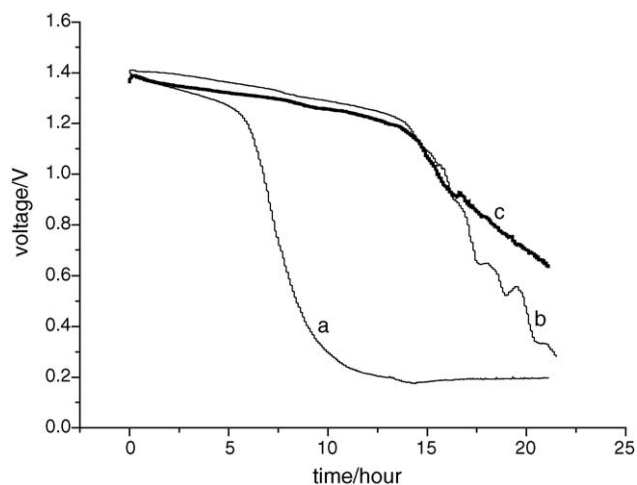


Fig. 3. Discharge characteristic of Zn- FeCl_3 batteries with various ferric chloride concentrations. The concentration of ammonium chloride is 5 M in the anode zone and 2 M in the cathode zone. The concentration of ferric chloride: (a) 1 M; (b) 2 M; (c) 3 M.

rents on a carbon felt electrode change linearly with potential over a very wide range, in agreement with Ohm's law.

3.2. Discharge characteristics of Zn- FeCl_3 batteries with various FeCl_3 concentrations

For batteries with a constant concentration of ammonium chloride of 5 M in the anode zone and 2 M in the cathode zone, the discharge characteristic is shown for 1–3 M ferric chloride in Fig. 3; the corresponding electromotive force E of the batteries is 1.697, 1.694 and 1.794 V, respectively. These values are all greater than the standard electromotive force of the battery, 1.534 V. The ordinate in Fig. 3 is voltage, V . $[V(\text{V}) - 0.006(\text{V})]$ is the deferent voltage of the battery, where 0.006 V is an instrumental correction factor. The discharge current in Fig. 3 can be calculated from the following formula:

$$I(\text{A}) = \frac{V(\text{V}) - 0.006(\text{V})}{5(\Omega)}$$

Fig. 3 shows that the voltage of the battery is 300–400 mV lower than the electromotive force. A voltage of more than 200 mV of this 300–400 mV was lost through the membrane and solution, with the remainder lost at the carbon felt cathode; no voltage loss occurred on the zinc electrode.

Fig. 3 shows that the discharge time of the battery increased with increasing ferric chloride concentration from 1 to 2 M, although the discharge time for 1 M FeCl_3 did not reach half of that for 2 M FeCl_3 . The reason for this is that there were some losses of FeCl_3 , because the color of the solution in the cathode zone became slightly yellow and opaque and there was some yellow powder at the bottom of the cathode zone after discharge. This means that there is not enough acidity in the solution when the FeCl_3 content was lower.

Fig. 3 also shows that when the FeCl_3 concentration reached 3 M, the discharge current decreased instead of increased. The reason for this is that when the FeCl_3 concentration increased,

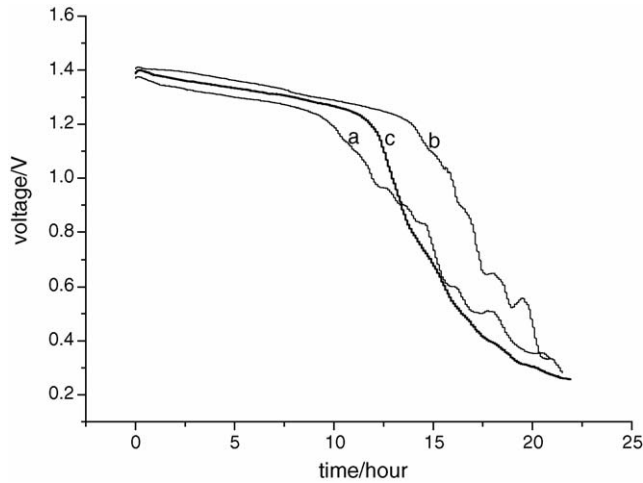


Fig. 4. Discharge characteristic of Zn-FeCl₃ batteries with various NH₄Cl concentrations in the cathode zone. The concentration of FeCl₃ was 2 M. Concentration of ammonium chloride: (a) 1 M; (b) 2 M; (c) 3 M in the cathode zone, and 5 M in anode zone.

the resistance of the solution increased. Thus, 2 M FeCl₃ represents an optimum concentration.

3.3. Discharge characteristics with varying NH₄Cl concentration in the cathode zone

Fig. 4 shows the discharge characteristic for 5 M ammonium chloride in the anode zone and 2 M ferric chloride in the cathode zone, with 1–3 M ammonium chloride in the cathode zone; the corresponding electromotive force of the batteries was 1.742, 1.694 and 1.741 V, respectively. Fig. 4 shows that 2 M ammonium chloride in the cathode zone is the optimum concentration. If the concentration of ammonium chloride is too high or too low, the resistance of the solution increases and the discharge characteristic deteriorates.

3.4. Discharge characteristic with a varying NH₄Cl concentration in the anode zone

Fig. 5 shows the discharge characteristic for 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and 3–5 M ammonium chloride in the anode zone. Fig. 5 shows that when the concentration of ammonium chloride in the anode zone increased from 3 to 4 M, the discharge current increased. However, with a further increase to 4 M, the discharge current increased slightly and the discharge time decreased. Thus, 4–5 M ammonium chloride in the anode zone is suitable for applications.

3.5. Charge/discharge characteristics of Zn-FeCl₃ batteries

For a battery with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and 5 M ammonium chloride and 1 M zinc chloride in the anode zone, charge/discharge curves are shown in Figs. 6 and 7, respectively.

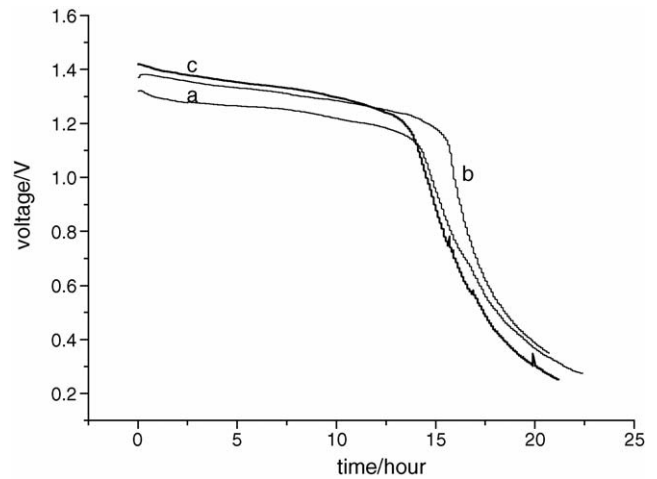


Fig. 5. Discharge characteristic of zinc-ferric chloride batteries with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and (a) 3; (b) 4; (c) 5 M ammonium chloride in the anode zone.

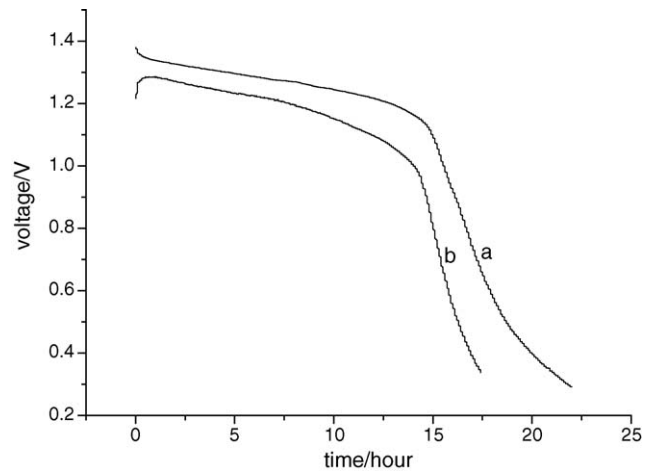


Fig. 6. Discharge characteristic of a zinc-ferric chloride battery with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and 5 M ammonium chloride and 1 M zinc chloride in the anode zone: (a) discharged for the first time and (b) discharged for the second time.

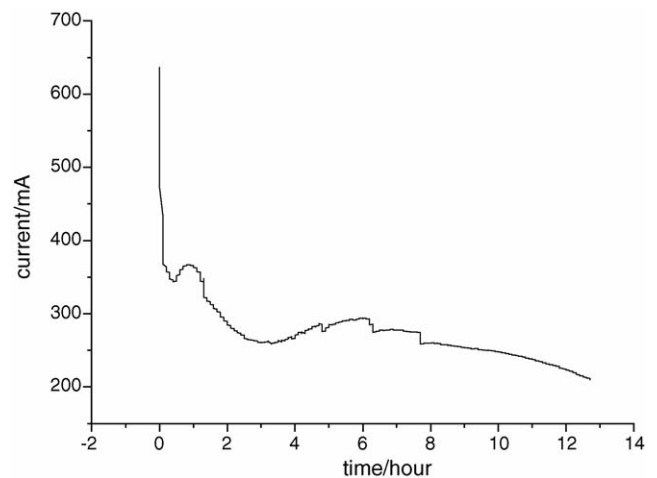


Fig. 7. Charge characteristic of a zinc-ferric chloride battery with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and 5 M ammonium chloride and 1 M zinc chloride in the anode zone at a constant voltage of 2 V.

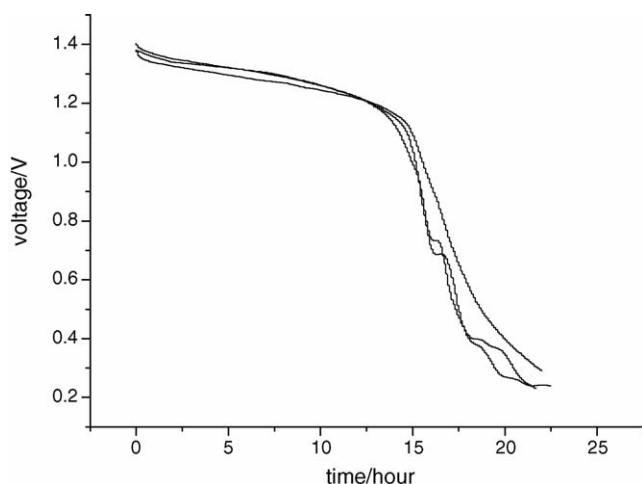


Fig. 8. Repeated-discharge experiments on three zinc–ferric chloride batteries with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone, and 5 M ammonium chloride and 1 M zinc chloride in the anode zone.

Fig. 6 shows that both the discharge current and the capacity are smaller for the second time than for the first, viz. the resistance of the batteries increases and the capacity degrades with cycling. Some ferric chloride permeates through the membrane and enters the anode zone during charging, but none crosses the membrane and enters the anode zone during discharge. This is possibly one of the causes of the increase in resistance and decrease in capacity of the battery. On the other hand, a voltage of more than 600 mV was lost at the membrane when the batteries were charged, but only 200 mV was lost when the batteries were discharged. Most of the electrochemical problems with such batteries are due to the zinc electrode [6]. Some dendrites and powder are produced during zinc electrodeposition. The use of additives and modified charging methods have not led to beneficial effects.

Therefore there are still some difficulties in using this zinc–ferric chloride battery as a rechargeable battery. However, it can feasibly be used as a fuel cell. Because both ferric chloride and ammonium chloride will not cause the membrane to corrode and the operating lifetime of zinc–ferric chloride fuel cell is very long.

3.6. Repeated-discharge experiments on zinc–ferric chloride batteries

Fig. 8 shows the repeated-discharge characteristic of three zinc–ferric chloride batteries with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone and 5 M ammonium chloride and 1 M zinc chloride in anode zone. Fig. 8 shows that the zinc–ferric chloride batteries possess a better return characteristic.

3.7. Influence of ZnCl in the anode zone on the discharge characteristic

The discharge characteristic of zinc–ferric chloride batteries with 2 M ferric chloride and 2 M ammonium chloride in the cath-

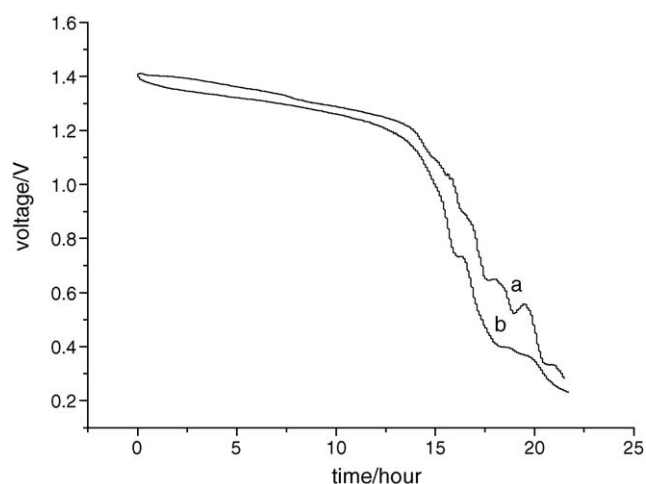
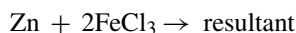


Fig. 9. Discharge characteristic of zinc–ferric chloride batteries with 2 M ferric chloride and 2 M ammonium chloride in the cathode zone, and 5 M ammonium chloride and (a) 0 M and (b) 1 M zinc chloride in the anode zone.

ode zone, and 5 M ammonium chloride and 0–1 M zinc chloride in the anode zone is shown in Fig. 9. The plot shows that an increase in zinc chloride concentration in the anode zone leads to a decrease in the discharge current. The reason for this is that the increase in zinc chloride in the anode zone makes the electrode potential of zinc more positive.

3.8. Calculation of energy density for Zn–FeCl₃ fuel cells

We calculate the energy density of Zn–FeCl₃ fuel cell according to the following reaction:



The mass of Zn + 2FeCl₃ is

$$65.38 \text{ g} + 2 \times 55.84 \text{ g} + 6 \times 35.45 \text{ g} = 389.8 \text{ g} = 0.3898 \text{ kg}$$

The theoretical energy density of Zn–FeCl₃ fuel cell is

$$\frac{1.534 \times 2 \times 9.6485 \times 10^4}{3600} = 211 \text{ Wh kg}^{-1}$$

While the theoretical energy density of Pb–PbO₂ battery is 170 Wh kg⁻¹.

The actual energy density of Zn–FeCl₃ fuel cell is calculated as follows: the mass of Zn + 2FeCl₃ + 7NH₄Cl (2 M NH₄Cl in the cathode zone and 5 M NH₄Cl in the anode zone) is

$$65.38 \text{ g} + 2(55.84 + 3 \times 35.45) \text{ g} + 7(35.45 + 18) \text{ g} \\ = 763.9 \text{ g} = 0.7639 \text{ kg}$$

The density of Zn, FeCl₃ and NH₄Cl is 7.13, 2.898 and 1.527, respectively. The volume of Zn + 2FeCl₃ + 7NH₄Cl is

$$\frac{65.38}{7.13} + \frac{2(55.84 + 3 \times 35.45)}{2.898} + \frac{7(35.45 + 18)}{1.527} = 366.1 \text{ ml}$$

The volume of solvent for Zn + 2FeCl₃ + 7NH₄Cl is 2000 – 366.1 = 1633.9 ml.

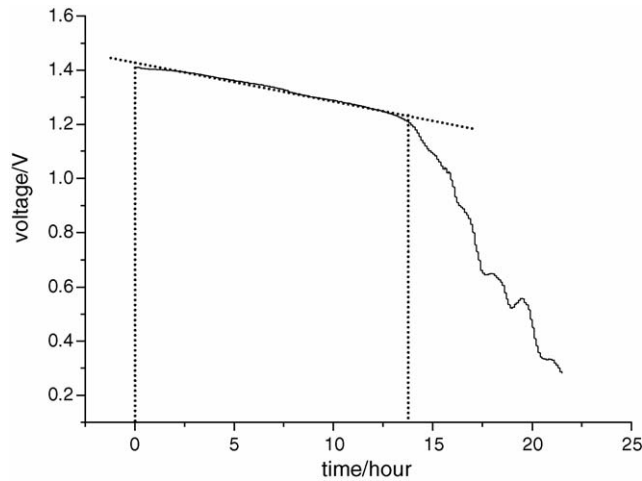


Fig. 10. Calculation of energy density for Zn-FeCl₃ fuel cell.

Supposing that the density of solvent is 1, thus, the mass of solvent is 1.6339 kg. The mass of Zn + 2FeCl₃ + 7NH₄Cl + solvent is 0.7639 + 1.6339 = 2.3978 kg.

The total mass of the fuel cell is 2.3978 kg (ignoring the mass of electrolytic cell). Supposing that the deferent voltage of the fuel cell change linearly with time:

$$V(\text{V}) = -\frac{1.43 - 1.22}{13.75}t(\text{h}) + 1.43$$

(see Fig. 10). Because the volume of 2000 ml solution is equal to the volume of 10 fuel cells, the actual energy density of Zn-FeCl₃ fuel cell is

$$\begin{aligned} \frac{10}{2.3978} \int_0^{13.75} \frac{(V - 0.006)^2}{R} dt &\approx \frac{10}{2.3978} \int_0^{13.75} \frac{V^2}{R} dt \\ &= \frac{10}{2.3978} \int_0^{13.75} \frac{1}{5} \left(-\frac{1.43 - 1.22}{13.75}t + 1.43 \right)^2 dt \\ &= 20.18 \text{ Wh kg}^{-1} \end{aligned}$$

While the actual energy density of Pb-PbO₂ battery is 17 Wh kg⁻¹ the actual energy density of a Zn-FeCl₃ fuel

cell is approximately equal to the actual energy density of Pb-PbO₂ battery. However the most remarkable advantages for a Zn-FeCl₃ fuel cell are that both zinc and ferric chloride are very cheap and environmentally friendly, with a flat discharge characteristic.

4. Conclusions

1. Zinc-ferric chloride batteries are suitable for use as fuel cells.
2. When a mixed solution of 2 M ferric chloride and 2 M ammonium chloride was used in the cathode zone with 4–5 M ammonium chloride in the anode zone, a better discharge characteristic was obtained, with a discharge time of approximately 14–15 h at 5 Ω.
3. At present there are still some difficulties in using the zinc-ferric chloride battery as a rechargeable battery, because zinc cannot be electrodeposited very well and a greater voltage is exerted on the membrane when the batteries are charged.
4. The actual energy density of a Zn-FeCl₃ fuel cell is approximately equal to the actual energy density of Pb-PbO₂ battery.
5. The most remarkable advantages for a Zn-FeCl₃ fuel cell are that both zinc and ferric chloride are very cheap and environmentally friendly, with a flat discharge characteristic.
6. Zinc-ferric chloride battery can feasibly be used as a fuel cell and the operating lifetime of the fuel cell is very long.

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