The zinc-chlorine battery: half-cell overpotential measurements

J. JORNÉ, J. T. KIM,* D. KRALIK†

Department of Chemical and Metallurgical Engineering, Wayne State University, Detroit, Michigan 48202, USA

Received 4 August 1978

The voltaic performance of the zinc-chlorine battery was investigated by measuring the individual potentials of the Zn and Cl₂ electrodes versus a reference electrode. The overpotential at the Zn electrode is very small for both the charging and the discharging processes, and the use of a flow-through porous Cl₂ electrode is advantageous. Energy efficiency in the region of 65% has been achieved for a complete cycle. Tafel polarization data for both the zinc and the Cl₂/graphite electrodes was obtained using rotating zinc hemisphere and graphite disc electrodes. Exchange current densities and Tafel slopes are reported.

1. Introduction

The zinc-chlorine battery concept is based upon the electrochemical reaction between zinc, chlorine and ZnCl₂ aqueous solution, and the simultaneous chemical reaction between chlorine and water [1]. The overall reactions are:

\[
\begin{align*}
\text{ZnCl}_2(\text{aq}) & \rightarrow \text{Zn}(s) + \text{Cl}_2(g) \\
\text{Cl}_2(g) + x\text{H}_2\text{O} & \rightarrow \text{Cl}_2\cdot x\text{H}_2\text{O}
\end{align*}
\]

\[x \approx 5.9.\]

The reactions are highly reversible. The e.m.f. of a Zn–Cl₂ cell under standard conditions is 2.12 V. During the charging process, the ZnCl₂ electrolyte is electrolysed, yielding a zinc deposit on an inert graphite substrate and Cl₂ evolution on a porous flow-through graphite anode. The Cl₂ gas is removed from the cell to another chamber where it is mixed with water at approximately 10°C and chlorine hydrate is formed.

During the discharging process, chlorine is evolved by heating the chlorine hydrate, mixed with the ZnCl₂ electrolyte, and passing it through the porous graphite electrode. Chlorine is consumed electrochemically while zinc dissolves at the other electrode. Coulombic inefficiencies are due mainly to the chemical recombination of zinc with dissolved chlorine. It has been shown by Kim and Jorné [2] that this process is limited by the mass transfer of dissolved chlorine to the zinc electrode. The kinetics and mass transfer of the chlorine electrode on a rotating graphite electrode has been investigated by Kim and Jorné [3] and the kinetic parameters and a kinetic mechanism have been proposed.

In this paper the voltaic behaviour of a single cell is investigated and the individual overvoltages are measured using zinc or calomel reference electrodes. The reference electrode was located in a separate compartment and connected by a tube to the interelectrode space. It is shown that the overpotential at the zinc electrode is very small (<50 mV) while the overpotential on the Cl₂ flow-through graphite electrode is about 100 mV. The ohmic drop can be decreased by adding KCl and NaCl as supporting electrolytes. Polarization data for the zinc electrode and Cl₂ electrode were obtained using a rotating zinc hemisphere and rotating graphite disc electrode, respectively.

2. Experimental

A single Zn–Cl₂ cell was used (EDA, Madison Heights, Michigan) [8]. The cell is shown in Fig. 1 and consists of a dense graphite electrode (Union Carbide ATJ Graphite) on which zinc is deposited,
and a porous flow-through graphite electrode (Union Carbide Porous Graphite Grade 60) on which chlorine is evolved. The thickness of the porous graphite electrode is 0.2 cm and the porosity is 0.52. The gap between the two electrodes is 0.2 cm. The apparent active area of the electrodes was 68 cm$^2$, the total current was 3 A and the charging process lasted for 1–2 hours. The experimental set-up is shown in Fig. 2. A 2.5 M ZnCl$_2$ (2 M) solution was circulated through a flow meter and the cell using a Kynar pump with a teflon gear (EDA modified micropump). The flow rate was 60 ml min$^{-1}$. The evolved Cl$_2$ was stripped during the charging by nitrogen bubbling throughout the experiment. Prior to each experiment the pH was adjusted by adding HCl and nitrogen was bubbled to remove oxygen and the remaining dissolved chlorine. The charging time was adjusted so that the amount of electricity was always the same, 0.080 A h cm$^{-2}$. The zinc deposits were peeled gently off the graphite substrate, washed thoroughly, dried and weighed. The ZnCl$_2$ concentration was 2 M and in some cases KCl and NaCl supporting electrolytes were added in order to reduce the ohmic resistance. In some cases the ZnCl$_2$ concentration was reduced down to 0.5 M.

During the discharge of the cell, Cl$_2$ gas was bubbled through the electrolyte reservoir and fed to the cell with the flowing ZnCl$_2$ solution. The discharging lasted until the cell was completely exhausted and all the Zn deposit was redissolved.

The reference electrode consisted of a Zn rod or SCE placed in a separate compartment filled with the cell’s ZnCl$_2$ solution. The reference electrode compartment was connected to the cell by a tube, and by small holes in the interelectrode spacing. The tops of the holes were located in the middle of the gap between the two graphite electrodes. The overpotentials were corrected for ohmic drop using the conductivities of the solutions.

The current was applied by an Udylite PC-10 constant current power supply. The potentials were measured by a Keithley 600 A electrometer and recorded on a multi-channel recorder (Honeywell Electronik 194) for the entire charging and