

Absorption of CO₂ by alkaline electrolyte and its effect on electrical discharge

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Freshly prepared 37% potassium hydroxide was exposed to the atmosphere. Samples were taken periodically to measure amount of absorbed CO₂ and their specific conductance. After exposure for 10 months, the solution was virtually neutralized by absorption of CO₂. Effects of CO₂ content and KOH concentration on the discharge characteristics of the silver-zinc cell were tested. Discharge capacity was decreased when CO₂ content reached beyond 3%, and KOH concentration dropped to below 30%. Polarization experiments on silver oxide and zinc electrodes showed that only the zinc electrode was affected. Observation of the current-time behaviour lead to the equation $(i - i_1) = kt_p^{-1/2}$, and X-ray diffraction showed that the passivation layer was ZnO.

1. Introduction

Most commonly used secondary cells or batteries, except the familiar lead-acid battery, use an alkaline electrolyte solution and potassium hydroxide is used with very few exceptions. Commercially available storage batteries offer a wide variety of physical design types and discharge performance characteristics. Other advantages include high cycle life, good performance under extreme environmental conditions, almost maintenance free, physical ruggedness, high energy density, very stable discharge voltage, low self discharge rates, immunity to electrical abuse and storage conditions. Alkaline electrolyte offers another advantage from an electrochemical point of view. The electrolyte is serving only as a charge carrier and is not actually reacting with the active materials as that in the lead-acid battery does. Besides many cell construction materials such as steel are not corroded by alkali.

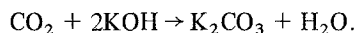
The general requirements of the alkaline electrolyte are high electrolytic conductance, low freezing point and inertness to electrodes in the open circuit condition. In the early stage of developing alkaline cells it was realized that potassium hydroxide electrolyte was superior to sodium and lithium hydroxide solutions with regard to conductance. For 1 mol dm⁻³ concentration, the

specific conductances of LiOH, NaOH and KOH at 25° C are 0.139, 0.158, and 0.184 × 10⁻³ ohm⁻¹ cm⁻¹, respectively [1]. Solubility of KOH is much better than the other two hydroxides, and so is the depression of the freezing point. Potassium hydroxide is a white crystalline material which rapidly absorbs moisture and CO₂ from air and deliquesces. The atmosphere contains approximately 0.033% of CO₂ even without the effects of pollution. The effects of CO₂ in KOH electrolyte and its discharge performance of silver-zinc cell are studied in this paper.

2. Experimental details and results

2.1. Absorption of CO₂

Potassium hydroxide was of reagent grade from Baker Chemical Co. and contained less than 1% K₂CO₃ according to the manufacturer's specification. Freshly prepared KOH solution was boiled in a beaker to drive off CO₂ and exposed to the atmosphere in the laboratory. A sample was pipetted from time to time to test its CO₂ content. When CO₂ was absorbed it reacted with KOH to form K₂CO₃



Testing of CO₂ content was performed at an inter-

Table 1. Absorption of CO_2 in KOH solution against time

Exposed time (months)	wt %			
	K_2CO_3	KOH	H_2O	Equivalent CO_2
0	0.41	36.67	62.92	0.13
2	10.35	28.60	61.05	3.30
4	19.55	21.13	59.32	6.23
6	28.98	13.48	57.54	9.24
8	41.86	3.1	55.04	13.35
10	45.54	4.3×10^{-2}	54.46	14.52

val of two months, and the results are shown in Table 1. The liquidus curve for the system $\text{KOH}-\text{K}_2\text{CO}_3-\text{H}_2\text{O}$ at 25°C is shown in Fig. 1 [2]. Above liquidus curve APC, the system is in the liquid state; below the curve the system is partly solid. At the intersection P , the solution is saturated with both KOH and K_2CO_3 . Curve EF is the composition change from freshly prepared solution at point E to solution after 10 month exposure in the atmosphere at point F, where the electrolyte had little hydroxide ion left and became useless for electric discharge.

2.2. Specific conductance of electrolyte

A special electrolytic cell as shown in Fig. 2 was made for measurement of specific conductance. A

constant current was passed between two stainless steel electrodes and the potential drop between them was measured with two calomel electrodes (Fisher Scientific Company No. 13-639-52).

The reference electrodes contained saturated KCl solution as liquid junction between the internal calomel element and the outside bulk KOH solution. A test against a homemade Hg/HgO electrode indicated a potential drifting of 0.25 mV h^{-1} over a period of 18 h. The cell had a passage area of 1.25 cm^2 and distance between two electrodes was 2.9 cm. The specific conductances of potassium hydroxide solutions against concentration by Lang [3] and this experiment are shown in Fig. 3, and those of potassium carbonate against concentration are shown in Fig. 4. As KOH electrolyte absorbed CO_2 , the concentration of less conductive K_2CO_3

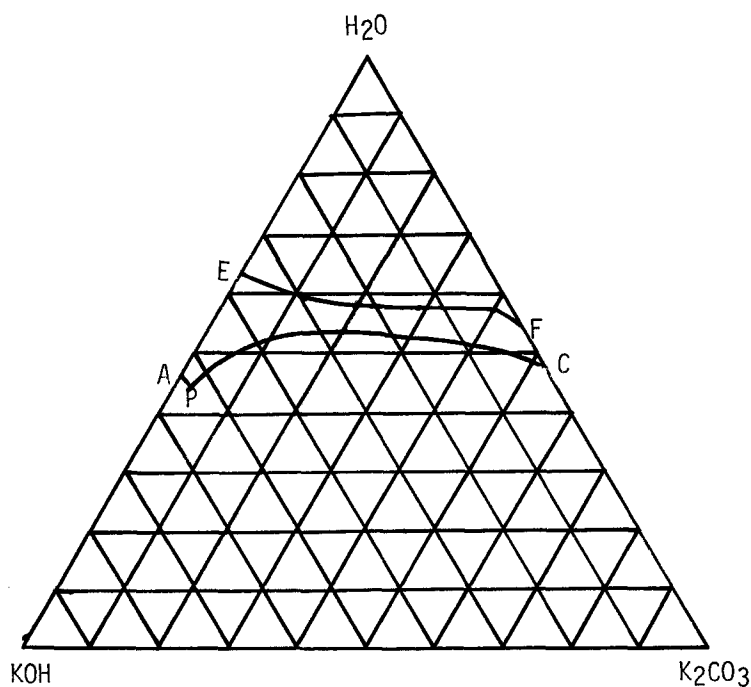


Fig. 1. Liquidus curve for the system $\text{KOH}-\text{K}_2\text{CO}_3-\text{H}_2\text{O}$ at 25°C .

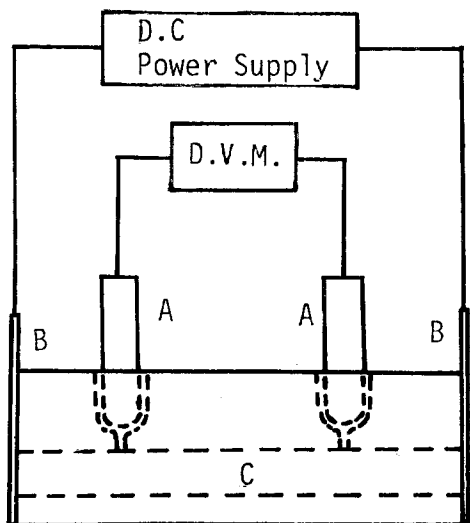


Fig. 2. Electrolytic cell for measurement of specific conductance. A. SCE reference electrodes. B. Stainless electrodes. C. Electrolyte channel.

was increased at the expense of more conductive KOH, and the specific conductances of 37% KOH mixed with controlled amounts of K₂CO₃ were measured and shown in Fig. 5.

2.3. Effect of K₂CO₃ concentration on discharge

The electrical cell contained 5 silver and 6 zinc electrodes of size 3 cm x 5 cm. The details of

construction have been described previously [5]. The cell was injected with 8 cm³ of electrolyte and discharged at a constant rate of 10 A controlled by a Hewlett-Packard 6269B d.c. power supply. The electrolyte was prepared by mixing KOH and K₂CO₃ so that the potassium ion concentration was kept constant. The effects of CO₂ concentration and KOH concentration on discharge capacity were shown in Tables 2 and 3, respectively. The cut-off voltage was 1.30 V. From Tables 2 and 3 one can see that potassium carbonate starts affecting discharge capacity at around 9% and begins deteriorating at 20%. These effects of electrolyte composition on discharge were tested by polarization experiments on separate silver and zinc electrodes. The electrode was discharged against a stainless steel counter electrode, and a saturated calomel electrode was used as a reference electrode. Two kinds of electrolyte were used for the experiment: 22.1% KOH solution with and without 18.4% K₂CO₃. The result showed that the CO₃²⁻ has no effect on the AgO electrode but affects the zinc one.

2.4 Passivation time of zinc electrode

Pure zinc metal sheet was abraded with No. 000 emery paper, and then rinsed with distilled water and degreased with boiling acetone [6]. A 1 cm²

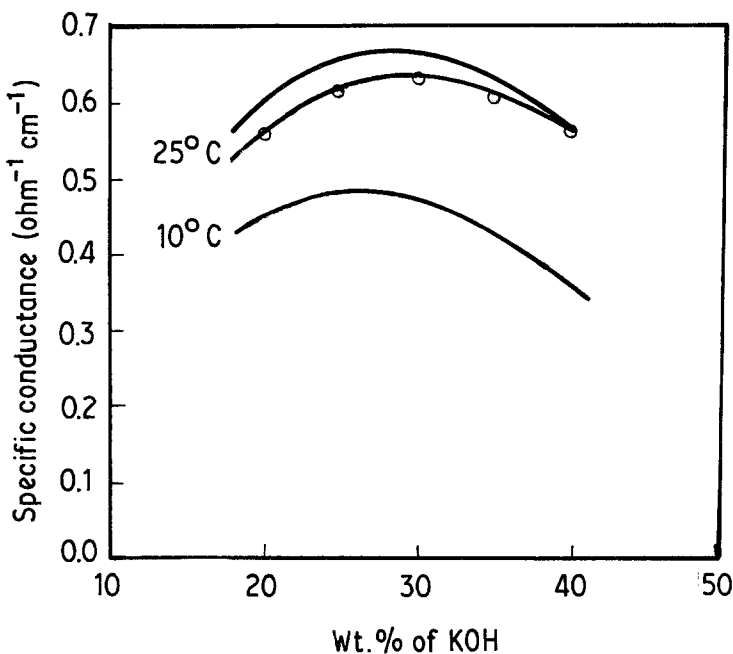


Fig. 3. Specific conductance against KOH concentration. ○ This measurement, — [3].

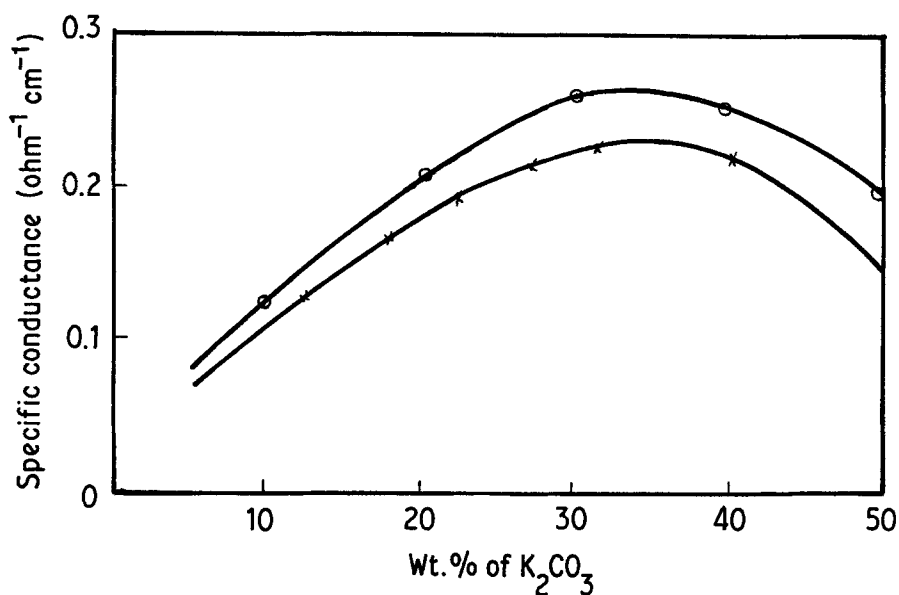


Fig. 4. Specific conductance against K_2CO_3 concentration at $25^\circ C \times [4]$, \circ this measurement.

piece of zinc sheet connected with electrical wire was immersed in electrolyte, and a constant current was passed through a counter electrode. Passivation time is determined from the polarization curve, where it is marked by a sudden rise in electrode potential. Three solutions, 37% KOH, 18.3% KOH, and 18.3% KOH + 23% K_2CO_3 , were used as electrolyte for comparison. Experimentally passivation time-current density data are conventionally expressed in the form [7, 8]

$$(i - i_1)t_p^{1/2} = k$$

where i is current density, i_1 the magnitude of transport process other than diffusion, t_p the passivation time, and k a constant. This is an equation derived from Fick's second law of diffusion based on semi-infinite linear diffusion [9]. Plots of i against $t_p^{-1/2}$ for three kinds of electrolyte are shown in Fig. 6. The data can be represented by linear square fit as following

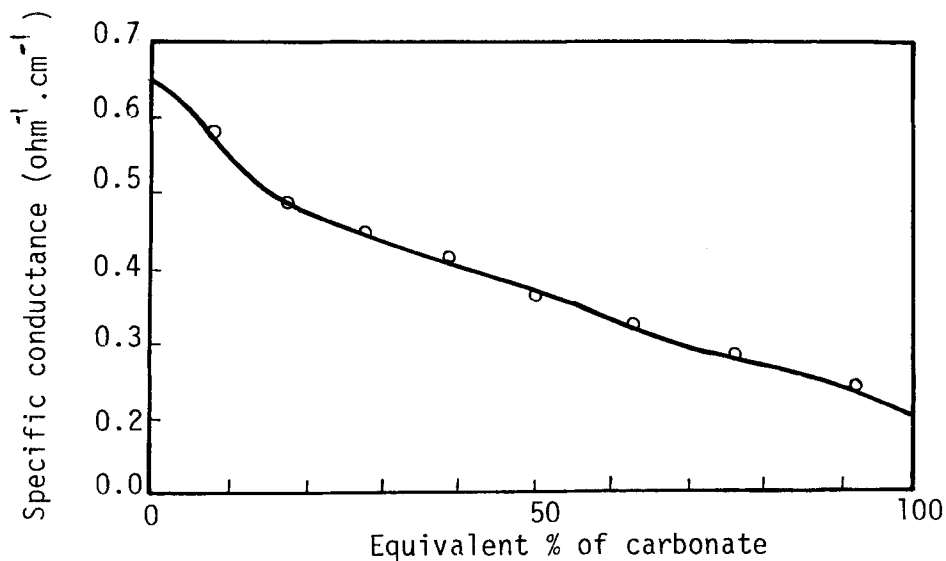


Fig. 5. Specific conductance of mixed KOH and K_2CO_3 electrolyte. (9. ON K^+).

Table 2. Effect of absorbed CO₂ on discharge capacity

Electrolyte composition		Discharge capacity (amp-minutes)
% K ₂ CO ₃	% KOH	
0	37	101-106
4.6	33.7	100-109
9.2	29.5	86-88
13.8	25.8	82-85
18.4	22.1	51-56
23.0	18.3	27-29

Table 3. Effect of KOH concentration on discharge capacity

% KOH	Capacity
37	101-110
33.7	101-106
29.5	92-95
25.8	86-92
22.1	62-67
18.3	63-65

equations:

$$i - 0.157 = 0.59t_p^{-1/2}$$

$$i - 0.16 = 0.48t_p^{-1/2}$$

and

$$i - 0.059 = 0.38t_p^{-1/2}$$

for 37% KOH, 27% KOH, and 27% KOH plus 10% K₂CO₃ solutions, respectively. These linear relations indicate that a diffusion process is involved in the discharge reaction. The relation-

ships between current density and time have also been studied by many authors [10-12]. Fig. 6 shows that 37% KOH solution has longer passivation time than 18% KOH solution, and electrolyte absorbed with CO₂ passivated much easier. The X-ray diffraction showed that the passivating layers in all three electrolytes were zinc oxide. This is in agreement with Powers' study [13]. Dirkse [14] has shown that at high Zn(OH)₄²⁻ ion concentration, it decomposes to form ZnO

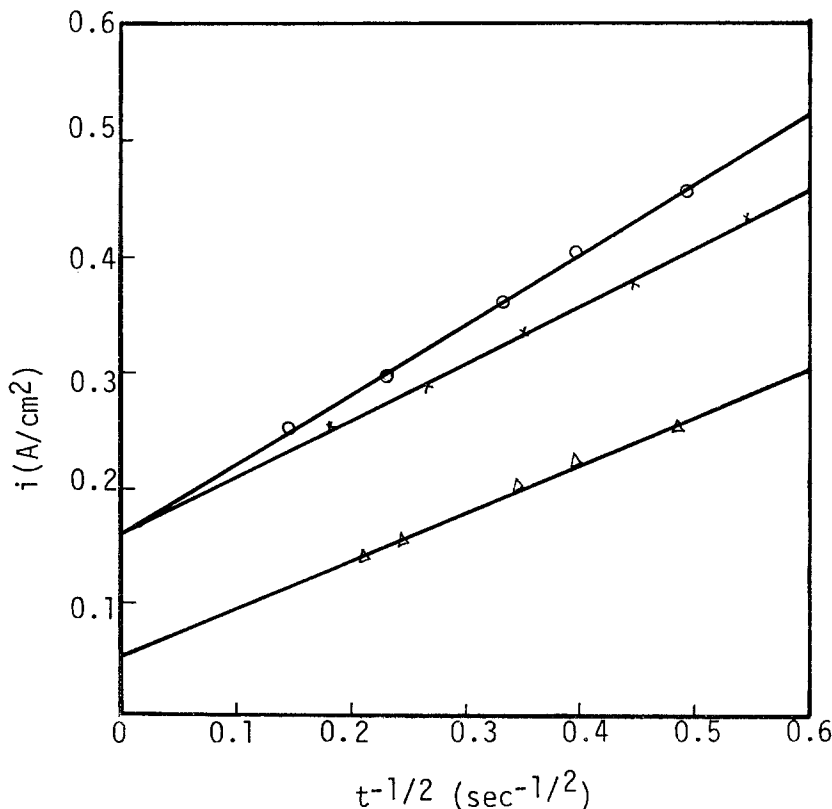
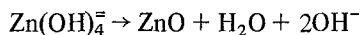
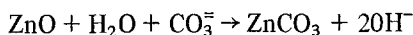


Fig. 6. Passivation time against current density of zinc electrode. ○ 37% KOH, × 18% KOH, and △ 18% KOH + 23% K₂CO₃.

precipitate:



The SEM observation shows that formation of ZnO is a nucleation and growth process, and occurs within the diffusion layer of the electrode [15]. No trace of ZnCO_3 was detected in the passivating film for electrolyte containing K_2CO_3 . Addition of 10% K_2CO_3 to 27% KOH solution saturated with ZnO did not result in any ZnCO_3 precipitation. A calculation of equilibrium constant (5.9×10^{-8}) from the thermodynamic data for the reaction



shows that enormous CO_3^{2-} concentration is needed to precipitate ZnCO_3 . The ZnCO_3 is very soluble in alkali solution.

3. Conclusions

The conclusions of this study can be summarized as follows:

1. The 37% KOH aqueous solution exposed to atmosphere for 10 months could absorb up to 14.5% of CO_2 , which is equivalent to 45.5% of K_2CO_3 , and left little hydroxide ion in the solution. The specific conductance of electrolyte decreased from 0.64 to 0.25 $\text{ohm}^{-1} \text{cm}^{-1}$ during this period.
2. The decrease in effective discharge capacity of Ag-Zn electric cell was caused by decreasing KOH concentration and increasing K_2CO_3 concentration. A study on polarization curves of silver oxide and zinc electrodes attributed this effect to the zinc electrode alone.

3. The relationships between passivation time and current can be represented by the familiar equation $(i - i_1) = kt_p^{-1/2}$. The X-ray diffraction analysis showed that ZnO was the passivation layer.

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