

EFFECT OF SILVER, COPPER AND PALLADIUM ADDITIVES ON THE PERFORMANCE OF CARBON ELECTRODES IN AN Li/SOCl_2 SYSTEM

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Summary

The effects of metallic additives on the performance of a carbon electrode in an $\text{Li}/\text{SOCl}_2\text{-LiAlCl}_4/\text{C}$ battery have been studied. It has been found that the electrode capacity increases on adding silver, copper or palladium. When the battery is discharged at a low rate (5 mA cm^{-2}), the capacity is more sensitive to the conductivity of the carbon electrode. However, at a high discharge rate (20 mA cm^{-2}), the capacity is controlled by the average pore diameter of the carbon electrode. Finally, the discharge overpotential of the carbon electrode has been studied using a galvanostatic transient method. In general, the addition of metallic powders is found to reduce the discharge overpotential.

Introduction

The carbon electrode is critical to the capacity and discharge performance of an Li/SOCl_2 battery, and consequently its technology has been the subject of considerable research [1]. For example, Behl *et al.* [2] have compared the efficacy of four different types of commercially available carbon as cathode materials; Dey [3] has emphasized that an optimum capacity can be achieved with a porosity in the range 70% - 80%; and Giattino [4] has pointed out that the performance and safety of the carbon electrode is improved with the addition of copper powder. Behl *et al.* [5] found that copper powders react with SOCl_2 to form cuprous chloride. Klinedinst and Murphy [6] prepared an electrode in which acetylene black was used as a supporting matrix for finely divided gold, platinum, nickel oxide, or cupric sulphide. Klinedinst [7] also observed that finely divided platinum on Shawinigan black increased both the capacity and the rate capability.

The aim of the present work is to study the effect of different metallic additives on the performance of the carbon electrode and, in particular, to examine the influence of these additives on the discharge overpotential. It is anticipated that a better understanding of the effect of such additives on

the kinetics of the carbon electrode will lead to an improvement in their preparation.

Experimental

Electrode preparation

Shawinigan acetylene black was mixed with Ag, Cu or Pd powder (10 wt %) and a Teflon binder (10 wt.%). The resultant mixture (weight: 0.15 g) was pasted onto a nickel screen (15 mm × 15 mm × 1.4 mm) and then pressed under 5.5×10^7 Pa for 30 s at 360 °C. Prior to experiment, the electrodes were stored in a vacuum oven at ambient temperature. The individual types of electrode were designated as follows: C₁ (with Ag additive); C₂ (with Cu additive); C₃ (with Pd additive); and C₄ (no additive)

The electrode was carefully weighed (w_A) and put in a near-vacuum (below 30 mmHg) flask for 30 min. The flask was filled with oil (80 °C) and, after 30 min, air cooled to room temperature. After absorbing outside oil the electrode was again weighed in atmosphere (w_B) and then in water (w_C). The electrode porosity ϵ was calculated according to the equation

$$\epsilon = \frac{w_B - w_A}{w_B - w_C} \frac{\rho_{H_2O}}{\rho_O} \times 100\%$$

where ρ_{H_2O} and ρ_O are the densities of water and oil, respectively, at the testing temperature

The surface area and average pore diameter of the carbon electrodes were measured by the BET method

Electrolyte preparation

SOCl₂ and triphenylphosphate (16 vol.%) were mixed and then distilled under a dry nitrogen atmosphere. The distilled portion at 75 - 77 °C was collected in a flask containing LiCl and AlCl₃. A 1.5 M solution of LiAlCl₄ was then prepared according to the procedure described by Szpak and Venkatasetty [8].

Lithium battery discharge

The test cells consisted of a carbon electrode (prepared as above), a lithium foil electrode and a solution (10 ml) of 1.5 M SOCl₂/LiAlCl₄. The cells were discharged at 5 and 20 mA cm⁻², respectively. The open-circuit voltage was measured to be 3.6 V and the cell was cut off at 1.7 V.

Galvanostatic transient method

A galvanostatic transient method was used to analyse the potential of the carbon electrode. The circuit diagram is shown in Fig. 1. Accurate readings of the ohmic drop, the activation overpotential and the concentration overpotential were recorded on an oscilloscope.

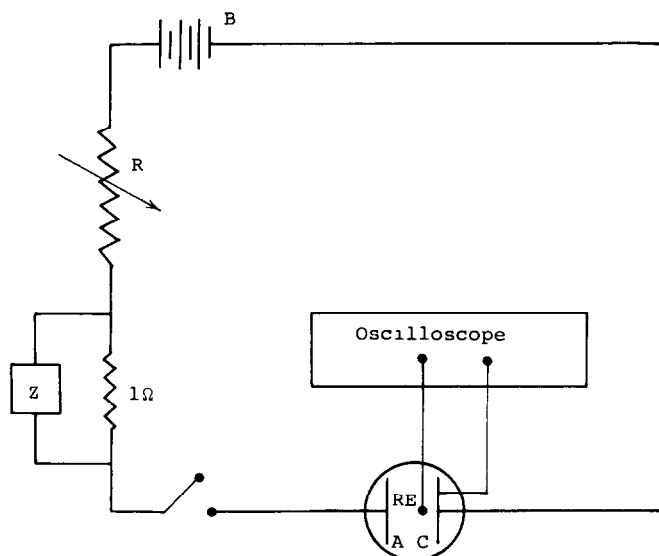


Fig 1 Circuit schema for measuring electrode overpotential A, anode, C, cathode, RE, reference electrode of test cell, R, variable resistance, B, 24 V, 240 A h lead/acid battery, Z, recorder

Results and discussion

Effect of metallic additives

The physical properties of the tested carbon electrodes are summarized in Table 1. Discharge data are given in Table 2. On close inspection, it can be seen that the capacity is most sensitive to the conductivity of the electrode when the discharge rate is low; the conductivity of the additives is C_1 (Ag) $>$ C_2 (Cu) $>$ C_3 (Pd). This order of conductivity (and capacity) remained unchanged when acetylene black was mixed with the different additives.

The average pore diameter follows a different order to that of conductivity and capacity, namely, $C_1 > C_3 > C_2 > C_4$. This parameter becomes a dominating factor when the discharge rate is high, and is due to the reaction rate of the electrode being controlled by the diffusion rate of the electrolyte.

TABLE 1

Physical properties of the various carbon electrodes

Electrode	C_1 (Ag)	C_2 (Cu)	C_3 (Pd)	C_4
Resistivity (Ω cm)	0 101	0 120	0 148	0 16
Average pore diameter (μ m)	0 55	0 36	0 48	0 11
Porosity (%)	70 00	76 90	75 20	76 21
Surface area (m^2 g $^{-1}$)	55 92	49 43	38 64	76 20

TABLE 2

Discharge performance of the various carbon electrodes

Discharge current density (mA cm ⁻²)	Electrode capacity (A h per g carbon)			
	C ₁ (Ag)	C ₂ (Cu)	C ₃ (Pd)	C ₄
5	4.46	4.21	2.75	1.98
20	1.04	0.98	1.06	0.78

Under this condition, a large average pore diameter (and hence a lower resistance to electrolyte diffusion) results in a higher capacity. However, there is one exception to this observation: the electrode with the Ag additive has a smaller capacity than that with the Pd additive, even though the former has a larger average pore diameter. This is probably due to the fact that Ag and SOCl₂ react to precipitate AgCl and this material may then obstruct the pores of the electrode. The AgCl deposit was identified by X-ray diffraction analysis (Fig. 2).

Finally, it can be concluded that there is no obvious trend in the influence of either the porosity or the surface area of the electrode on the resulting capacity.

Analysis of discharge overpotential

A galvanostatic transient method has been successfully used in our previous work to study the discharge overpotential of a tubular lead/acid

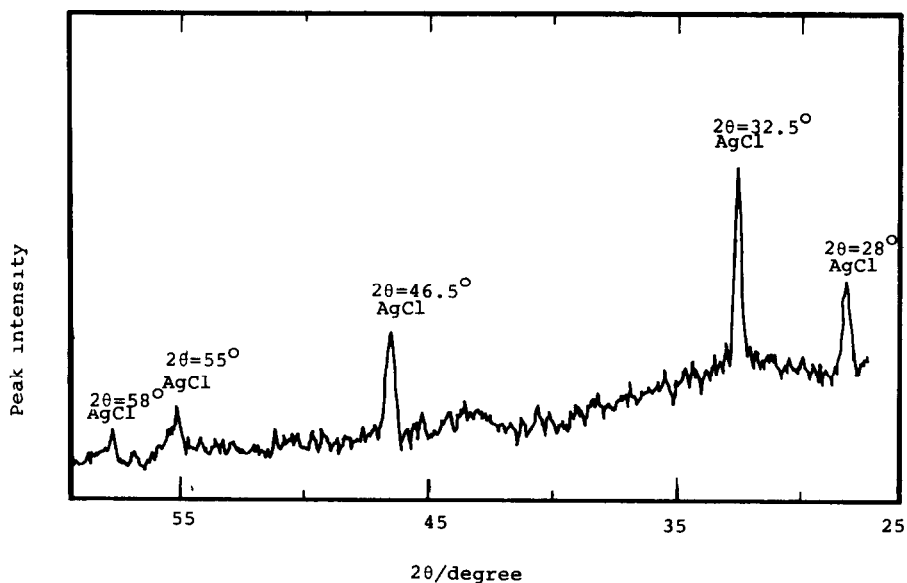


Fig 2 X-ray diffraction pattern of electrode C₁ (with Ag) in SOCl₂ electrolyte

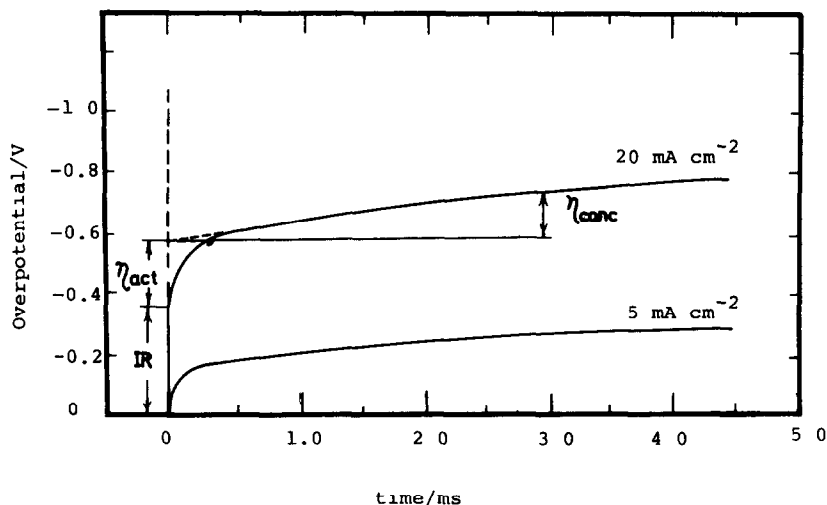


Fig 3 Typical discharge curve of a carbon electrode at the indicated discharge rates

electrode [9] In the present study, this method has been applied to the investigation of the discharge overpotential of the carbon electrode in an Li/SOCl_2 battery. Figure 3 shows typical transient discharge curves for this electrode at different discharge rates. The relationship between the discharge current density i and either the activation overpotential η_{act} or the concentration overpotential η_{conc} is presented in Figs. 4 and 5, respectively.

From Figs 4 and 5, it can be seen that the addition of metal to the carbon electrode reduces both the activation overpotential and the concentration overpotential. In general, as the conductivity of the electrode increases, the activation overpotential decreases. On the other hand, it is noted that electrode C_3 has the lowest concentration overpotential. This may be associated with the fact that there are more active sites in electrode C_3 since, unlike electrodes C_1 or C_2 , the additive contained therein (*i.e.* Pd) does not react with SOCl_2 .

The major contribution to the discharge overpotential comes from the activation overpotential and the i.r. drop. We suggest that the addition of metal to the carbon electrode results in more nucleation and active sites, thus providing a lower true current density and a smaller concentration gradient with a consequently lower concentration overpotential.

When the activation overpotential is greater than 0.05 V, the Tafel equation (*viz.* $\eta = a + b \log i$) can be applied. The exchange current density i_0 can be obtained by extrapolation of the plot in Fig. 4 to zero overpotential. The values of i_0 for the various carbon electrodes are: C_1 (Ag): 2.24 mA cm^{-2} ; C_2 (Cu): 1.51 mA cm^{-2} ; C_3 (Pd): 1.29 mA cm^{-2} ; and C_4 : 0.85 mA cm^{-2} . The significant increase of exchange current density after the addition of metallic powders demonstrates the effect of metallic additive on the reduction of activation overpotential. The detailed mechanism of this process requires further study.

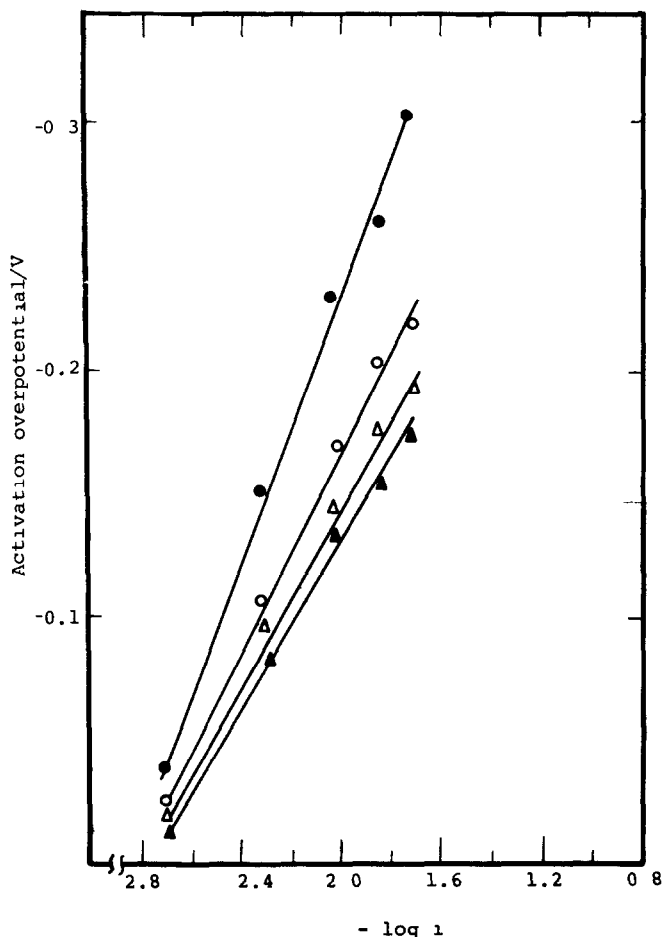


Fig 4 Plot of activation overpotential against current density for ▲, C₁ (with Ag), △, C₂ (with Cu), ○, C₃ (with Pd), and ●, C₄ (no additive)

Conclusions

From the studies reported in this paper, we may make the following conclusions.

(1) The capacity of the carbon electrode in an Li/SOCl₂ battery is sensitive to electrode conductivity at a low discharge rate (5 mA cm⁻²). When the electrode is discharged at a high rate (20 mA cm⁻²), the average pore diameter of the electrode becomes the controlling factor.

(2) Metallic additives such as silver, copper or palladium powders not only increase electrode conductivity but also significantly reduce electrode overpotential.

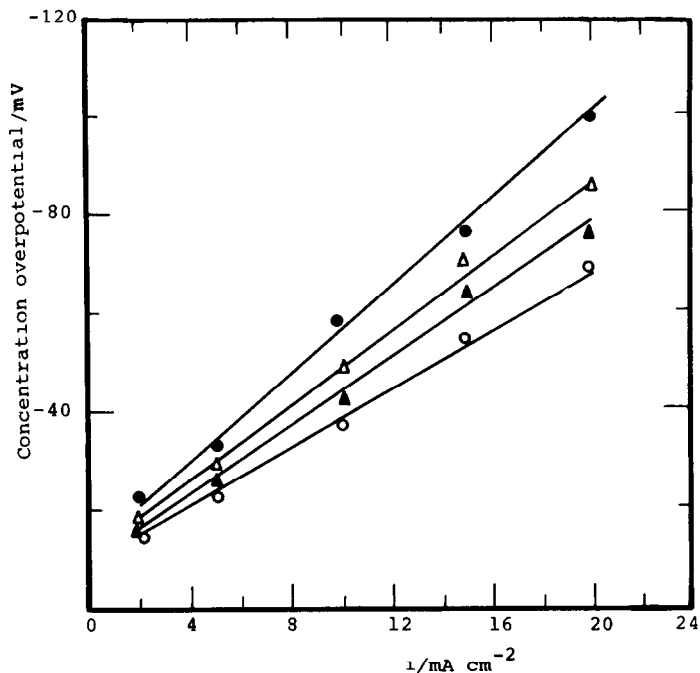


Fig 5 Plot of concentration overpotential (at 4.5×10^{-3} s) against current density for ▲, C₁ (with Ag), △, C₂ (with Cu), ○, C₃ (with Pd), and ●, C₄ (no additive)

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