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Effective conductivities of a negative electrode in an Li-Al/FeS cell at different states of charge

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Effective conductivities of porous negative electrodes containing Li–Al or Al as the initial active material were experimentally determined at 450° C for different states of discharge by means of an a.c. impedance bridge. When a negative electrode having a theoretical loading density of 0.83 Ah cm^{-3} was discharged, the effective conductivity decreased from approximately 20 to 5 ohm^{-1} cm^{-1}. This decline in the effective conductivity is attributed to the decrease in the volume fraction of conductive materials (Li–Al and Al) in the electrode. A theoretical calculation shows that the total volume fraction of conductive Li–Al and Al governs the resistance behaviour of the negative electrode because of little effect of change in the pore electrolyte conductivity and of low volume fraction of the solid salt precipitated.

1. Introduction

For better understanding of the charge–discharge behaviour of a high-temperature Li–Al/FeS secondary cell, we carried out separate determinations of effective conductivities of each positive and negative electrode, respectively. The results for a porous FeS positive electrode have been reported in previous papers [1, 2], in which its unique resistance behaviour was described. The effective conductivity of the FeS positive in the LiCl-rich electrolyte decreases as the discharge proceeds, but towards the end of discharge it starts to increase. In the LiCl–KCl eutectic electrolyte, the effective conductivity decreases much more sharply at low utilizations, for example, at about 44% utilization for a discharge at 100 mA cm^{-2}, indicating that the effective conductivity during discharge is strongly affected by the LiCl-concentration in the LiCl–KCl electrolyte.

In this paper we report the results of experiments undertaken to examine changes of Li–Al negative electrode resistance during charge and discharge in the electrolytes containing varied LiCl concentration. These results and methods are useful in determining the effects of electrode additives and characteristics of separators as well as for designing of the cells.

2. Experimental procedure

Aluminium powder (– 100, + 150 mesh) or Li–Al alloy powder (49 atom % Li, Lithium Corporation of America; – 60, + 100 mesh) was used as the initial active material. As electrolyte, eutectic LiCl–KCl (58.2 mol % LiCl–KCl, Anderson Physics Laboratory) or an LiCl–rich LiCl–KCl (67.4 mol % LiCl–KCl) was employed. A mixture of the active material (Al or Li–Al) and the electrolyte powder was cold-pressed to make a test electrode of 1 cm diameter and 0.4 cm thickness. This electrode was placed in a BN electrode housing with a stainless steel current collector. The theoretical capacity and utilization were calculated assuming that the fully charged composition in Li–Al alloy is 49 atom % Li. The counter electrode was a mixture of FeS, Fe and Li_2S. The cell was operated at 450° C in an argon atmosphere glove box. Charge and discharge were carried out by an automatic cycler (Hokuto Denko, HJ-201) at constant

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current densities of 20–150 mA cm^{-2}. The impedance measurements were made by a vector impedance meter (Hewlett-Packard, 4800A) after interrupting the charge or discharge current. For usual calculations impedance values at 20 kHz were used. The electrode potentials were measured against an Ni/Ni_3S_2 reference electrode [3]. The potentials shown in the figures are *IR*-free. The cell assembly and the other detailed procedure have been described previously [1, 2].

3. Results and discussion

3.1. *Experimental effective resistance*

Typical changes in the effective specific resistance of the Li–Al electrode in the eutectic electrolyte are shown in Fig. 1. Similarly, the effective specific resistance in the LiCl-rich electrolyte when started with Al instead of Li–Al is shown in Fig. 2. In both cases the electrodes were cycled at 50 mA cm^{-2}. When the Li–Al alloy was used as the initial active material, the discharge capacity of the first cycle was extremely low. The reproducible results were obtained after the second to fourth cycle. When a negative electrode containing the Li–Al alloy as the initial active material was charged to the fully-charged state, its potential changed from that of $(\alpha + \beta)$ Li–Al to a more negative level at 60–70 % charged state, indicating the formation of γ-phase [4–6]. This is probably due to poor current collection because of low volume fraction of the active material with insufficient compaction.

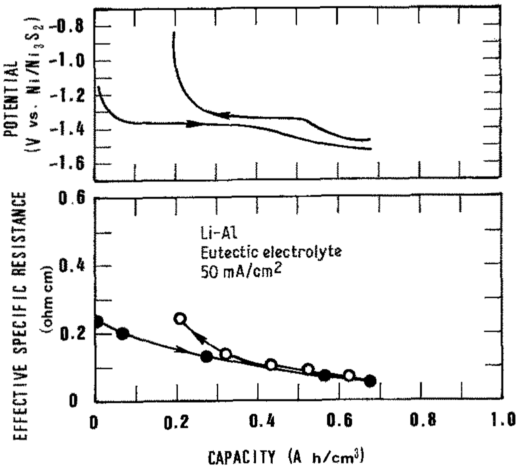

Fig. 1. Change in the effective specific resistance of a negative electrode which was initially Li–Al alloy, during a charge–discharge cycle. Loading density: 0.68 Ah cm^{-3}, current density: 50 mA cm^{-2}, eutectic electrolyte.

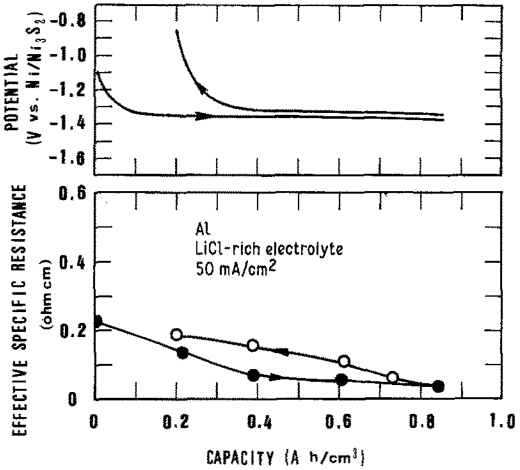

Fig. 2. Change in the effective specific resistance of a negative electrode, which was initially Al, during a charge–discharge cycle. Loading density: 0.83 Ah cm^{-3}, current density, 50 mA cm^{-2}, LiCl-rich electrolyte.

Fig. 3 shows the effect of current density on the resistance behaviour during discharge of a negative electrode with a theoretical capacity of 0.83 Ah cm^{-3} in the LiCl-rich electrolyte. The effective resistance increased almost linearly from approximately 0.05 at the fully-charged state to 0.2 ohm cm at the end of discharge within the range of current densities examined. Identical results were obtained for negatives which contained the Li–Al alloy initially in either the eutectic or LiCl-rich electrolyte.

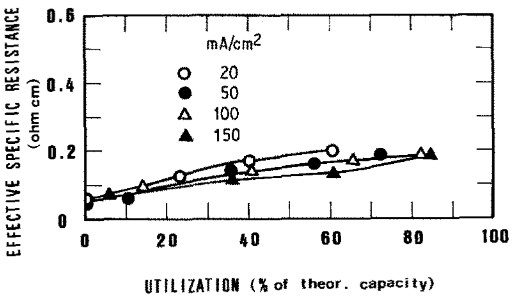

Fig. 3. Change in the effective specific resistance during discharge at different current densities. Starting material: Al, loading density: 0.83 Ah cm^{-3}, LiCl-rich electrolyte.

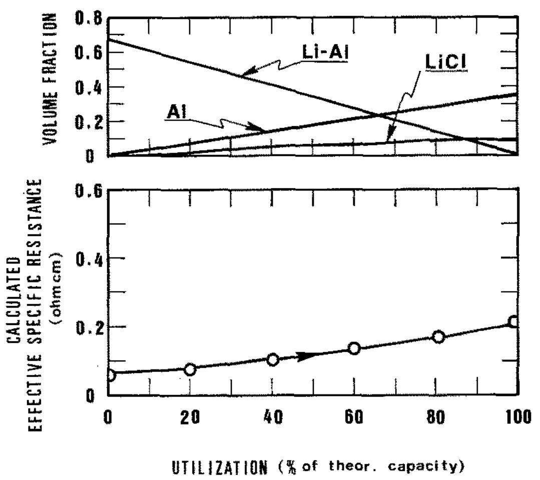

Fig. 4. Calculated effective specific resistance and volume fraction of LiAl, Al and precipitated LiCl during discharge of an Li–Al negative electrode in LiCl-rich electrolyte. Loading density: 0.9 Ah cm^{-3}, current density: 100 mA cm^{-2}.

3.2. *Calculated effective resistance*

A theoretical calculation of the effective resistance using the Meredith–Tobias equation [7] was made to examine how each parameter contributes to the electrode resistance. It was similar to that made in a previous work [2] for the FeS positive. Fig. 4 shows the calculated change of the effective resistance, and volume fraction of the Li–Al, Al and solid LiCl precipitated on a negative electrode with a loading density of 0.9 Ah cm^{-3} which was discharged in the LiCl-rich at 100 mA cm^{-2}. The calculation results show good agreement with the experimental results. In this calculation, we made some assumptions: that the electrochemical reactions take place uniformly in the electrode and that during discharge β-LiAl is directly converted to Al. A conductivity of 1.5×10^5 ohm^{-1} cm^{-1} was used for both Al and the β-LiAl. The densities for Al and β-LiAl used were 2.70 and 1.75 g cm^{-3}, respectively. The other parameters were specified in Table 1 of a previous work [2].

Fig. 4 shows that on discharge at 100 mA cm^{-2}, solid LiCl begins to precipitate at about 10% utilization but its volume fraction is as low as 0.1 even at the end of discharge, showing little effect on the electrode resistance. The LiCl deposition in porous Li–Al anodes which were discharged at high current densities (250 mA cm^{-2}) has been observed experimentally by Vallet *et al.* [8].

4. Conclusion

The effective resistance of the Li–Al negative electrode decreases on charge and increases on discharge. The magnitude of its change is much smaller than that of the FeS positive electrode. It is, therefore, concluded that the greater part of the change in the cell resistance of an Li–Al/FeS cell comes from the resistance change in the positive electrode. The resistance profiles were not very sensitive to the initial form of the active material (Al or Li–Al), LiCl-concentration in the electrolyte and charge–discharge current density. A theoretical calculation shows that the total volume fraction of Al and Li–Al present in the negative electrode governs the resistance behaviour.

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