

ELECTROCHEMICAL BEHAVIOR OF GRAPHITE INTERCALATED BY FLUORINE

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Summary

The discharge potentials of graphite fluorides, $(CF)_n$ and $(C_2F)_n$, were almost the same at low current densities, but $(C_2F)_n$ gave a higher discharge potential, by 0.3 - 0.4 V, than $(CF)_n$ with increasing current density. The discharge of the electrodes made by mixing $(CF)_n$ and $(C_2F)_n$ showed that $(C_2F)_n$ was preferentially discharged, followed by the discharge of $(CF)_n$. The dependence of their overpotentials on the structures is discussed on the basis of the X-ray diffraction and ESR measurements.

Introduction

There are two kinds of graphite fluorides, $(CF)_n$ and $(C_2F)_n$. When natural graphite is used as a starting material, $(CF)_n$ and $(C_2F)_n$ are prepared at around 600 °C and at 350 - 400 °C, respectively. A mixture of $(CF)_n$ and $(C_2F)_n$ is formed between these temperatures. The chemical composition varies from 1.0 to 0.58 with decreasing temperature from 600 to 350 °C [1]. Below 300 °C, F_2 gas is almost inert to graphite. However, it has been found that fluorine is intercalated into graphite with a small amount of metal fluoride [2]. This type of intercalation compound has an ionic bond between carbon and fluorine, and the graphite layer is still planar, while graphite fluorides have cyclohexane-carbon rings with covalent bonds. In this paper, the discharge characteristics of these fluorine-intercalated graphites are reported.

Experimental

Graphite fluorides and the intercalation compound were prepared from Madagascar natural graphite in F_2 gas of 1 atm at 380 - 600 °C, and at under 300 °C, respectively. The products were analyzed by X-ray diffraction and elemental analysis. The galvanostatic discharge of these compounds was made in 1M $LiClO_4$ -PC solution with Li anodes at 25 or 30 °C. The discharge potential was monitored relative to a Li reference electrode.

Results and discussion

Figure 1 shows the discharge curves of graphite fluorides of different compositions, prepared at different temperatures. Their colors varied from black ($\text{CF}_{0.62}$ prepared at 380°C) to white ($\text{CF}_{1.00}$ prepared at 600°C). The discharge potentials increased with decreasing F/C ratio by 0.4 V, while the capacity decreased inversely. The utilizations of fluorine were 96 - 99%. The galvanostatic polarization curves are shown in Fig. 2, where the discharge potentials are almost the same at low current densities, but the difference in the potentials between $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ reached 0.3 - 0.4 V with increasing current density. As the OCVs are the same for both $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ [3], the overpotential is lower in $(\text{C}_2\text{F})_n$ by the above value. Thus $(\text{C}_2\text{F})_n$ is more easily discharged than $(\text{CF})_n$. Figure 3 shows this more clearly. The electrode made by mixing $(\text{CF})_n$ and $(\text{C}_2\text{F})_n$ gave stepwise discharge potentials, namely, $(\text{C}_2\text{F})_n$ was preferentially discharged, followed by the discharge of $(\text{CF})_n$ (Fig. 3). This was confirmed by the X-ray diffraction analysis of the electrodes discharged to various percentages. The diffraction line corresponding to $(\text{C}_2\text{F})_n$ (9.7° in 2θ by $\text{Cu K}\alpha$) disappeared in the X-ray diagram after 40% discharge, while that for $(\text{CF})_n$ remained unchanged. After 100% discharge, the peak of $(\text{CF})_n$ (15.1° in 2θ by $\text{Cu K}\alpha$) also disappeared. As $(\text{C}_2\text{F})_n$ normally contains $(\text{CF})_n$ as an impurity, the discharge potential of $(\text{C}_2\text{F})_n$ would be inferior in flatness.

The discharge reaction proceeds by intercalation of solvated Li^+ ions into graphite fluoride with the formation of a ternary intercalation compound of lithium fluoride. The Li^+ ion transfer in the diffusion layer would be responsible for the observed overpotential because no activation overpotential was detected by the current interrupter method. The overpotential of $(\text{CF})_n$ decreased with increasing d_{001} and β_{001} of the (001) diffraction line

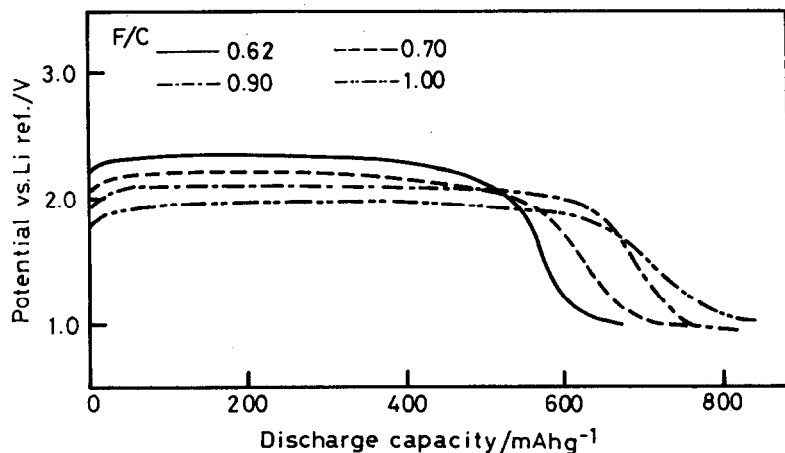


Fig. 1. Galvanostatic discharge curves of graphite fluoride electrodes of various compositions.

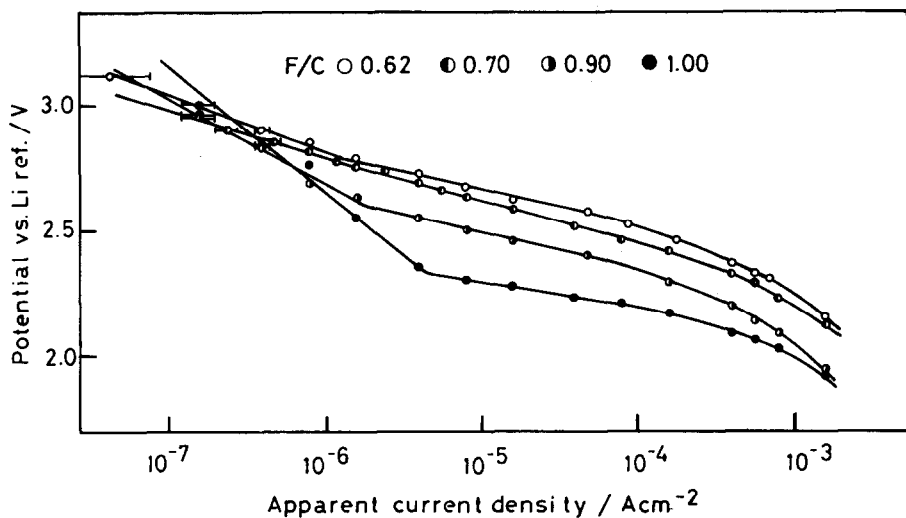


Fig. 2. I - V curves of graphite fluoride electrodes of various compositions.

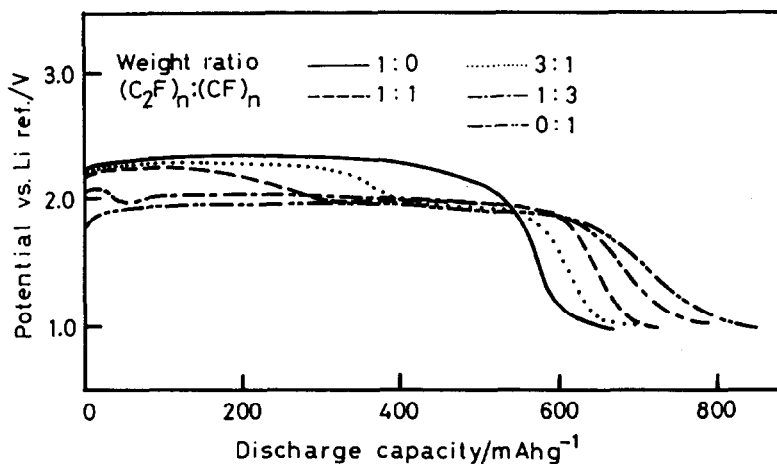


Fig. 3. Galvanostatic discharge curves for mixtures of $(CF)_n$ and $(C_2F)_n$.

of $(CF)_n$. This would be because the increase in the space between the monolayers of $(CF)_n$ and the decrease in the thickness of the crystallite along the c -axis increase the rate of Li^+ ion transfer in the diffusion layer. On the other hand, it is difficult to prepare $(C_2F)_n$ with a large difference in d_{001} and β_{001} since the starting carbon materials and reaction temperatures are limited in this case. From ESR measurements $(C_2F)_n$ was found to contain many defects. When it was treated in F_2 gas at high temperatures, the defects were reduced and the color changed from black to white with

increasing heat treatment temperature. Corresponding to this phenomena, the discharge potential was also decreased, approaching that for $(CF)_n$. The defects in $(C_2F)_n$ would facilitate the decomposition of the ternary intercalation compound and give the short circuiting paths for the transfer of Li^+ ion in the diffusion layer. The higher discharge potential of $(C_2F)_n$, compared with that of $(CF)_n$, is mainly attributed to the effect of the defects contained in $(C_2F)_n$.

The graphite intercalation compound of fluorine and metal fluoride exhibited higher initial OCVs (3.4 - 4.2 V) and discharge potentials (2.8 - 2.5 V at 40 - 400 $\mu A\ cm^{-2}$) than graphite fluorides. The discharge reaction is almost the same as that of graphite fluoride.

References

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