

# Polycarbofluorides for lithium sources of current with nonaqueous electrolyte

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## Introduction

Fluorinated carbon used as a cathode substance in lithium cells with a high and stable discharge potential is of great practical and theoretical importance. Its electrochemical activity has been reported earlier [1–3] to be determined in many respects by the nature of fluorinated substance, degree of fluorination, particle size and crystal lattice parameters. The latter two factors are of paramount importance and can be controlled in technological conditions of fluorination.

We have studied 25 types of fluorocarbon substances which differ both in nature, initial substances and the conditions of fluorination.

## Experimental

The substance obtained was tested as the cathode in cells of graded size 1126 and 2325.

Open-circuit voltages (OCV) of cells with polycarbofluorides under investigation varied from 2.89 to 3.48. The effect of fluorine mass% on open-circuit voltage is shown in Fig. 1 (curve 1).

As is seen on curve 1, the OCV value of the cell decreases with the increase of fluorine concentration in  $(CF_x)_n$ . This phenomenon is explained by the difference in

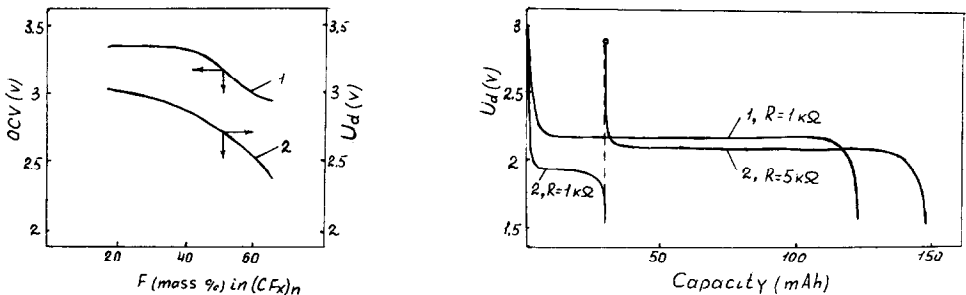


Fig. 1. Effect of fluorine mass concentration (%) in  $(CF_x)_n$  on curve (1): OCV, and curve (2):  $U_d$ .

Fig. 2. Step-by-step discharge of cells 2325 with polycarbofluoride cathodes, curve (1):  $(CF_{0.62})_n$ , and curve (2):  $(CF_{0.84})_n$ ; electrolyte propylene carbonate +  $LiClO_4$ .

structure and the amount of mobile fluorine with a weak bonding in the molecule  $(CF_x)_n$ .

It is of interest to compare the data on curve 1 with the value of the initial discharge cell voltage in discharge by  $R = 5 \text{ k}\Omega$  (curve 2). The data obtained demonstrate that cells with various polycarbofluoride cathodes operate with various excess voltage. With the increase of fluorine concentration in  $(CF_x)_n$  molecule the cathode polarization increases, respectively. The problem is likely to be the more stable covalent F—C bond and the low mobility of fluorine in the  $(CF_x)_n$  structure. As to the degree of fluorination, we differentiate two forms, viz.,  $(CF)_n$  and  $(C_2F)_n$ .

According to ref. 3, F—C bond is less stable in samples of the type  $(C_2F)_n$ . This enables greater mobility and electrochemical activity. Besides these, greater lattice defect density and longer distances between the layers in  $(C_2F)_n$  than those in  $(CF)_n$  enable a better penetration of solvated lithium ion deep into the crystal. In this case, the reduction proceeds with less excess voltage.

Experimental results demonstrate, that cells with polycarbofluoride cathodes similar to  $(C_2F)_n$  are capable of sustaining greater current intensity than those of  $(CF)_n$  structure. It should be noted, however, that the latter have greater capacity. Therefore, one should prefer polycarbofluorides either of this or that form, depending on the application.

Elucidation of this factor is simplified with the help of gradual step-by-step discharge through various resistance (Fig. 2).

## Conclusion

From the foregoing, we may conclude that cells with polycarbofluoride cathode  $(CF_{0.62})_n$  can sustain heavier current intensity than those of the  $(CF_{0.84})_n$  form. The aggregate capacity spent at all the discharge steps is somewhat higher for the second structure than that for the first one. Substance  $(CF_{0.62})_n$  may be used for cell formation with current intensity of  $1 \text{ mA/cm}^2$ . The substance of composition  $(CF_{0.84})_n$  is advisable in low-current cells for a long period of time.

Composite combination of both forms is advisable for the cells of multipurpose use.

Voltamperometry with linear potential scanning was applied for the identification of the reduction mechanism of polycarbofluoride  $(CF_{0.62})_n$  structure. The current of peak polycarbofluoride reduction as a linear function of the square root of potential scanning rate is shown in Fig. 3.

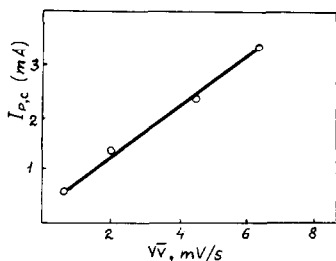


Fig. 3. Dependence of  $I_{p,c}$  on  $\sqrt{v}$  for  $(CF_{0.62})_n$ .

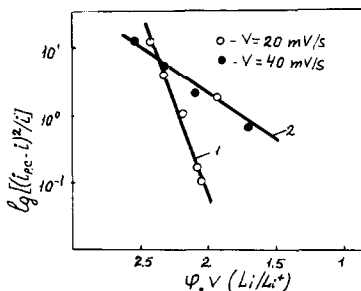
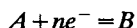


Fig. 4.  $\log[(I_{p,c} - i)/i]$  vs.  $\nu$  for  $(CF_{0.62})_n$ .

According to ref. 4, a linear dependence of  $I_{p,c}$  versus  $\sqrt{\nu}$  is evidence for a reversible process of the electroreduction of  $(CF_{0.62})_n$  via the reaction:



where  $A$  is the oxidized form, and  $B$  the reduced one.

Figure 4 shows the data in coordinates  $\log ((I_{p,c} - i)/i)$  for two scanning rates.

As shown in the graph, the straight line has a lesser slope to the potential axis with the increase of potential scanning rate, and defines the shift of the reversible process towards an irreversible one. Irreversible process can proceed, and the value of current intensity is equal to  $11 \text{ mA/cm}^2$ . The current values mentioned above may be achieved by making a porous cathode with the corresponding structure and selection of the proper electrolyte.

The effect of temperature on discharge characteristics of cells 1126 is shown in the Figs. 5-7. Figures 5-7 show that the effect of temperature on discharge voltage and the spent capacity are dissimilar and depend on the electrolyte.

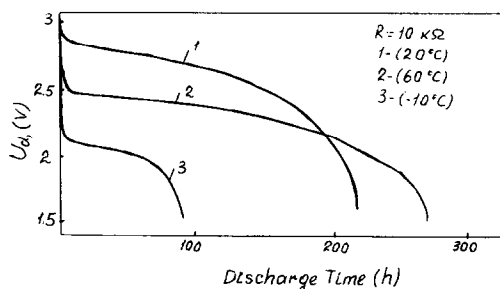


Fig. 5. Discharge curves of cells 1126 at various temperatures; electrolyte: propylene carbonate + dimethoxyethane +  $\text{LiClO}_4$ .

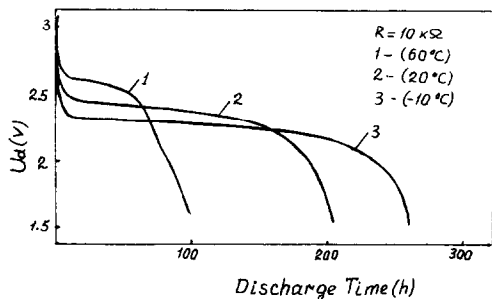


Fig. 6. Discharge curves of cells at various temperatures; electrolyte: propylene carbonate + dimethoxyethane +  $\text{LiBF}_4$ .

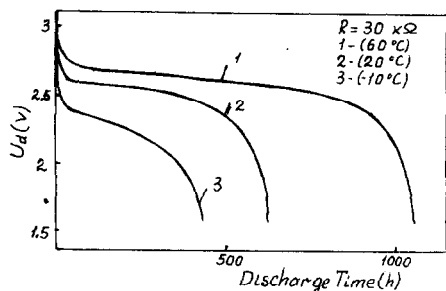


Fig. 7. Discharge curves of cells at various temperatures; electrolyte: propylene carbonate + dimethoxyethane +  $\text{LiCF}_3\text{SO}_3$ .

Perchlorate electrolytes are preferable at room temperature. Deterioration of characteristics at 60 °C is likely to be connected with the higher corrosion activity of lithium.

Tetrafluoroborate electrolytes are preferable at temperature below 0 °C. Electrolytes based on  $\text{LiCF}_3\text{SO}_3$  are promising at higher temperatures.

## References

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