

A STUDY OF POSITIVE ELECTRODE MATERIALS FOR BATTERIES OPERATING IN A HALIDE-ALUMINATE MEDIUM

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Summary

The behaviour of cathodes made of different types of carbon and graphite intercalation compounds was investigated in halide-aluminate media with emphasis on the oxidation and reduction processes of halide compounds. Concerning carbon, it is shown that in chloride medium, the reduction of fixed chlorine proceeds via two steps corresponding probably to two different bond energies (intercalated chlorine and adsorbed chlorine).

In mixed bromide-chloride medium, a single reduction wave was observed characterized by a very flat plateau at 1.65 V *vs.* Al/(Al³⁺).

The behaviour of several intercalated halide compounds has been investigated; the reduction of the transition metal ion and of excess chlorine was observed. Mass capacities of the order of 80 mAh/g were found. In every case, however, a degradation of the compound was observed during charge-discharge cycling due to leaching out of the intercalated halides. The compounds are, therefore, unsuitable for use as cathodes in secondary batteries where long cycle life is required, but they may have applications in special types of primary battery.

Résumé

Le comportement de cathodes constituées soit par différents carbones, soit par des composés d'insertion du graphite, a été étudié en milieu halogéno-aluminate en ce qui concerne les processus d'oxydation et de réduction des composés halogénés. En ce qui concerne les carbones, on a montré qu'en milieu chlorure, la réduction du chlore fixé sur les carbones s'effectue en deux étapes correspondant à vraisemblablement deux énergies de liaison différentes (Cl inséré et Cl adsorbé). En milieu mixte chlorures-bromures, on n'observe sur les graphites qu'une seule vague de réduction caractérisée par un palier très horizontal situé à un potentiel de 1.65 V par rapport à l'échange Al/(Al³⁺). Le comportement de plusieurs composés halogénés d'insertion du graphite a été étudié; on met en évidence la réduction de l'ion métallique de

transition et celle du chlore excédentaire, des capacités massiques de l'ordre de 80 mAh/g ont été trouvées. Cependant, dans tous les cas, on observe une dégradation du composé au cours des cycles de charge-décharge due au passage en solution des halogénures insérés. Par conséquent, ces composés sont inutilisables en tant que cathodes d'accumulateurs où une grande durée de vie est indispensable mais peuvent trouver des applications dans certains types de piles.

Introduction

In recent years much research work has been carried out on high temperature electrochemical systems with the aim of achieving batteries with high specific mass energies. Most successful systems, primary and secondary, operate in the temperature range 400 to 600 °C. Such high temperatures result in certain obvious disadvantages and our investigations have been directed at ways of avoiding some of these. As early as 1973 [1] we found that a suitable system would feature an operating temperature of less than 150 °C, if possible, and an electrochemical cell generating an e.m.f. of more than 2 V. To date, electrolytes composed of a mixture of halide-aluminates seem to be the most likely answer to these requirements since, unlike solid and organic electrolytes, they have a high conductivity. With this option, the material for the negative electrode must be chosen from metals such as Al or Ti, and the positive electrodes from substrates for halogen electrodes of the first kind, or compounds for electrodes of the second kind. These systems are in fact able to function at a temperature below 200 °C due to the relatively low melting point of chloro-aluminates. (The eutectic of the AlCl_3 -NaCl mixture is situated at 110 °C, and that of the AlBr_3 -NaBr mixture at 90 °C.) Moreover, their energy properties are high (for the Al- Cl_2 cell, theoretical mass energy of 1370 Wh/kg and theoretical OCV of 2.1 V) and the reagents are plentiful and cheap [2]. For all these reasons, several research teams have studied this type of storage battery in recent years [3 - 6]. Giner and Holleck studied a primary battery in conjunction with a chlorine storage tank. The work of Seegmiller and colleagues has mainly contributed to our knowledge on chloro-aluminate electrolytes as well as on MoCl_5 based electrodes.

Our research work has been devoted to developing an electrode that does not depend on any evolution of halogen. This is necessary since most applications prohibit any recourse to a chlorine storage tank in order to respect battery safety standards.

This paper will only deal with results obtained in an investigation on the suitability of graphite and certain of its intercalation compounds as materials for positive electrodes.

Suitability of graphite and graphite compounds as an electrode material

Most metals (apart from W and Mo) are subject to severe corrosion in chloro-aluminate media [7]. Graphite was therefore recommended as a material for the positive electrodes. Generally graphite is chosen on the grounds of its properties with respect to the evolution and reduction of chlorine gas. In our case, we have studied the retention properties of chlorine on carbon electrodes while avoiding the release of chlorine gas. Graphite is stable in halide-aluminate media and can attach variable quantities of halogen depending on its structure and the nature of the halogen. Intercalation compounds formed with chlorine are only stable at low temperature ($T \cong -70^\circ\text{C}$). Above normal temperature, only residual chlorine remains fixed to the lattice defects or to the surface. On the contrary, bromine intercalation compounds are stable at normal temperature and the most saturated, C_8Br , gives a mass capacity of 280 mAh per gram of graphite. Despite energy properties that are less than those of the Al- Cl_2 cell (530 Wh/kg; OCV 1.75 V), this system seems more promising because of its stability. Graphite intercalation compounds have been thoroughly investigated [8] but their electrochemical application is recent [9, 10]. Electrochemical research on halogen electrodes has been mainly of a technological nature, and fundamental data on the $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ exchange on a carbon electrode are not yet available. However, a thorough investigation of this mechanism is essential to understand the behaviour of the intercalated compounds. A variety of intercalated metal chlorides have been used as electrodes. The initial idea is that the metal chloride will not only participate in the electrochemical reaction through its redox system, but will also separate the graphite planes, thereby increasing the halogen storage capacity by acting on both the intercalation rate and the number of available sites. Moreover, halogens form ternary intercalation compounds with the metal halides, especially AlCl_3 and FeCl_3 [11].

Experimental

The measurement cell, which was isolated from the atmosphere, was made from Teflon (Fig. 1). The auxiliary electrode and the reference electrode were of aluminium. The working electrode was composed of 50 mg of the test powder, pressed between a molybdenum collector and a porous Teflon disc. Its apparent surface area was 1 cm^2 . The cell was heated in a crucible furnace, the temperature of which was regulated by a thermocouple. The temperature of the bath was controlled locally by a thermometer ($\pm 1^\circ\text{C}$). The alkali salts were dried out at high temperature. Prolabo 99.99% purity aluminium chloride was used to give a bath with a low impurity content. For experiments in a chloride medium the electrolyte was composed of a binary mixture AlCl_3 (60%) and NaCl (40%) for a temperature above 110°C , and a ternary mixture AlCl_3 (60%) NaCl (20%) KCl (20%) for a temperature of 110°C . In a bromide medium, where the melting points are lower, a NaBr

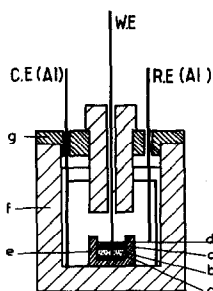


Fig. 1. Test battery schematic drawing. a, Mo collector; b, active powder; c, glass wool; d, perforated Teflon sheet; e, f, g, Teflon vessel.

(40%) AlBr_3 (60%) mixture was usable at 110°C (eutectic at about 90°C). Mixed media with variable alkali bromide contents were used above 110°C : AlCl_3 (60%) NaBr or KBr ($x\%$) NaCl [$(20 - x)\%$], where $x = 10, 20, 30$. Experiments were carried out at constant current using a potentiostat. In the first stage the current was generally 10 mA. During the first part of the charge, the potential varied very little; at the end of the charge it suddenly increased to values that were more anodic corresponding to the evolution of chlorine. To analyze the reduction process, a charge at least equal to the maximum capacity that can be recovered in reduction, was carried out. The curves characterizing the reduction kinetics were obtained by polarising the electrodes as cathodes with a 3 mA current.

Behaviour of carbon electrodes

Influence of the carbon structure

The experiments were carried out on purified Ceylon graphite (Carbone Lorraine 9900), graphites with a high specific surface area ($165\text{ m}^2/\text{g}$ and $295\text{ m}^2/\text{g}$), BP 70 ($550\text{ m}^2/\text{g}$), Ketjen black ($1000\text{ m}^2/\text{g}$) and carbon blacks with different surface areas: BP 800 ($250\text{ m}^2/\text{g}$), Vulcan P ($150\text{ m}^2/\text{g}$), annealed at very high temperature and consequently well graphitized. At 140°C in a chloride medium, the potential after charging all the samples was 2.1 V. On the graphites and the Ketjen black, the discharge curves show two domains (Fig. 2); the first, corresponding to the most anodic potentials, seems to be the same for all the samples and corresponds to a capacity of about 30 mAh/g; the second, corresponding to more cathodic potentials, was larger the greater the specific surface area. However, when the capacity of graphite with a $295\text{ m}^2/\text{g}$ surface area is compared with that of carbon black BP 800, assuming that the chlorine has been adsorbed, there should be a difference between the two of some 20%. In fact, there is a difference of a factor of 8. So, specific surface does not define adsorption but is associated with the variation of another parameter, such as the ratio of internal and surface defects, characterizing the carbon materials. Under these conditions, the chlorine can be assumed to be attached in two forms: at the most anodic potentials, in a weak bond form

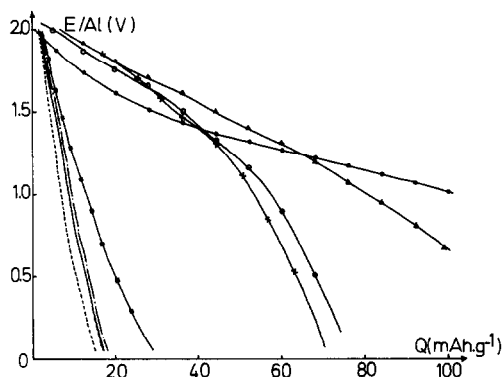


Fig. 2. Discharge curves of different carbons in NaCl-AlCl_3 electrolyte at 140°C . - - -, Vulcan P; —, BP 800; - . -, BP 70; —■—, BP 800 (2700 under Ar); —○—, purified Ceylon graphite; —×—, graphite $165\text{ m}^2/\text{g}$; —▲—, graphite $295\text{ m}^2/\text{g}$; —●—, graphite Ketjen black.

corresponding to both inserted chlorine and Cl_2 adsorbed in the bulk of the material; at the more cathodic potentials, in a stronger bond form. Two suggestions can be put forward concerning the type of bond. The first is that the number of sites is probably greater the greater the number of internal structural defects, this defect density being itself related to the specific surface area; in this case there could be intercalated chlorine. The second that there is a strong adsorption on surface defects such as plane edge atoms.

Influence of the electrolyte

Ceylon graphite was studied in electrolytes of different compositions. In a chloride medium, at 170°C , two waves were seen, probably corresponding to two chlorine bond states (Fig. 3). At lower temperature these waves were no longer visible. On the other hand, in bromide medium, a single well-defined plateau was distinguished at a height depending on temperature. At

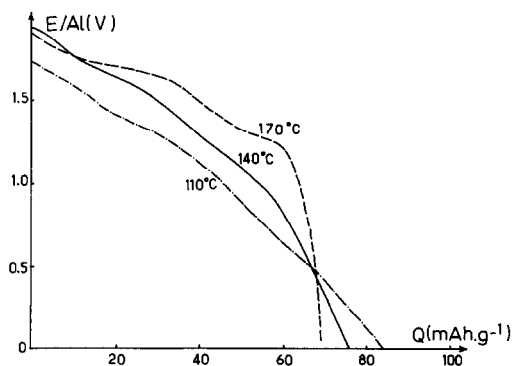


Fig. 3. Discharge curves of purified Ceylon graphite in NaCl-AlCl_3 electrolyte at 110, 140 and 170°C .

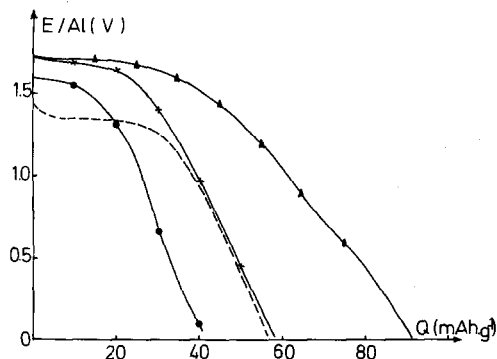
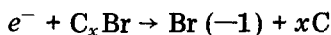
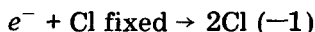


Fig. 4. Discharge curves of purified Ceylon graphite in various electrolytes at 110 °C. ---, NaBr (35%)–AlBr₃ (65%); —●—, NaBr (20%)–KBr (20%)–AlCl₃ (60%); —×—, NaBr (20%)–NaCl (20%)–AlCl₃ (60%); —▲—, NaBr (10%)–NaCl (30%)–AlCl₃ (60%).

110 °C, in a purely bromide medium, this plateau was at 1.3 V (Fig. 4). For mixed media, with variable alkali bromide content (10%, 20% and 40% KBr), the plateau was at 1.65 V. The existence of these plateaus suggests that there is a well-defined intercalation compound. Under these conditions, in a mixed medium, it could be a bromochloride inserted compound, BrCl, with a redox potential situated between the characteristic exchange potentials:



When the bromine content was decreased, there was an increase in capacity corresponding to the intercalation of BrCl (60 mAh/g for 20% Br, and 90 mAh/g for 10% Br). This result can be explained by the existence of an optimum Cl/Br ratio, such that, for a given current, the oxidation rate for bromide and chloride is the same. For higher bromide contents an intercalated compound of Br₂ and BrCl was formed (for 40% NaBr there was in fact an intermediate plateau between 1.3 V and 1.65 V). For steric reasons, BrCl is probably more easily intercalated than Br₂, so that the intercalation observed in this case was lower than that obtained for lower Br contents. When the temperature was increased the stability of the bromine intercalated compounds decreased and at 140 °C the capacity obtained in a bromide medium was negligible. However, even at 110 °C, the capacity was much less than that corresponding to C₁₂Br, which is considered stable up to 120 °C (that is, 187 mAh/g).

Study of graphite insertion compounds

Electrochemical behaviour and interpretations

With intercalation compounds, the redox system of the intercalated molecule contributes to the charge–discharge reactions. In addition, the con-

ditions are apparently suitable for an increase in the amount of intercalated chlorine (stabilization of chlorine in a ternary intercalation compound, and higher intercalation rates due to the separation of the planes). The compounds investigated were lamellar; the intercalated molecules were metal chlorides (FeCl_3 , SbCl_5 , CrCl_3 , AlCl_3 , CuCl_2 , NiCl_2 , HgCl_2 , MoCl_5 , TaCl_5) or metal fluorides (TiF_4 and SbF_5).

The formulae were determined by gravimetry, assuming that the intercalated cation had its maximum valency. However, this assumption must be treated with circumspection since much of the experimental data furnish evidence to the contrary, in particular for MoCl_5 . Determinations carried out by microanalysis on various compounds of the C_xMoCl_5 type (gravimetric formula) lead to the conclusion that the majority of the halide was not intercalated in the form of MoCl_5 but in the form of a mixture of MoCl_5 , MoCl_4 and MoCl_3 . Moreover, the considerable difference observed between the value of the reduction plateaus of the compounds that were subjected to electroreduction directly after a preliminary anodic charge, tends to corroborate the fact that for MoCl_x as for FeCl_x , there was only a low content of intercalation compound in the form of MoCl_5 or FeCl_3 . We have therefore every reason to believe that traditional determinations of the constituent elements by gravimetry or by chemical microanalysis are frequently inadequate. For instance, for C_xMoCl_5 these traditional methods may give formulae of the type $\text{C}_{13}\text{MoCl}_4$. Yet the Debye-Sherrer X-ray diagrams for the same compound indicate a 5th order, that is a formula of the type $\text{C}_{64}\text{MoCl}_4$. Figures 5 and 6 show the change in potential of several compounds during constant current reduction (3 mA) after a charge of 166 mA corresponding to a quantity of electricity at least equal to saturation of the compound (beginning of evolution of chlorine gas). In order to analyze the electrochemical properties of these compounds more thoroughly it is convenient to class them in 3 families.

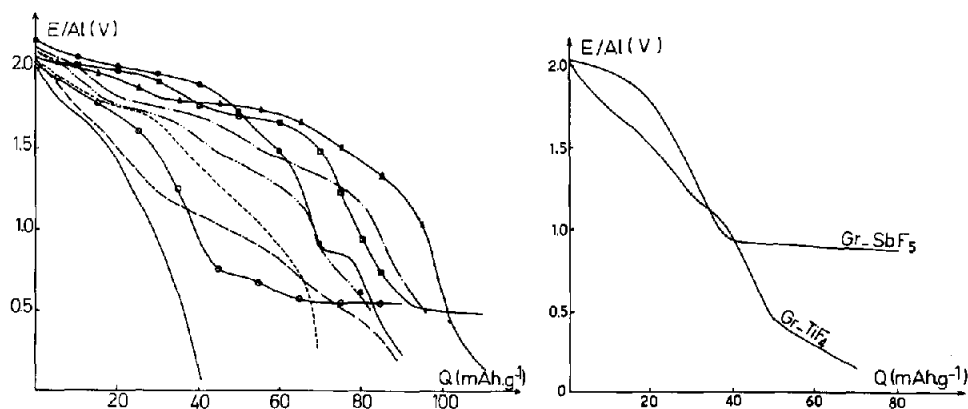


Fig. 5. Discharge curves of various intercalated chlorides in NaCl-AlCl_3 electrolyte at 140°C . —▲—, $\text{C}_{27}\text{MoCl}_5$; —□—, $\text{C}_{7.4}\text{FeCl}_3$; —●—, $\text{C}_{24}\text{SbCl}_5$; —○—, $\text{C}_{25}\text{TaCl}_5$; —·—, $\text{C}_{207}\text{NiCl}_2$; —·—, $\text{C}_{67}\text{WCl}_6$; —·—, $\text{C}_{20}\text{HgCl}_2$; —·—, $\text{C}_{29}\text{CrCl}_3$; ———, $\text{C}_{9.4}\text{AlCl}_3$.

Fig. 6. Discharge curves of intercalated fluorides in NaCl-AlCl_3 electrolyte at 140°C .

Compounds with very low intercalation content

Theoretically the redox system has little influence on the measured capacity. For instance, for the nickel compound the total capacity for the reduction of NiCl_2 would be about 20 mAh/g. We should expect, then, that the behaviour of these compounds would be very similar to that of graphite studied under the same conditions. From Fig. 7 we see that total capacity was effectively only slightly higher than that of graphite, but on the other hand the appearance of the curve that corresponds in the main to the reduction of the chlorine, is very different from the curve for graphite at 140 °C and very similar to the graphite curve at 170 °C. It would in fact appear that a very low intercalation content increases the rate of the reduction steps of the intercalated chlorine. This kinetic effect may be due either, to a change in the spacing of the layers that outcrop at the grain boundaries, or indirectly to surface activation during treatment of the compound. In practice, it is therefore possible to have available at lower temperature, the capacity corresponding to the reduction of chlorine in a more anodic potential domain.

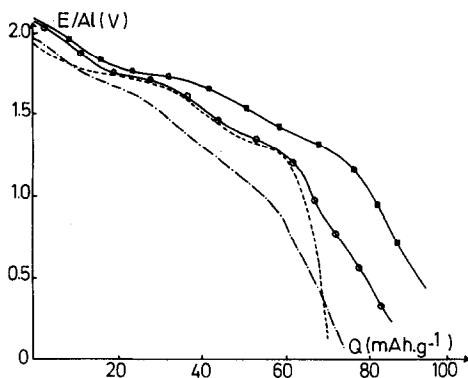


Fig. 7. Discharge curves of intercalated chloride with very low content in $\text{NaCl}-\text{AlCl}_3$ electrolyte. —, purified Ceylon graphite at 140 °C; - - -, purified Ceylon graphite at 170 °C; —○—, $\text{C}_{67}\text{WCl}_6$; —□—, $\text{C}_{207}\text{NiCl}_2$.

Compounds with an intermediate intercalation content

The typical example is that of MoCl_5 where between 2 V and 1.75 V a wave was observed corresponding to the reduction of the chlorine. Experiments carried out on MoCl_5 dissolved in the electrolyte (the electrode was vitreous carbon) showed that when the reduction of MoCl_5 to MoCl_3 takes place, a reduction wave of between 1.75 and 0.75 V was produced. As the binding energies of this intercalation compound are very weak, it is probable that the equilibrium potential of the intercalated redox system is not very different from that of the dissolved system. The reduction states around 1.9 V must therefore be attributed to the reduction of chlorine which was found to take place at a higher rate than on pure graphite, producing a pseudo-plateau. We note that the capacity corresponding to the wave between 1.75

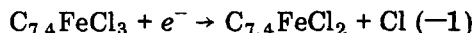
and 0.75 V (that is about 50 mAh/g) is in good agreement with the reduction of the compound $C_{60}MoCl_5$:



Compounds with high intercalation content

For $C_{9.4}AlCl_3$, the capacity found was that of the chlorine intercalated on the graphite, since the $AlCl_3$ system cannot be reduced. The chlorine reduction kinetics appeared unchanged.

For $FeCl_3$, experiments carried out on $FeCl_3$ dissolved in the electrolyte and reduced on a vitreous carbon electrode, showed that the reduction $FeCl_3 \rightarrow FeCl_2$ may occur at 2 V and continue to 0.7 V. Under these conditions we can reasonably attribute the whole of the curve found from 2 V to 0.75 V to the reduction:



The presence of a first plateau at potentials between 2 and 1.3 V is explained by the fact that during this first polarization step the intercalated chlorine is reduced at the same time as Fe^{3+} . When the chlorine content decreased, the current was mainly applied to the reduction of Fe^{3+} . However, whereas the total capacity of the compound was of the order 85 mAh/g, when the capacity corresponding to the reduction of the chlorine is subtracted, the reduction $Fe^{3+} \rightarrow Fe^{2+}$ would only leave 65 mAh/g, corresponding to a formula of the order $C_{20}FeCl_3$. However, the preparation of this compound gave a formula $C_{7.4}FeCl_3$. So we see that during the earlier period when it was in contact with the electrolyte (initial reduction then anodic charge) part of the $FeCl_3$ originally intercalated has left the lattice and dissolved in the electrolyte. This phenomenon was clearly evident in the cycling tests described later.

The possibilities of using intercalation compounds as cathodes in chloro-aluminate media

Comparison of the characteristics of the 1st discharge curves

These curves are shown in Fig. 5. For the various compounds investigated, we observed: (i) the "useful" specific mass capacity, *i.e.* limited to potentials that are more anodic than 1.2 V; (ii) the mean potential of the plateaus or pseudo-plateaus.

We see that the best values for specific mass capacities were given by $C_{60}MoCl_5$, $C_{207}NiCl_2$ and $C_{20}FeCl_3$. For compounds of the type $C_{67}WCl_6$, $C_{24}SbCl_5$, the capacity was of the order 70 mAh/g. All the other compounds gave lower values. The best results for mean plateau potential were given by $C_{60}MoCl_5$, $C_{20}FeCl_3$, and $C_{24}SbCl_5$. The other compounds gave no well-defined plateau.

Suitability of the compounds for battery applications

For secondary battery use cathode materials must be stable for long periods under charge-discharge conditions. Of the two compounds with best

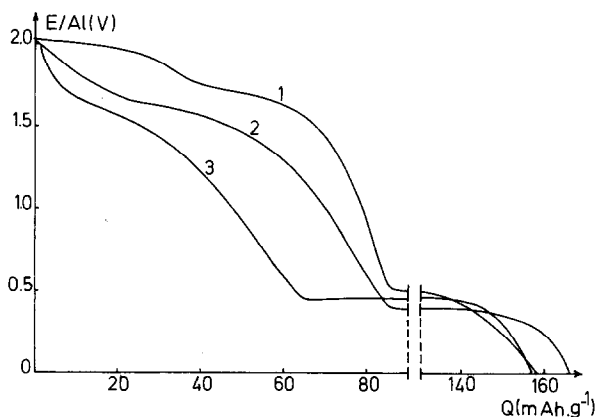


Fig. 8. Evolution of the $C_{7.4}FeCl_3$ discharge curve during cycling ($NaCl-AlCl_3$ electrolyte at $140^\circ C$.)

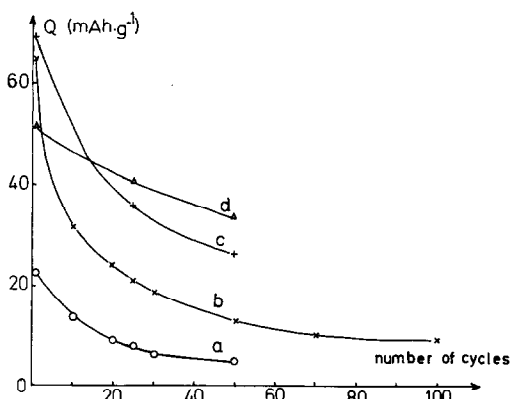


Fig. 9. Mass capacity of $C_{14.2}MoCl_{3.9}$ in $NaCl-AlCl_3$ electrolyte as a function of cycle number. a, $T = 140^\circ C$; end of discharge: 1.75 V; b, $T = 140^\circ C$; end of discharge: 1.60 V; c, $T = 140^\circ C$; end of discharge: 1.20 V; d, $T = 120^\circ C$; end of discharge: 1.60 V.

mass energies and potential, $FeCl_3$ is very soluble in chloro-aluminates. The change in the discharge curve for the iron compound at $110^\circ C$ over the first three cycles is shown in Fig. 8. A considerable deterioration was also observed at the same temperature for $MoCl_5$ which is less soluble. The capacity also decreased noticeably over less than 100 cycles, whatever the temperature and degree of discharge (Fig. 9). The performance of these compounds is therefore inadequate for them to be considered for use as cathode materials in secondary batteries where the requirement is for reasonable stability over at least 500 cycles.

In the case of primary batteries long storage life is frequently of great importance, and since these compounds are inactive until the electrolyte becomes molten, at temperatures in excess of $90^\circ C$, their use should result in batteries with good storage characteristics. The fact that they have to be heated to be activated limits their use to special applications, e.g. thermal

and fuse batteries. In such applications, discharge times usually range from a few minutes to one or two hours and so long term stability in the active state is not required. Therefore these compounds should be suitable for this type of cell, some support for this view may be drawn from the fact that FeCl_3 and MoCl_5 have already been successfully used in some types of thermal cell [12].

Conclusions

The present work has shown that a significant capacity can be obtained with graphites in a chloride-aluminate melt. This capacity is related to the reduction of chlorine and is therefore highly dependent on the structure of the graphite.

On graphites in a medium containing alkali bromides to the extent of about 20%, a mixed chlorine-bromine intercalation compound is formed which is reduced at 1.65 V.

On intercalation compounds, even with low intercalation content, the chlorine intercalation kinetics are altered.

Caution must be exercised in applying basic formulae, particularly in the case of MoCl_5 which is intercalated in the form of a mixture of MoCl_5 , MoCl_4 and MoCl_3 .

For a number of compounds capacities of 100 mAh/g can be obtained from both the chlorine and the redox systems. From the point of view of practical applications, none of the intercalated compounds have sufficient long term stability in chloro-aluminate melts, even at 110 °C, for them to be suitable for use as cathode materials in secondary cells. However, they have possible applications in thermally activated primary cells.

Acknowledgement

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