

ELECTROCHEMICAL BEHAVIOUR OF NEW CATHODIC MATERIALS USABLE IN LITHIUM BATTERIES: $\text{AgBi}(\text{CrO}_4)_2$ AND $\text{Bi}_2\text{O}(\text{CrO}_4)_2$

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Resumé

Le comportement électrochimique de deux nouveaux chromates $\text{AgBi}(\text{CrO}_4)_2$ et $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ a été étudié sur électrodes minces dans le carbonate de propylène par rapport à une électrode de lithium. La réduction de ces deux matériaux se produit en deux phases principales, la seconde étant partiellement réversible, spécialement dans le cas de $\text{AgBi}(\text{CrO}_4)_2$. Dans ce dernier composé, la réduction de l'argent intervient dans la première phase au potentiel où le chrome est partiellement réduit. L'énergie volumique importante obtenue avec ce matériau, associé au lithium, ainsi qu'une très bonne stabilité des composants, permet de réaliser avec ce couple un générateur électrochimique de haute densité d'énergie et de longue durée de vie.

Summary

An examination of the electrochemical behaviour of two new chromates, $\text{AgBi}(\text{CrO}_4)_2$, and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, has been investigated with experimental thin electrodes in PC 1M LiClO_4 , vs. the lithium electrode. The reduction of these two compounds occurs in two main steps, the second one being partially reversible, especially in the case of $\text{AgBi}(\text{CrO}_4)_2$. Silver reduction takes place for this material in the same voltage range as the first chromium reduction step. The energy density obtained with $\text{AgBi}(\text{CrO}_4)_2$ associated with the lithium anode and the very good stability of the components, makes this electrochemical couple a good system for a high energy density cell with long life applications.

1. Introduction

The prime role of the chromate ions in the discharge mechanism of the Li-Ag₂CrO₄ battery system has already been noted during the study of the electrochemical reduction of Ag₂CrO₄ [1, 2]. It has been shown that the electrochemical reduction of this compound occurs at a relatively high drain when Cr(VI) reduction is involved. During the discharge, the reduction of Ag(I) is then catalysed by the intermediate formation of Cr(V). After Ag(I) reduction, Cr(VI) leads, at the end of the discharge, to the formation of Cr(IV).

Following this study, other metallic chromates have been tested. Among these compounds, AgBi(CrO₄)₂ has engaged our attention, since the presence of silver and chromate ions should lead to an electrochemical behaviour similar to that of Ag₂CrO₄. In order to specify the role of Bi(III) during the discharge of this new cathodic material [3], we have also undertaken the synthesis and study of another cathodic material, the bismuth oxochromate: Bi₂O(CrO₄)₂ [4].

2. Experimental

2.1. Electrochemical study

The electrochemical study was carried out with "membrane" electrodes, which are models of those used in lithium batteries. Their area is 1 cm² and their thickness between 0.2 and 0.3 mm. Small quantities of active material (about 5 mg) are mixed with 90% of graphite (Koch-Light), of purity 99.99%. The method of preparation of these electrodes consists of pressing the mixture on a stainless steel grid.

The electrolyte used is propylene carbonate 1M LiClO₄. The experimental equipment allows the use of a small quantity of electrolyte (less than 5 ml). The electrode faces a lithium "counter electrode" and the potentials are measured *vs.* a lithium reference electrode, Li/LiClO₄ 1M in PC, *via* a capillary close to the working electrode.

The usual electrochemical methods such as cyclic voltammetry and zero current potentiometry were used in this work.

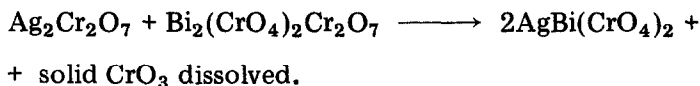
The results obtained with experimental electrodes of AgBi(CrO₄)₂ were compared with those obtained with lithium button cells using the same cathodic material and electrolyte: the cathode was obtained by pelleting a mixture of AgBi(CrO₄)₂ (95% by weight) and graphite (5% by weight). The outside diameter of the cell was 21 mm and its thickness 9 mm, representing a volume of 3.12 cm³. The theoretical capacity of this prototype was 850 mA h.

2.2. Preparation of AgBi(CrO₄)₂

The synthesis of AgBi(CrO₄)₂ has been described in detail previously [5] where a structure analysis of this chromate is also described. The first step consists of the precipitation of the compound Bi₂(CrO₄)₂Cr₂O₇ by

the addition of solid bismuth nitrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, to an aqueous solution saturated with CrO_3 at 20 °C.

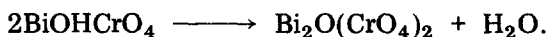
In the second step, $\text{Bi}_2(\text{CrO}_4)_2\text{Cr}_2\text{O}_7$ was allowed to react with silver bichromate in aqueous medium:



2.3. Preparation of bismuth oxychromate

Hydroxochromate of bismuth, BiOHCrO_4 , is well known and is easily prepared by the addition of a soluble bismuth salt, for example, the nitrate, to an aqueous solution of CrO_3 . Two allotropic forms exist, the structures of which have been determined [6].

The thermolysis of BiOHCrO_4 was carried out in oxygen at atmospheric pressure, at a heating rate of 300 °C per hour (Fig. 1). A first plateau distinctly appears between 320 and 500 °C. The observed loss of mass: 2.53%, is in accordance with the calculated value: 2.63%, for the dehydration reaction:



This loss of mass occurs without modification of the degree of chromium oxidation which remains equal to six. The compound obtained gives a specific Debye-Scherrer diagram, which is rather complex. It was not possible to specify the crystallographic characteristics of this compound because of the inability to prepare monocrystals: the proposed method of preparation always leads to a powder. Furthermore, heating above 500 °C results in a decrease in the degree of oxidation of chromium without any fusion.

Chemical literature at the turn of the century mentions the formulae of bismuth chromates Bi_2O_3 , 2CrO_3 or $(\text{BiO})_2\text{Cr}_2\text{O}_4$, the stoichiometry of which is, indeed, $\text{Bi}_2\text{Cr}_2\text{O}_9$ [7].

The possibility of obtaining $\text{Bi}_2\text{Cr}_2\text{O}_9$ from BiOHCrO_4 , where separate CrO_4 tetrahedrons exist, suggests that these tetrahedrons remain after dehydration, and that $\text{Bi}_2\text{Cr}_2\text{O}_9$ is an oxychromate of bismuth, $\text{Bi}_2\text{O}(\text{CrO}_4)_2$.

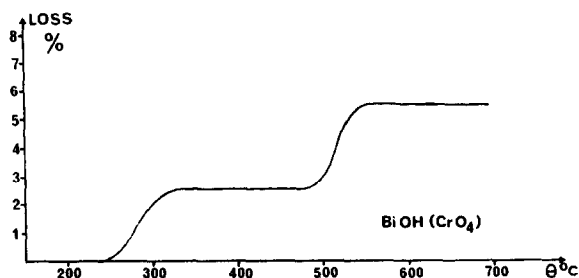


Fig. 1. Thermolysis of BiOHCrO_4 .

3. Electrochemical study with model electrodes

3.1. Discharge characteristics

The elements which can be reduced in $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ are Ag(I), Cr(VI), Bi(III). Figure 2(a) and (b) shows the reduction curves, at several constant currents, of $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, respectively, at 60°C . The discharges of these two cathodic materials behave nearly identically, beginning at about 3.1 V and then carrying on into a step of decreasing potential between 3 and 2 V. In the case of $\text{AgBi}(\text{CrO}_4)_2$, the reduction process which occurs at 3.1 V for low drains, is broken down into two separate plateaux, when the current density increases. In this case, the capacity involved on the first step never exceeds 1 F/mole of $\text{AgBi}(\text{CrO}_4)_2$.

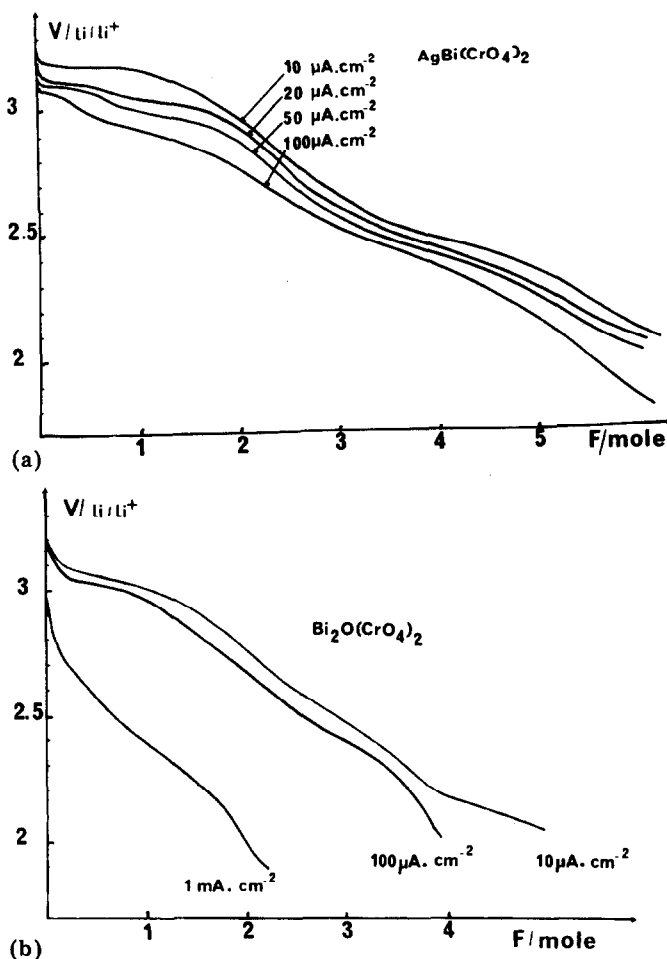


Fig. 2. Discharge curves of electrodes, at 60°C , for several current drains. (a) $\text{AgBi}(\text{CrO}_4)_2$; (b) $\text{Bi}_2\text{O}(\text{CrO}_4)_2$.

For a reduction of these compounds to a cut off voltage of 2, the amount of metallic bismuth formed represents less than 1% of the Bi(III) initially present in the electrode. This result shows that the electrochemical reduction of Bi(III) is not involved in this voltage range. It has been demonstrated previously that, for Bi_2O_3 [8] and even for mixed bismuth-lead oxides [9], the reduction of Bi(III) only occurs in the 1.5 V range. In addition, metallic silver is characterized at the beginning of discharge, for silver-bismuth chromate.

The overall faradaic efficiencies obtained are in accordance with a reduction of Ag(I) to Ag(0), and a decrease of the mean degree of oxidation of chromium from 6 to 4, as is the case for silver chromate.

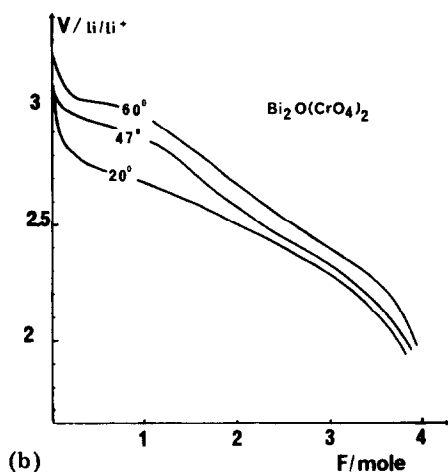
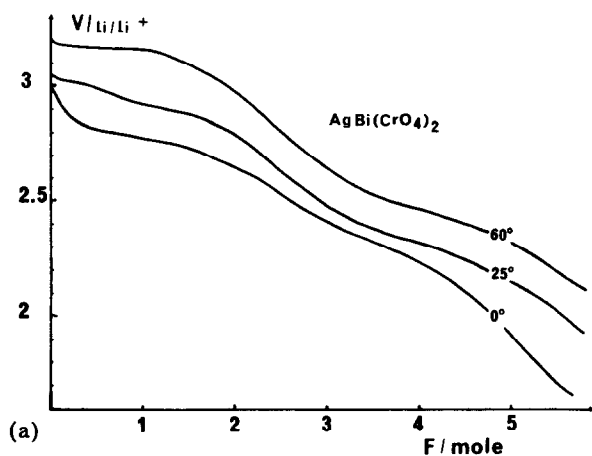


Fig. 3. Discharge curves of electrodes at several temperatures. (a) $\text{AgBi}(\text{CrO}_4)_2$, $10 \mu\text{A cm}^{-2}$; (b) $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, $100 \mu\text{A cm}^{-2}$.

On comparison of the discharge curves, Fig. 2(a) and (b), it can be seen that the reduction of silver and a part of the chromium in $\text{AgBi}(\text{CrO}_4)_2$ occurs simultaneously in the first, nearly flat plateau, since the capacity so obtained, from low drain, corresponds to more than twice the capacity of the silver alone. This compound differs noticeably from Ag_2CrO_4 , of which the well defined first flat plateau is due to silver reduction only [1, 2]. At a higher drain, it seems that two processes can be distinguished. In this case, the first step should correspond to silver reduction (1 F/mole).

In Fig. 3(a) and (b) the discharge curves at constant current and several temperatures are shown. The same observations were made, and it will be noted that the polarisation effect is more pronounced on the first plateau than on the second, sloped step.

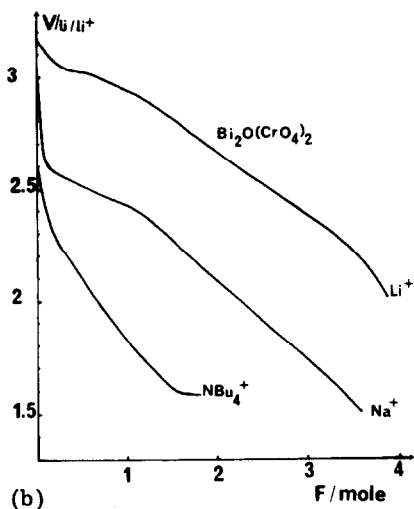
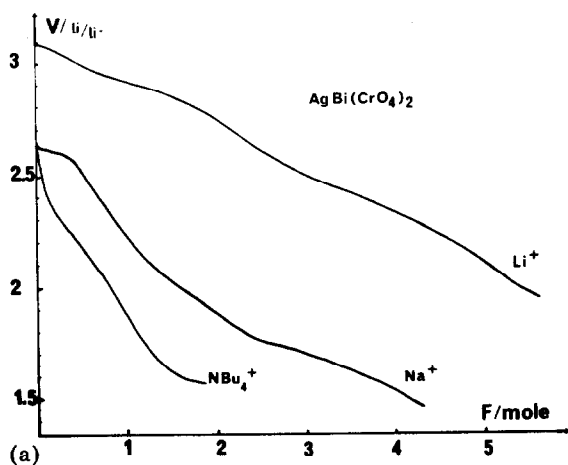


Fig. 4. Influence of the electrolyte MClO_4 ($\text{M} = \text{Li}^+$, Na^+ and $n\text{NBu}_4^+$) on the reduction curves at 60°C . (a) $\text{AgBi}(\text{CrO}_4)_2$, $10 \mu\text{A cm}^{-2}$; (b) $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, $100 \mu\text{A cm}^{-2}$.

We have established that the rates of electrochemical reduction of $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ are considerably reduced by the substitution of Li^+ ions by other, bigger cations (Fig. 4(a) and (b)); this result, also obtained during the study of Ag_2CrO_4 [1, 2] or other cathodic materials [10, 11], shows that the primary process in the reaction is an insertion of Li^+ ions into the crystal lattices.

3.2. Cyclic voltammetry

The cyclic voltammetry experiments (Fig. 5) allowed us to find the same electrochemical processes as those experienced during the potentiostatic study. One can observe for $\text{AgBi}(\text{CrO}_4)_2$ an initial additional wave, at about 3.1 V, which can be due to $\text{Ag}(\text{I})$ reduction. The first and second steps of $\text{Cr}(\text{VI})$ reduction occurred in the same voltage range for the two materials.

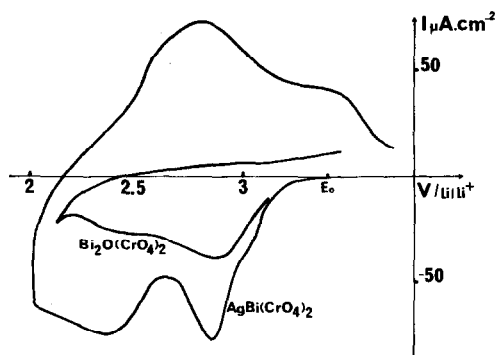


Fig. 5. Cyclic voltammetry on $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$, vs. Li/Li^+ electrode, at 60°C , 6 mV min^{-1} .

When the cathodic sweep is limited to about 2 V, the consecutive anodic sweep shows that the reversibility of the electrochemical process occurring in the reduction of $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ is less important than that of $\text{AgBi}(\text{CrO}_4)_2$.

The reoxidation of $\text{AgBi}(\text{CrO}_4)_2$, previously reduced up to 3 V or 2.8 V (Fig. 6(a)), gives only one small anodic wave between 3.4 and 3.5 V, corresponding to the oxidation of the silver produced.

In contrast to the first reduction process of $\text{AgBi}(\text{CrO}_4)_2$, the second step, occurring between 2.5 and 2 V, is almost reversible. This result suggests that, during the primary phase of reduction, a compound is formed with a particular structure which is thereafter able to insert Li^+ ions in a reversible way.

In the case of $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ (Fig. 6(b)), this insertion of Li^+ ions after partial reduction of the material only appears almost reversible when the sweep rate is increased (60 instead of 6 mV min^{-1}), suggesting that the insertion compound so formed is not really stable.

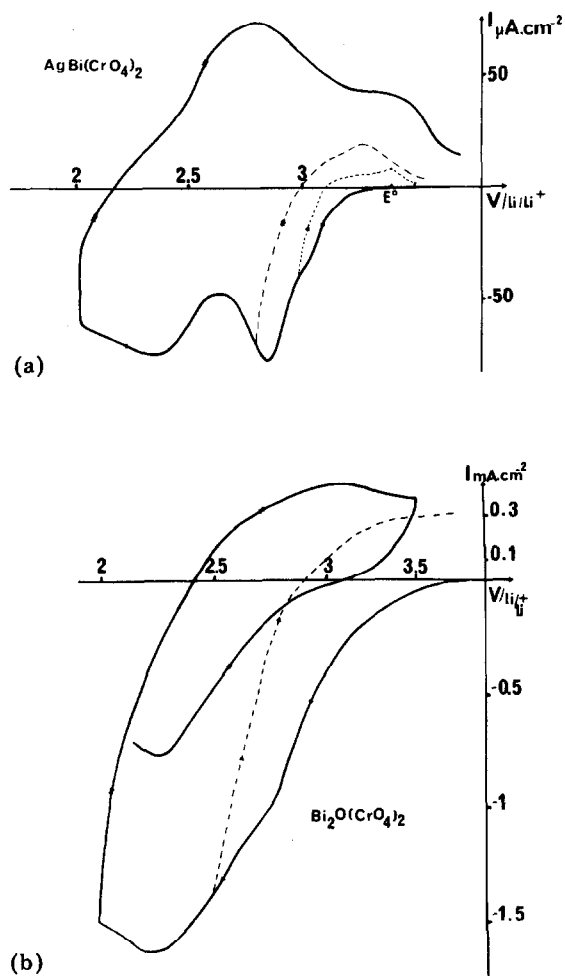


Fig. 6. Effect of the depth of reduction on the consecutive anodic sweep (60 °C). (a) $\text{AgBi}(\text{CrO}_4)_2$ 6 mV min^{-1} ; (b) $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ 60 mV min^{-1} .

3.3. Charge/discharge cycles

The reversibility after a previous partial reduction is also shown in Fig. 7(a) and (b), where curves of recharge at constant current, after different depths of discharge, are reported for the two materials.

The slope variation, occurring at 3.4 V for $\text{AgBi}(\text{CrO}_4)_2$, must be due to silver formed during discharge. It can be seen that the magnitude of this step does not depend on the depth of the previous reduction, indicating that silver is reduced at the beginning of discharge. This result has been confirmed by radiocrystallographic analysis of partially discharged cell cathodes.

The reversibility of the Li^+ ions insertion after partial reduction is only temporary. This can be established through the decrease in the amount of electricity recovered during cycling, especially in the case of $\text{Bi}_2\text{O}(\text{CrO}_4)_2$.

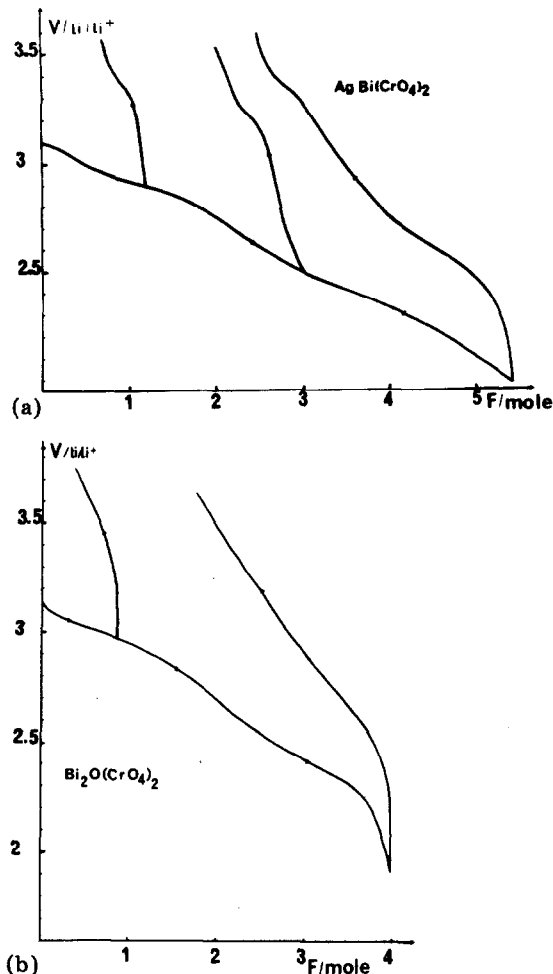


Fig. 7. Recharge curves of experimental electrodes after partial or complete reduction at $100 \mu\text{A cm}^{-2}$. (a) $\text{AgBi}(\text{CrO}_4)_2$; (b) $\text{Bi}_2\text{O}(\text{CrO}_4)_2$.

In this reaction, the insertion of the Li^+ ions may occur in a single phase [12], as is the case for some chromium oxides where the degree of oxidation of the metal is, on average, between 6 and 5 [13]. The incorporation of Li^+ ions would therefore be improved by a partial reduction of Cr(VI).

The formation of octahedral sites during discharge, where the chromium would have 6 coordination, from the initial tetrahedral sites of CrO_4^{2-} , could explain this behaviour [14].

3.4. Zero-current potential evolution

Figure 8 shows the equilibrium potential after recovery, at 60°C , of $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ electrodes at different depths of reduction.

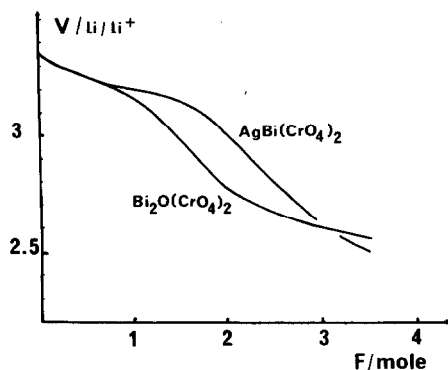


Fig. 8. Equilibrium potential at 60 °C of $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ electrodes, after recovery at different depths of discharge.

A significant change in the slope of the curves will be noticed at an average oxidation degree of 5.5 for the chromium ions. This corresponds to the step where the reversibility occurs according to a single phase equilibrium.

Furthermore, the silver reduction in $\text{AgBi}(\text{CrO}_4)_2$ cannot be distinguished from the initial chromium reduction.

Below a voltage range of 2, Bi(III) can be reduced in two successive steps, 1.7 - 1.8 V and 1.4 - 1.5 V. These two electrochemical processes are similar to those observed during the discharge of Li-Bi₂O₃ cells [8].

4. Discharge of Li-AgBi(CrO₄)₂ button cells

Button cells were produced using the construction technique defined by SAFT for lithium-silver chromate cells [15].

These prototypes were discharged under various conditions of current drain and temperature. Figure 9 shows the influence of temperature on the discharge profile. In Fig. 10, the discharge curves at 37 °C under various loads are reported; this work is still in progress.

At a low drain, the first discharge step, up to 3 V, corresponds to a reduction of 2 F/mole of $\text{AgBi}(\text{CrO}_4)_2$. Neither discharge rate nor temperature induces any modification in the discharge profile, other than of the kinetic polarisation effect.

The drain capability is somewhat lower than that obtained with Li-Ag₂CrO₄ cells of the same type. The energy density on a volume basis, obtained at low drain and good efficiency ($\cong 90\%$) is about 650 W h/dm³, which is similar to that of silver chromate (700 W h/dm³).

The exceptional stability of this electrochemical couple, even at a temperature as high as 70 °C, suggests that it is a good high energy density system with long-life applications.

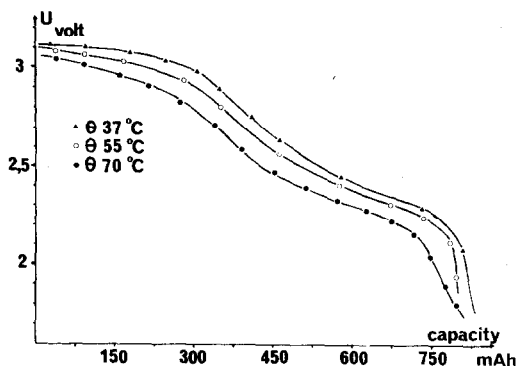


Fig. 9. Discharge curves of $\text{LiAgBi}(\text{CrO}_4)_2$ button cells (3.2 cm^3) under a $15 \text{ k}\Omega$ load at different temperatures. Theoretical capacity: 850 mA h .

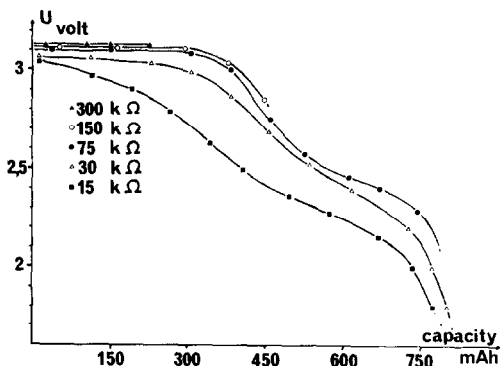


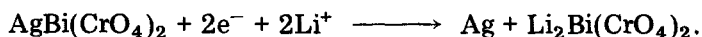
Fig. 10. Discharge curves of $\text{Li-AgBi}(\text{CrO}_4)_2$ button cells (3.2 cm^3) under several loads at $37 \text{ }^\circ\text{C}$. Theoretical capacity: 850 mA h .

5. Discussion

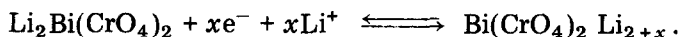
The electrochemical reduction of $\text{AgBi}(\text{CrO}_4)_2$ and $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ leads in a first step to a compound, the Li^+ containing structure of which allows an almost reversible insertion of more Li^+ ions. The average oxidation state of chromium in this compound is about 5.5.

In the case of $\text{AgBi}(\text{CrO}_4)_2$, both silver and chromium ions are reduced in a single step, between 3.3 and 3 V. A separate plateau of $\text{Ag}(\text{I})$ reduction may appear, when the reduction rate increases.

For a low discharge rate, the first electrochemical reduction step of $\text{AgBi}(\text{CrO}_4)_2$ can be written as:

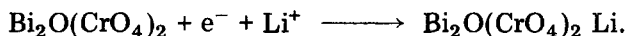


At the end of this process, $\text{Li}_2\text{Bi}(\text{CrO}_4)_2$ is reduced, according to the equation:

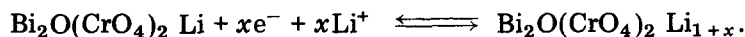


The stability of this insertion compound is not complete and it should decompose into separate phases, leading to the different oxides of Cr, Bi and Li. The electrochemical reduction of Bi(III) occurs only below 2 V, after the complete reduction of Cr(VI) to Cr(IV).

The reduction mechanism of $\text{Bi}_2\text{O}(\text{CrO}_4)_2$ must be similar to that of $\text{AgBi}(\text{CrO}_4)_2$: the first step, involving 1 F/mole above 3 V, leads to a compound where the average oxidation state of chromium is also about 5.5:



This phase can then be reduced, in an almost reversible way, into:



The stability of this compound is also not complete, and the reduction of the cathode can be carried on up to 4 F/mole, *i.e.*, Cr(IV).

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