

BEHAVIOUR OF $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ AS A POSSIBLE CATHODE FOR LITHIUM CELLS

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Summary

The electrochemical reduction of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes occurs in a nearly continuous way from 3.5 V to 2 V/ Li^+/Li and leads to a final oxidation state of about III for chromium ions. Three reduction steps can be distinguished:

- Cr(VI) reduction leading approximately to Cr(V)
- Ag(I) reduction to Ag(0)
- Further reduction of chromium, leading approximately to Cr(III) in a quasi-reversible way.

A loss of capacity was observed, however, during repeated charge/discharge cycles.

Résumé

La réduction intensiostatique d'électrodes modèles de $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ se produit de manière pratiquement continue entre 3.5 V et 2 V/ Li^+/Li et aboutit en définitive à la formation probable de Cr(III). On peut néanmoins mettre en évidence trois étapes de réduction:

- passage de Cr(VI) jusqu'à un stade voisin de Cr(V)
 - réduction de Ag(I) en Ag(0)
 - une étape quasi réversible aboutissant à la formation de Cr(III).
- Cependant, la phase formée à l'issue de la réduction de Ag(I) est peu stable, comme le montrent les cycles charge/décharge du matériau.

1. Introduction

Cathodes containing chromium(VI) are of considerable interest for application in lithium non-aqueous battery systems, because of their generally high specific capacity. We have already proposed a mechanism for the

discharge of Li-Ag₂CrO₄ [1, 2] and Li-AgBi(CrO₄)₂ [3] battery systems: electrochemical reduction of Cr(VI) leads to Cr(IV) formation at potentials ranging from 3.2 to 2 V.

In the case of Ag₂CrO₄, it has been shown that Ag(I) reduction is catalysed through Cr(V) formation, involving an Ag(I)-Cr(V) intermediate compound. Following Ag(I) reduction, Cr(VI) reduction occurs in two steps, leading successively to Cr(V) and Cr(IV) [4]. In the case of AgBi(CrO₄)₂, Ag(I) and Cr(VI) are simultaneously reduced at the beginning of the discharge. The resulting compound, where chromium has an oxidation state close to V, has a particular structure which allows Li⁺ insertion in an almost reversible way and subsequent reduction to Cr(V). Bi(III) reduction does not occur up to a cut-off voltage of 2 V.

The silver bismuth dichromate, AgBi(Cr₂O₇)₂, which was synthesized and tested in a lithium cell [7] has recently engaged our attention, as its theoretical specific capacity is close to that of silver chromate. In order to investigate the role of Ag(I) during the electrochemical reduction of this new material, we have also studied a similar compound: TlBi(Cr₂O₇)₂.

2. Experimental

The electrochemical study was carried out with "membrane" electrodes. A small quantity of active material was mixed with 90% by weight of pure graphite and the mixture was pressed on a stainless steel grid. The membrane obtained was about 0.3 mm thick with an area of 1 cm². Potentials were measured against a lithium reference electrode through a capillary close to the working electrode. A lithium sheet was used as the counter electrode.

The electrolyte was a 1M LiClO₄ solution in propylene carbonate, containing less than 200 ppm of water, and the active material was prepared from a saturated solution of chromium trioxide, bismuth nitrate and Ag₂Cr₂O₇ [5]. The unit formula of this dichromate is AgBi(Cr₂O₇)₂. The crystallographic study shows that this compound crystallizes in the non-centrosymmetric tetragonal space group *I4* [6].

3. Results and discussion

(i) Discharge characteristics

Figure 1 shows AgBi(Cr₂O₇)₂ reduction curves at several temperatures under a current density of 0.1 mA cm⁻². During discharge, the potential decreases nearly continuously from 3.5 V to 2 V. The Faradaic balance, at 40 and 60 °C exceeds the 9 *F*/mole expected for Ag(I) → Ag(0) and Cr(VI) → Cr(IV) reductions.

As Bi(III) is not reducible in this range of potentials, it appears that Cr(VI) is being reduced nearly to Cr(III). This process does not seem to occur during the reduction of metallic chromates.

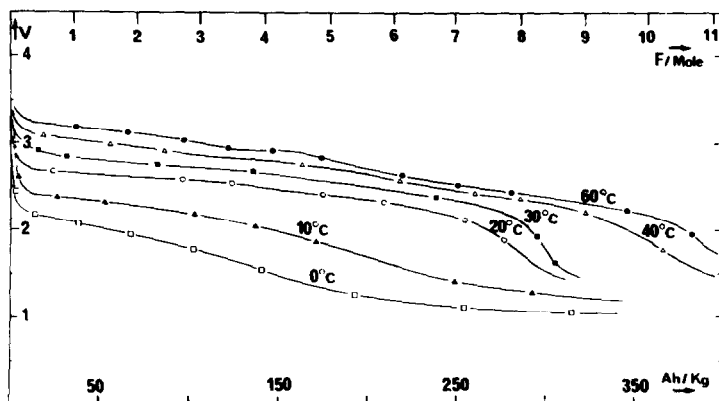


Fig. 1. Discharge characteristics of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes. Temperature effect at 0.1 mA cm^{-2} ($A = 1 \text{ cm}^2$, $I_d = 100 \mu\text{A}$).

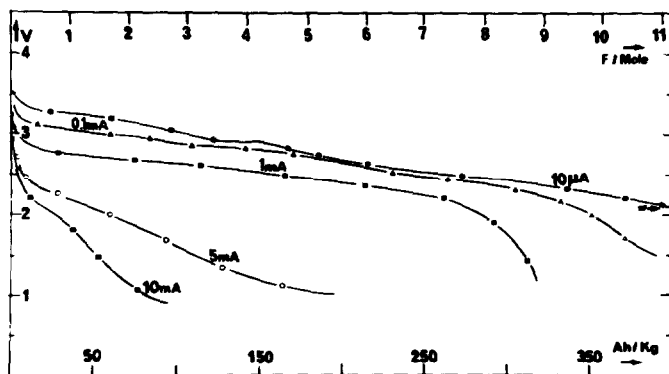


Fig. 2. Discharge characteristics of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes. Current density effect at 40°C ($A = 1 \text{ cm}^2$).

Between 20 and 60°C , the specific capacity and the reduction potentials are only slightly temperature dependent, but below 10°C an important loss of capacity is recorded. At a constant temperature of 40°C a sudden loss of capacity is also observed (Fig. 2), when the current density exceeds 1 mA cm^{-2} . At a current density of 10 mA cm^{-2} , the specific capacity is lower than 50 A h/kg for a cut-off voltage of 2 V .

Under the best discharge conditions, *i.e.*, high temperature or low current density, a plateau is observed at 2.9 V , involving about 1 F/mole of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$. This plateau is more evident in Fig. 3, where open circuit voltage values are plotted against the depth of discharge. These open circuit voltages are the stable equilibrium potentials achieved after the discharge current has been switched off. The absence of such a plateau in the $\text{TlBi}(\text{Cr}_2\text{O}_7)_2$ O.C.V. curve, suggests that it is a characteristic of Ag(I) reduction.

We can conclude, therefore, that the Cr(VI) reduction begins at the first step of the discharge, before Ag(I) reduction. This process is different in

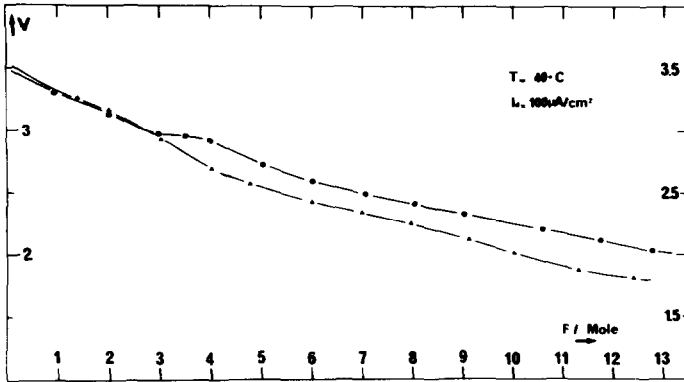


Fig. 3. O.C.V. curves as a function of the D.O.D. ● = $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$, ▲ = $\text{TlBi}(\text{Cr}_2\text{O}_7)_2$ ($T = 40^\circ\text{C}$, $I_d = 100 \mu\text{A}/\text{cm}^2$).

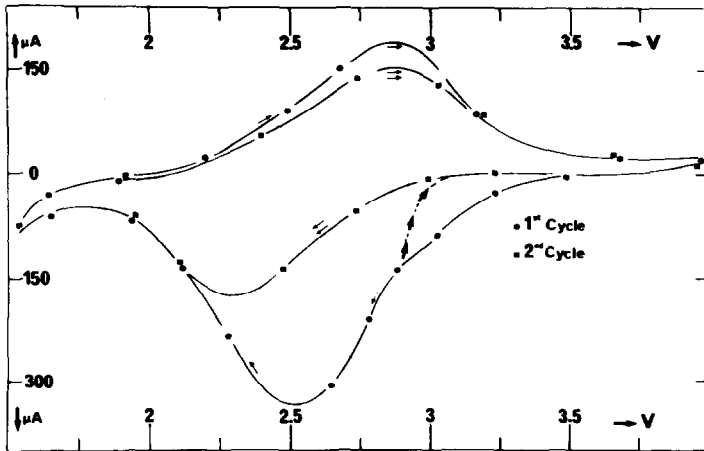


Fig. 4. Voltammograms of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes ($T = 40^\circ\text{C}$, $6 \text{ mV}/\text{mn}$).

$\text{Li}-\text{AgBi}(\text{CrO}_4)_2$ cells where $\text{Ag}(\text{I})$ and $\text{Cr}(\text{VI})$ reductions occur simultaneously [3]. In Fig. 3, the Faradaic balance of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ and $\text{TlBi}(\text{Cr}_2\text{O}_7)_2$ confirm that $\text{Cr}(\text{VI})$ reduction leads almost to $\text{Cr}(\text{III})$.

(ii) Linear sweep voltammetry investigations and reversibility

Voltammetric studies (Fig. 4), show that the continuous process of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ reduction is somewhat reversible, as it is for $\text{AgBi}(\text{CrO}_4)_2$. The first stage of $\text{Cr}(\text{VI})$ reduction is not reversible (dashed line). Voltage sweep reversal allows an anodic process to appear only if the cathodic potential has reached 2.9 V, *i.e.*, $\text{Ag}(\text{I})$ reduction potential.

In order to clarify this behaviour, we have tested the reversibility of partially reduced electrodes. Charging curves for $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ and for $\text{TlBi}(\text{Cr}_2\text{O}_7)_2$ electrodes, at constant current density (0.01 mA cm^{-2}) and after different depths of discharge are shown in Fig. 5. Re-oxidation was

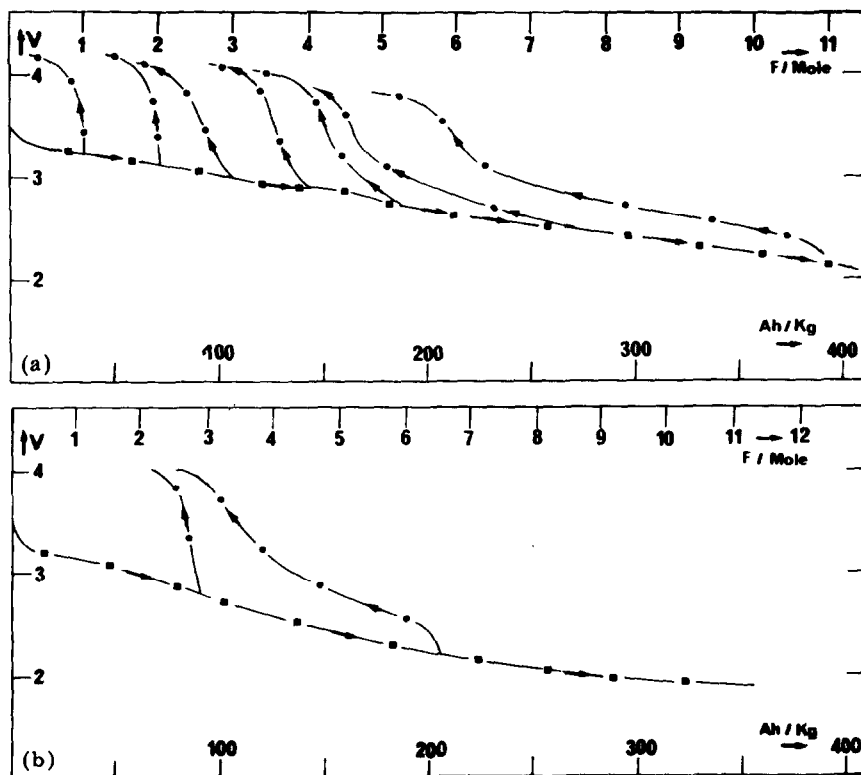


Fig. 5. (a) Discharge/charge curves of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes ($T = 40^\circ\text{C}$, $I = 10 \mu\text{A}/\text{cm}^2$); (b) discharge/charge curves of $\text{TlBi}(\text{Cr}_2\text{O}_7)_2$ electrodes ($T = 40^\circ\text{C}$, $I = 10 \mu\text{A}/\text{cm}^2$).

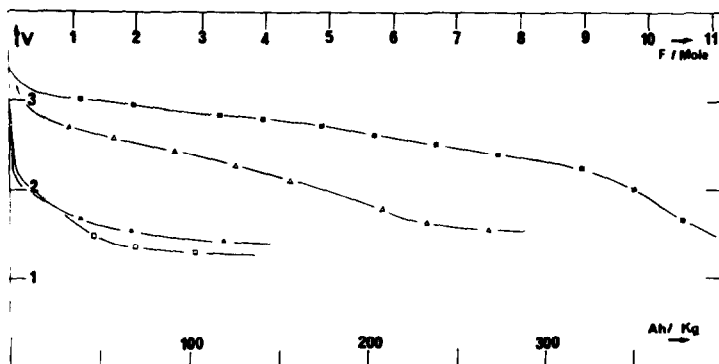


Fig. 6. Cation size effect for $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes. \blacksquare = 1M LiClO_4 , \blacktriangle = 1M NaClO_4 , \blacktriangle = $1\text{M Mg}(\text{ClO}_4)_2$, \square = $1\text{M NBu}_4\text{ClO}_4$ ($T = 40^\circ\text{C}$).

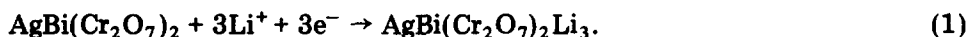
observed as soon as the oxidation state of chromium was close to V (D.O.D. $\cong 4$ F/mole). From this state, the amount of electricity recovered during the recharge was almost a linear function of the depth of discharge.

(iii) Discharge mechanism

Reduction characteristics depend on the size of the electrolyte cation; the bigger the ionic radius of the cation, the lower is the rate of the electrochemical process (Fig. 6). Such a result has been described for chromate reduction [1] which confirms that the primary process of the reaction is Li^+ insertion into the crystal lattice of the cathodic material.

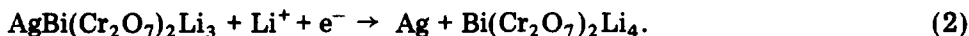
By analogy with $\text{AgBi}(\text{CrO}_4)_2$ reduction, the following 3-stage scheme may be suggested for $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ reduction:

(a) *Between 3.5 and 2.9 V.* The chromium reduction involves 3 F/mole and corresponds to an Li^+ insertion into the lattice as:

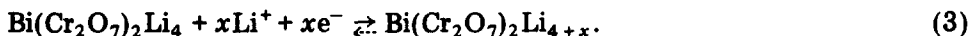


The oxidation state of chromium in this insertion compound is close to V (formally 5.25).

(b) *At 2.9 V.* Ag(I) reduction occurs as:



(c) *Between 2.9 and 2 V.* The Li^+ insertion occurs reversibly:



with x values between 0 and 9.

The charge/discharge cycles of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes, however, show that the reversibility of Li^+ insertion, occurring between 2.9 V and 2 V, is only temporary. The specific capacity is reduced by half between the second and the twentieth cycles (Fig. 7).

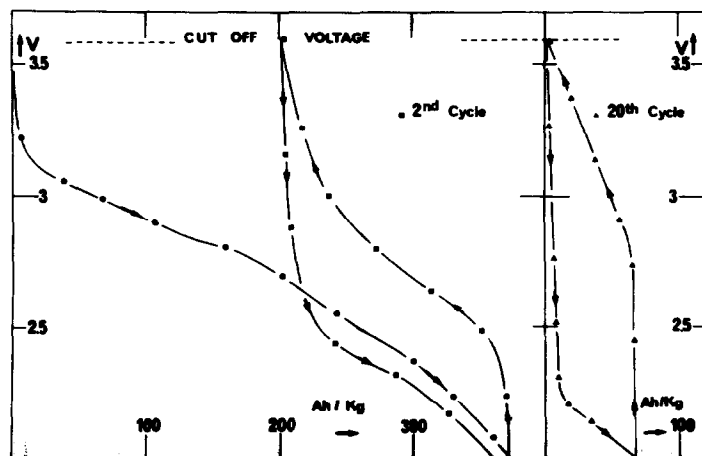


Fig. 7. Charge/discharge cycles for $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ electrodes ($I_d = I_c = 0.1 \text{ mA/cm}^2$, $T = 40^\circ\text{C}$).

4. Conclusion

As is the case for $\text{AgBi}(\text{CrO}_4)_2$, $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ is not an interesting material for secondary Li cells. The high specific capacity of this compound, however, suggests that it could be used in primary cells.

The solubilities of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ and its discharge products are lower than those of $\text{Ag}_2\text{Cr}_2\text{O}_7$ due to Bi(III), but those solubilities are high compared with Ag_2CrO_4 or $\text{AgBi}(\text{CrO}_4)_2$ compounds in non-aqueous media, for example, propylene carbonate. This problem is the major obstacle to the further development of $\text{AgBi}(\text{Cr}_2\text{O}_7)_2$ as a useful cathode material for primary Li cells.

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