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## Silver as Anode in Cryolite—Alumina-Based Melts

<sup>a,b</sup>M. KUCHARÍK\*, <sup>b</sup>P. CHAMELOT, <sup>b</sup>L. CASSAYRE, and <sup>b</sup>P. TAXIL

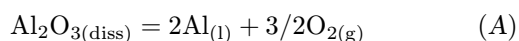
<sup>a</sup>*Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovakia*  
*e-mail: uachkuch@savba.sk*

<sup>b</sup>*Laboratoire de Génie Chimique (LCG), UMR 5503, Université Paul Sabatier,*  
*118 route de Narbonne, 31062 Toulouse Cedex 04, France*

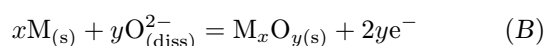
The anodic behaviour of silver was investigated in cryolite—alumina-based melt. Silver has a lower melting point (*ca.* 960 °C) than the other metals considered as possible inert materials for aluminium electrolysis. The working temperature used in aluminium industry is approximately 960 °C, depending on the melt composition. Therefore, the stability of silver during the anodic process was tested at 870 °C in an acidic electrolyte consisting of 65.5 mass % Na<sub>3</sub>AlF<sub>6</sub> + 22.9 mass % AlF<sub>3</sub> + 5.7 mass % CaF<sub>2</sub> + 3.9 mass % LiF + 2 mass % Al<sub>2</sub>O<sub>3</sub> with the melting point *ca.* 850 °C. The electrolyte without alumina was prepared as well, with the melting point *ca.* 860 °C. The resulting cryolite ratio (CR =  $n(\text{NaF})/n(\text{AlF}_3)$ ) for both electrolytes was equal to 1.6. The behaviour of the silver anode was studied by voltammetry measurements. The electrochemical study showed that an oxidation reaction occurred at a potential below the oxygen evolution potential. Silver was not found to be stable under oxygen evolution. The degradation of the silver anode was apparent after electrolysis.

**Keywords:** silver electrode, cryolite, alumina, low-temperature electrolyte

Nowadays, the industrial production of primary aluminium is carried out exclusively by the Hall—Héroult process. The consumable carbon anodes used in this process produce large amounts of CO<sub>2</sub> and other environmentally hazardous gases, *e.g.* CO, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>. The replacement of carbon anodes by inert materials is a key problem in the development of new procedure in aluminium electrolysis. The cell reaction with inert anodes is as follows



The majority of the metal-based anodes will be covered by an oxide layer during the electrolysis [1]. The formation of oxide layer on the anode caused by dissolved alumina can be represented by the following electrochemical equation



This concept involves the formation of a dense and stable electrically conducting oxide layer at the surface of the anode, which protects the metal phase from further oxidation. The solubility of the oxide layer in the melt must be low as well [2].

*Belyaev and Studentsov* [3—5] investigated various pure metals, oxides, and ferrites as candidate materials for the inert anodes as early as during the thirties of the last century. The iron rods with different metal coatings (Cu, Ni, Cr, and Ag) were used [3]. It was concluded that the coatings of the mentioned pure metals were unresisting as anodes at 935 °C. In the case of pure Cu, Ni, and Cr coatings the electrochemical reactions occurred between the metal and electrolyte followed by the dissolution of reaction products in elec-

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\*The author to whom the correspondence should be addressed.

trolyte. In the case of the silver coating the melting of the metal was observed during the electrolysis even below the melting point of Ag [3].

Cermet anodes consist of the mixture of a ceramic phase and a metal phase. Cermet anodes are attractive since they combine the advantages of ceramics and metal [1].

In order to increase electrical conductivity *Ray et al.* [6–12] included silver into an inert cermet anode. The ceramic phase comprised nickel and iron oxide. The alloy phase, containing copper and silver, was interspersed throughout the ceramic phase. The optimal composition of silver in the Cu—Ag alloy was within about 0.5 mass % and 8 mass % of silver, according to the Cu—Ag phase diagram [9].

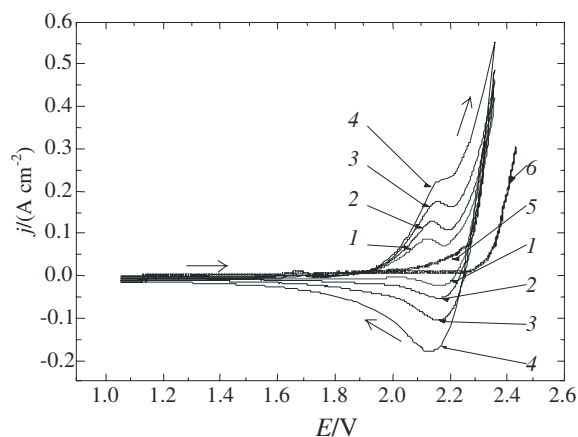
In this work, the anodic behaviour of pure silver metal in cryolite-based melts up to 870 °C is presented.

For the preparation of the electrolytic bath, the following chemicals were used: Na<sub>3</sub>AlF<sub>6</sub> (Cerac, 99.5 %), AlF<sub>3</sub> (Acros, 99.9 %), CaF<sub>2</sub> (Merck, 99.99 %), LiF (Merck, 99.99 %), Al<sub>2</sub>O<sub>3</sub> (Cerac, 99.5 %). Silver and tungsten (Goodfellow, 99.9 %, *d* = 1 mm) as well as gold and platinum (Goodfellow, 99.9 %, *d* = 0.5 mm) were employed for metal electrodes.

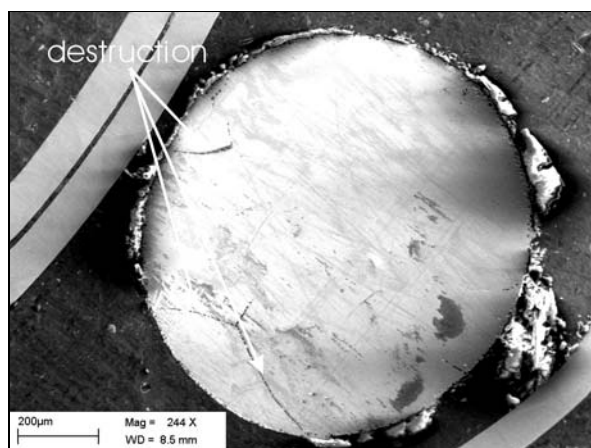
Vitreous carbon crucible containing 200 g of the mixture was placed in the cell and its content was initially dehydrated under vacuum for 24 h at 250 °C. The electrochemical experiments were carried out at the working temperature of 870 °C under the inert argon atmosphere (less than 1 ppm O<sub>2</sub>) in Autolab PG stat10 potentiostat controlled by GPES software. Detailed description of the experimental set-up was presented elsewhere [13].

Potentials were measured with respect to platinum wire immersed in the bath acting as a reference electrode. The platinum electrode potential was related to the aluminium deposition potential by cathodic polarization of a tungsten electrode [14].

The electrolyte with the melting point of 910 °C (lower temperature as that reported by *Belyaev and Studentsov* [3]) was used in order to determine the behaviour of Ag anode during electrolyses. However, the melting of the silver electrode was still observed during polarization at working temperature 920 °C. Therefore, electrolyte (65.5 mass % Na<sub>3</sub>AlF<sub>6</sub> + 22.9 mass % AlF<sub>3</sub> + 5.7 mass % CaF<sub>2</sub> + 3.9 mass % LiF + 2 mass % Al<sub>2</sub>O<sub>3</sub> with melting point *ca.* 850 °C) with even lower melting point was prepared. An alumina-free electrolyte (65.5 mass % Na<sub>3</sub>AlF<sub>6</sub> + 22.9 mass % AlF<sub>3</sub> + 5.7 mass % CaF<sub>2</sub> + 3.9 mass % LiF with melting point of 860 °C) was used in order to compare the behaviour of Ag electrode in alumina-containing and alumina-free electrolytes as well. In both cases no melting of the silver electrode was observed at the working temperature. The temperatures of primary crystallisation of the electrolytes were calculated according to the empiric equations by *Solheim et al.* [15]. The calculated standard reversible potential for oxy-

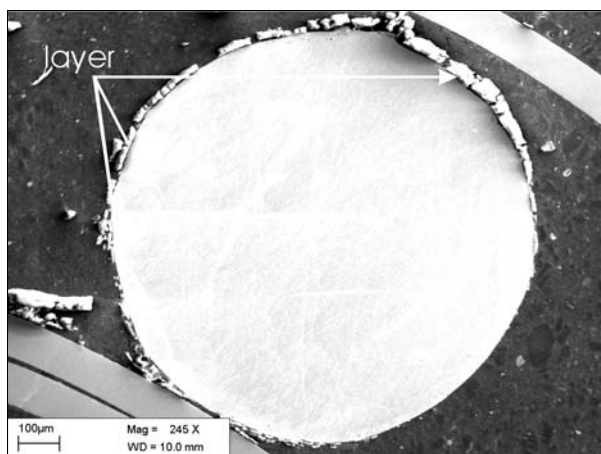


**Fig. 1.** Cyclic voltammetry on silver electrode in the melt comprising alumina. Sweep rates 0.05 V s<sup>-1</sup> (1), 0.10 V s<sup>-1</sup> (2), 0.20 V s<sup>-1</sup> (3), 0.50 V s<sup>-1</sup> (4). Comparison with the linear sweep voltammetry on Ag (5) and Au (6) electrode at the sweep rate of 0.002 V s<sup>-1</sup>.

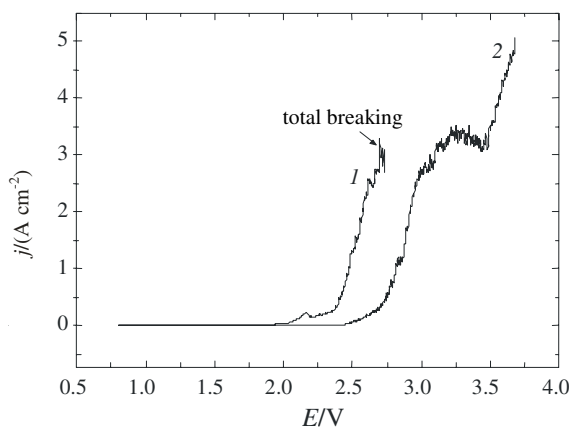


**Fig. 2.** Silver electrode after 12 cyclic voltammetry measurements in cryolite-based melt containing alumina.

gen evolution (eqn (A)) at 870 °C is 2.27 V [16]. The cyclic voltammograms on the silver electrodes (sweep rates 0.05–0.5 V s<sup>-1</sup>) and linear sweep voltammograms on silver and gold electrode (sweep rate 0.002 V s<sup>-1</sup>) in the melt with alumina are shown in Fig. 1. The oxidation peaks with maxima in the potential range 2.12–2.17 V *vs.* Al/AlF<sub>3</sub> depending on the sweep rate were observed. These maxima were observed at the potential below the standard potential for oxygen evolution (2.27 V). The upper limit of the applied potential was 2.5 V *vs.* Al/AlF<sub>3</sub>. Three cycles were recorded at each sweep rate. Altogether, twelve cycles were performed with one silver electrode. After this procedure SEM image of the cross-section of the silver electrode was recorded (Fig. 2) evidencing the damage to the silver anode. In order to determine the nature of the process at *ca.* 2.17 V *vs.* Al/AlF<sub>3</sub>, a new silver electrode was polarized at this potential for 20 min followed by



**Fig. 3.** Silver anode polarized for 20 min in cryolite-based melt containing alumina at the potential of 2.17 V *vs.* Al/AlF<sub>3</sub> and quickly lifted from the melt.



**Fig. 4.** Voltammograms (0.002 V s<sup>-1</sup>) on silver (1) and gold (2) electrodes in the cryolite-based electrolyte containing no alumina.

quick lifting. SEM image of the cross-section of this for long time polarized silver electrode is shown in Fig. 3. No damage of the electrode was observed though the polarizing time was significantly longer than the overall duration of the cyclic voltammetry measurements with one electrode. Thus, the silver electrode seems to be stable up to 2.17 V *vs.* Al/AlF<sub>3</sub>. In Fig. 3 a layer coating the silver electrode was observed. Thus, the nature of the silver anode surface was examined by EDX (Oxford, INCA 2000) showing that the anode coating contained no silver but the electrolyte elements solidified on the electrode surface. This observation confirmed the stability of silver electrode up to the potential of 2.17 V *vs.* Al/AlF<sub>3</sub> as well. However, from this experiment the nature of the process at given potential cannot be deduced.

Linear sweep voltammograms on silver and gold electrodes in the electrolyte containing no alumina are shown in Fig. 4. On gold electrode the anodic potential

was slowly increased (sweep rate 0.002 V s<sup>-1</sup>) from the open circuit potential. Voltammogram curve in the potential range 2.3–3 V *vs.* Al/AlF<sub>3</sub> was assigned to the evolution of oxygen. At the potential of about 3 V *vs.* Al/AlF<sub>3</sub> current density of 2.6 A cm<sup>-2</sup> was reached. In the interval 3–3.5 V *vs.* Al/AlF<sub>3</sub> the current density was approximately constant. Further increase of the potential resulted in further increase of the current density. Cassayre *et al.* [17] determined the dissolution potential of the gold electrode in the oxide-free cryolite melt at 3.2 V *vs.* Al/AlF<sub>3</sub> at 1000 °C. Consequently, the part of gold voltammogram curve above 3.5 V *vs.* Al/AlF<sub>3</sub> can be assigned to the dissolution of the gold electrode at the applied working temperature of 870 °C. From the measurement realized with the gold electrode it can be deduced that some traces of alumina had to be present in the molten electrolyte though no alumina was added. The most probable source of alumina impurities was cryolite.

In the case of the silver electrode the anodic potential was slowly increased analogously to the experimental procedure applied during the measurement with the gold electrode. An oxidation peak is observed at the potential 2.17 V *vs.* Al/AlF<sub>3</sub>. The current density started to increase rapidly above *ca.* 2.3 V *vs.* Al/AlF<sub>3</sub>. The silver electrode was damaged after reaching the current density of around 3 A cm<sup>-2</sup>.

Electrochemical measurements and the SEM observation clearly showed that silver used as anode is oxidized at the potential lower than the value corresponding to oxygen evolution. It can be concluded that silver as a pure metal is not a suitable construction material for inert anodes used in aluminium-producing industry.

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