

Tin Oxide and Nickel Ferrite Anodic Behaviour in Molten Chlorides

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INTRODUCTION

At present, metal production from molten salt electrolytes containing dissolved oxides has a big challenge in finding a new anode material to replace the traditional carbon anode. When carbon anodes are used in processes involving a metal oxide as raw material, two important problems are encountered: a large amount of CO₂ gas is produced, and the anode is consumed. This is a major challenge in the production of primary aluminium metal and in other molten salt electrolysis processes where a metal oxide is used as raw material, such as the proposed FFC Cambridge process [2].

An inert anode is an anode that does not react chemically or electrochemically in the process, but in reality an inert anode will be slowly consumed by processes like chemical dissolution, reduction by dissolved metal, disintegration, grain boundary attack and electrochemical decomposition. Galasiu et al. [1] defined an acceptable wear rate in aluminium electrolysis to be 10 mm/year or lower.

The aluminium industry has made an extensive research to find a suitable material for an oxygen evolving inert anode, within the material types of metals, ceramics and a mixture of metals and ceramics: cermets. Stainless steel based materials, SnO₂ and nickel ferrite based materials seem to be the most promising. So far none of these materials has fulfilled the requirements.

This paper presents some results from using tin oxide and nickel ferrite based materials in molten chlorides. With the development of several new processes for the production of metals from chloride melts, it is interesting to map the behaviour of the materials in chlorides.

EXPERIMENTAL

Nickel ferrite based anodes were prepared from NiO, Fe₃O₄, Cu and Ni, while tin oxide based materials (Stannex E, D and ELR) was bought from Dyson Industries Ltd. The laboratory experiments were performed in a tube furnace with a closed cell setup under argon atmosphere. In all experiments, argon 5.0 (purity of 99.999 %) was used as the purging gas, and the chemicals were not exposed to air after being heated above 200 °C. Only during the few seconds that it would take to insert or replace an electrode was the cell open to air. The Argon 5.0 gas was led through an alsint tube to the surface of the molten electrolyte, in order to rapidly transport any oxygen gas away from the electrolyte. The materials, see Table 1, were tested in CaCl₂ - NaCl and LiCl - KCl based electrolytes.

Table 1: Composition of tested anode materials (wt %)

	NiFe ₂ O ₄	NiO	Cu	Ni	SnO ₂
1	80	0	17	3	-
2	63	17	17	3	-
3	80	0	10	10	-
4	63	17	10	10	-
Stannex D	-	-	-	-	98
Stannex E	-	-	-	-	98.5
Stannex ELR	-	-	-	-	98.5

RESULTS

Cyclic voltammetry with Stannex electrodes in eutectic LiCl-KCl at 450 °C shows an anodic reaction starting at around 1 V vs. Ag⁺/Ag, which is Cl₂-gas evolution. Also, a background current prior to the Cl₂-evolution can be seen. Closer inspections with the more sensitive method square wave voltammetry reveals two anodic peaks in this region. This might be due to very small amounts of oxides in the electrolyte. Addition of Li₂O resulted in an increase in this background current. Since it seems to be at least two reactions contributing to this background current, it might be a mixture of oxidation reactions, both oxygen evolution and possibly formation of lithium stannates.

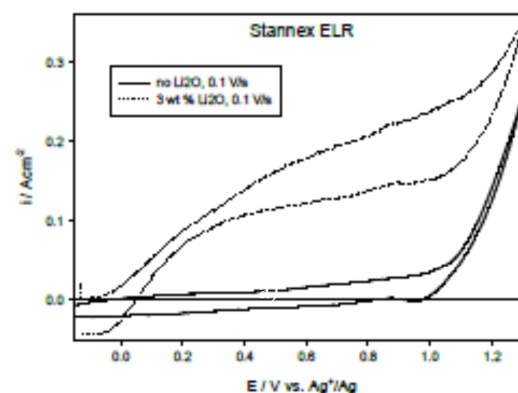


Fig. 1. Cyclic voltammetry (0.1 V/s) in molten LiCl-KCl at 450 °C on SnO₂ (Stannex) electrodes before and after addition of Li₂O.

5 hour electrolysis was also carried out in the eutectic LiCl-KCl at 450 °C and the Stannex anodes showed a good performance. After electrolysis the electrodes had not changed in shape, but the color was slightly darker.

REFERENCES

- I. Galasiu, R. Galasiu and J. Thonstad, Inert Anodes for Aluminium Electrolysis, p. 6, 1st ed., Aluminium-Verlag, Düsseldorf, Germany, 2007.
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