



Electrochemical growth of a corrosion-resistant multi-layer scale to enable an oxygen-evolution inert anode in molten carbonate

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ABSTRACT

An *in-situ* formed three-layered scale consisting of a Cu-rich layer and two oxide layers on the surface of Ni₁₀Cu₁₁Fe alloy enables an inert anode for oxygen evolution reaction in molten Na₂CO₃-K₂CO₃. The outermost layer is mostly NiFe₂O₄, the middle layer mainly consists of NiO, and the innermost is a Cu-rich metal layer. The dense NiFe₂O₄ layer is resistant to molten salts and prevents O²⁻ diffusing inwards, the middle NiO layer conducts electrons and functions as a buffer layer to increase the mechanical robustness of the whole scale, and the third copper-rich layer could help to slow down the oxidation rate of the alloy. This low-cost inert anode with a multi-layered scale is able to survive for more than 600 h in molten Na₂CO₃-K₂CO₃ electrolysis cell, generating O₂ and thereby enabling a carbon-free electro-metallurgical process.

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1. Introduction

With the exception of noble metals (e.g., Au, Pt, Ir, etc.), a corrosion-resistant oxide layer is requisite for pure metals and alloys surviving as an anode in a high-temperature atmosphere or oxide-ion containing molten salts. Low-cost transition-metal alloys have been considered as promising inter anode candidates in molten-salt electrolysis cells, such as Hall-Héroult [1,2], FFC Cambridge [3–5], molten oxide electrolysis [6–8], molten carbonate electrolysis [9–12]. The vector of electrochemical metallurgy points towards green process development featuring low energy consumption and zero-emissions. Therefore, a low-cost inert anode is key to accomplishing an environmentally sound electrolysis process, without producing CO₂ and toxic byproducts, but generating oxygen.

In addition to the widely used molten halide electrolytes in the current electrolysis industry, molten carbonate has been in the past

few years found to be an electrolyte capable of producing iron, nickel, and cobalt and oxygen with a low-cost Ni₁₀Cu₁₁Fe inert anode [10–12]. Unlike molten halide electrolytes, molten carbonate has a narrow electrochemical window but less corrosivity. Besides ceramics and cermets, metallic inert anodes are promising candidates due to their low cost, high electronic conductivity, ease of fabrication, excellent thermal shock resistance, and mechanical robustness [13]. Amongst the metallic inert anodes, the nickel-based alloys have been intensively studied due to their low cost, mechanical robustness and formation of a nickel ferrite coating [14–23]. Generally, transition metals and their alloys can be oxidized prior to the oxygen evolution because of their lower electronegativity than oxygen. In order to make the low-cost transition metallic alloys work as inert anodes, a dense and electrically conductive oxide layer on the surface of the alloys should be constructed to protect the bulk metal anode and subsequently enable oxygen evolution [24]. After the electrically conductive oxide layer forms, the oxygen evolution reaction takes place at the interface of the oxide layer and electrolyte, providing electrons to the metallic anode underneath the oxide layer, and then the electrons are transferred through the external circuit to the cathode for reduction reactions. Therefore, constructing a dense and stable protective oxide layer, while maintaining its electrical conductivity,

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oxygen catalytic activity, mechanical robustness and an appropriate thickness, is crucial to the success of the metallic inert anode.

Direct electrochemical formation of a functionally protective oxide scale on the surface of alloys is a straightforward approach, taking advantage of electrochemical corrosion of metal anode in a short term and thereby enabling a long-term stability. Herein, the electrochemical growth of the protective oxide scale and its structure are studied to reveal the oxide growth process and structures, which allows us to have a better understanding of the electrochemical corrosion mechanism of Ni10Cu11Fe in molten carbonate, and thereby inspiring future inert anode development.

2. Materials and methods

2.1. Materials and experimental setup

Ni10Cu11Fe anode was fabricated by casting the mixed nickel, copper and iron powders (79:10:11 in mass ratio, analytical purity (>99.9%), Sinopharm Chemical Reagent Co. Ltd., China) in an alumina crucible (20 mm in inner diameter) protected in an Ar atmosphere at 1600 °C, and the alumina crucible was heated by a MoSi₂ pole furnace. A porous Fe₂O₃ pellet was attached to an iron wire (2 mm in diameter) working as a cathode, and the as-prepared Ni10Cu11Fe was employed as an anode for electrolysis [10]. The electrolysis cell was contained in an alumina crucible containing 500 g anhydrous Na₂CO₃-K₂CO₃ (59:41 in molar ratio, analytical purity (>99.9%), Sinopharm Chemical Reagent Co. Ltd., China), and the salt was dried in air at 250 °C for 48 h in a closed-end sealed stainless steel (SS) reactor. Then the temperature of the SS reactor was raised to 750 °C to melt the salt with the protection of Ar flow. Pre-electrolysis was performed under a constant cell voltage of 1.8 V between a Ni10Cu11Fe alloy anode and a foamed nickel cathode for 2 h to further remove residual water and, if any, other impurities from the molten salts.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) measurements were conducted in a three-electrode setup controlled by a CHI1140a electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China). Nickel, iron, copper, platinum wires (1 mm in diameter, Alfa Aesar), and Ni10Cu11Fe alloy were respectively employed as a working electrodes, with a graphite rod (6 mm in diameter) counter electrode and a Ag/Ag₂SO₄ reference electrode. The onset potential begins at open circuit potential (OCP). The reference electrode was made by inserting a silver wire (2 mm in diameter) into a eutectic carbonate melt (Li₂CO₃:Na₂CO₃:K₂CO₃ = 43.5: 31.5: 25 mol %) containing Ag₂SO₄ (0.1 mol/kg) in a mullite cylinder. Electrochemical impedance spectroscopy (EIS) tests were conducted to test the conductivity of the formed oxides coating of Ni10Cu11Fe anode by an electrochemical workstation (Autolab 302 N, Metrohm), and the excitation ac signal with amplitude of 5 mV in a frequency domain from 1 Hz to 10 kHz was applied and the DC potential was controlled at the open circuit potential. The Ni10Cu11Fe rod served as working electrode, an iron sheet (3 cm × 4 cm) was used as a counter electrode, and the Ag/Ag₂SO₄ was the reference electrode. All experiments were performed under the protection of high purity argon flow (>99.999%).

2.3. Oxide scale formation and characterization

A two-electrode electrolysis cell consisting of a sintered Fe₂O₃ pellet cathode, the casted Ni10Cu11Fe anode, and a molten Na₂CO₃-K₂CO₃ electrolyte was assembled in the SS test vessel to *in-situ* form an oxide scale and test the stability of the inert anode covered with

the oxide scale. The electrolysis cell was operated under constant cell voltage and controlled by a battery testing system (Shenzhen Neware Electronic Ltd., China). After the Fe₂O₃ pellet cathode was completely reduced to Fe, new Fe₂O₃ pellets were refilled at regular intervals to supply O²⁻ and enable the anode to work under certain current densities with the same electrolyte and anode. The resistance of the anode under different electrolysis durations was measured by EIS. After electrolysis, the grown protective layer on the surface of the anode was cross-sectioned and analyzed by scanning electron microscopy (SEM, FEI Sirion field emission, including second and backscattered electron imaging), X-ray diffraction spectroscopy (XRD, Shimadzu X-ray 6000 with Cu K α 1 radiation at $\lambda = 1.5405 \text{ \AA}$) and energy-dispersive X-ray spectroscopy (EDX, EDAX GENESIS 7000). The outlet gas from the electrolysis chamber was analyzed by gas chromatography (GC) (Shanghai Kechuang).

3. Results and discussion

3.1. Thermodynamic analysis

The theoretical electrochemical window of molten Na₂CO₃-K₂CO₃ is 2.34 V at 750 °C, and the anodic and cathodic limit reactions are oxygen evolution and sodium deposition, respectively. If an inert anode was made of noble metal, like platinum, is employed, oxygen can be generated at the anode. Thermodynamic data of the molten carbonate system were analyzed in detail by Van et al. [25]. Thermodynamically, the transition-metal will be oxidized in molten carbonate under anodic polarization. The Gibbs free energy of the anodic reactions of Ni, Fe and Cu in molten Na₂CO₃-K₂CO₃ was obtained from *HSC Chemistry 6*. The standard dissociation potentials of the reactions are calculated from the Nernst equation ($\Delta G = -nFE$, the chemical activity of all species is assigned as unity, n is the number of transferred electrons, and F is the Faraday constant). As shown in Fig. 1, the oxides scale could form on the surface of Ni, Fe and Cu electrodes prior to oxygen evolution. Among these three metals, iron oxides preferentially form, then nickel oxide forms, and copper oxides form lastly. At the very beginning of electrolysis, the electrochemical oxidation of anode takes place at the alloy/electrolyte interface. Afterwards, the oxides grow at alloy/oxides interface, and simultaneously compounding reactions could occur inside the oxide scale and further oxidation could give rise to the formation of the spinel NiFe₂O₄ at the scale/metal interface. There are two kinds of reactions taking place spontaneously. One reaction is named a displacement

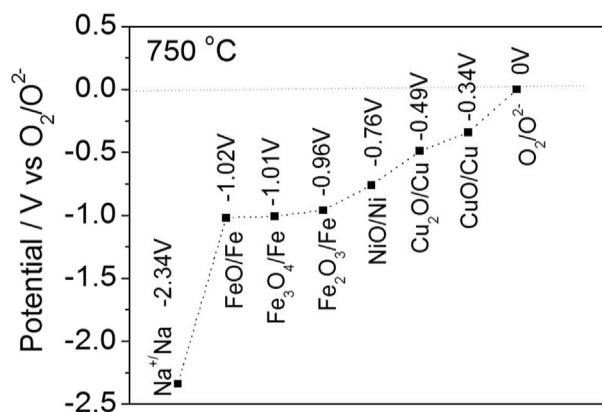


Fig. 1. Standard potentials of the half reactions versus oxygen evolution potential at 750 °C, all thermodynamic data are obtained from HSC Chemistry 6.

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