



# Unusual temperature effect on the stability of nickel anodes in molten carbonates



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## ABSTRACT

The stability of nickel anode in a eutectic molten  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  electrolysis cell was systematically investigated over the temperature range of 450 °C to 750 °C. An unusual temperature effect was observed involving a critical activation-passivation transition temperature at 575 °C for the nickel in the melt; rapid dissolution of nickel was found to occur below 575 °C under anodic polarization, whereas its surface became passivated above this temperature, and the stability of the passivation film was further improved by increasing the temperature up to 750 °C. A blackish oxide film forms on nickel surfaces that retard the anodic dissolution of nickel. The composition and structure of the oxide film, as well as its formation mechanism, were studied by electrochemical measurements combined with X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) characterization. Two temperature sensitive oxidation states of nickel (i.e., Ni(II) and Ni(III)) formed during the anodic polarization. Ni(III) tended to combine with  $\text{Li}_2\text{CO}_3$  to form the more soluble  $\text{LiNiO}_2$  during anodic polarization at lower temperature, and its content in the film decreased dramatically with increasing temperature. Thus, a stable and protective film consisting of NiO can form at temperatures above 575 °C.

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## 1. Introduction

Molten carbonate electrolysis (MCE) has been demonstrated to be a promising approach towards green metallurgy without  $\text{CO}_2$  emissions [1–4] and  $\text{CO}_2$  utilization (CCU) [5,6]. A robust inert anode for oxygen evolution in high temperature molten salts is crucial for the success of these processes [1,3,7]. In this regard, Au, Pt, Ir and  $\text{SnO}_2$  have been shown to be stable in molten carbonates [6,8], but Au, Pt, Ir are noble metals and  $\text{SnO}_2$  exhibits poor catalytic activity for oxygen evolution in the melt [6,9]. Consequently, Ni-based alloys are attractive anode candidates for industrial-scale applications in molten salts for their high corrosion resistance [10–13], excellent high-temperature mechanical properties [14–16] and relatively low cost [17]. In fact, Ni-based lithiated NiO ( $\text{Li}_x\text{Ni}_{1-x}\text{O}$ ) cathodes have been applied in molten carbonate fuel cells (MCFCs) for over 5000 h at 600 °C [18,19]. Many data exist concerning the NiO MCFC cathode, but less is known concerning the MCE anode.  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  maintains a cubic NiO structure for  $0 < x < 0.3$ , but shifts to a hexagonal  $\text{LiNiO}_2$  structure for  $0.3 < x$

$< 0.5$  [20]. The stability and solubility of the lithiated nickel oxide was widely investigated in molten carbonates, which depends on  $\text{CO}_2$  and  $\text{O}_2$  partial pressure or the cathode potential [21]. The anode of the MCE process, however, functions in a more positive potential than that of the MCFC cathode. The  $\text{O}_2$  evolution reaction (OER) occurs on the former electrode, whereas the  $\text{O}_2$  reduction reaction (ORR) occurs on the latter electrode. The  $\text{O}_2$  and  $\text{CO}_2$  are released from the anode of the MCE process, where the ratio of  $\text{O}_2/\text{CO}_2$  and the rate of the gas production are determined by the working potential [22]. The operating condition of the MCE anode is quite different from the MCFC cathode. Nevertheless, nickel and nickel-based alloys have been demonstrated as promising candidates for anodic materials in the MCE processes at temperatures beyond 750 °C [1,2].

Although temperature dependence of the solubility of NiO in MCFCs has been reported in several papers [18,23,24], none of the electrochemical studies have specifically addressed the temperature effect on the stability of the nickel anode in a MCE bath. Serious corrosion of nickel and a Ni-10wt%Cu-11wt%Fe alloy anode was observed at 500 °C in a  $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  eutectic melt [6]. However, our group demonstrated nickel alloy to be a long-term stable anode in molten  $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$  at 750 °C [1]. Licht et al. reported that Inconel alloy and nickel anode remained stable in

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molten  $\text{Li}_2\text{CO}_3$  in the temperature range from 750 °C to 950 °C [2]. To the best of our knowledge, the abnormal temperature effect of nickel anodes as described above has not been fully investigated. A thorough understanding of the mechanism is crucial for developing a satisfactory inert anode for molten carbonate electrolysis in a wide temperature range and for protecting the corrosion of nickel and nickel alloys in molten carbonate devices (MCFCs and solar thermo-power plants) and technologies (MCEs).

In the present work, the stability of nickel under anodic polarization was investigated by linear sweep voltammetry in the temperature range from 450 °C to 750 °C in a ternary molten carbonate of a  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$  eutectic. The critical temperature of the activation-passivation transition of nickel electrode was determined for the first time. Furthermore, the mechanism of the special anodic behaviour was explored by cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD).

## 2. Experimental

### 2.1. Materials and electrochemical measurements

An alumina crucible filled with 500 g of anhydrous  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$  (mixed in a eutectic molar ratio of 43.5:31.5:25.0) was placed in a sealed stainless steel reactor. All the reagents were of analytical purity and purchased from the Sinopharm Chemical Regent Co. Ltd., China. The mixed salt was dried at 300 °C for 24 h in air and then melted at 850 °C in an argon atmosphere. The temperature was then cooled in preparation for the electrochemical measurements. Nickel and platinum wire (each 1 mm in diameter) were sealed in alumina tubes by high-temperature cement mixed with nano- $\text{Al}_2\text{O}_3$  powder, with 10 mm of the wire exposed from the alumina tubes to function as the working electrode. NiO or  $\text{Ni}_2\text{O}_3$  loaded platinum electrodes were manufactured by dipping platinum wires into a NiO (AR, 98%) or  $\text{Ni}_2\text{O}_3$  (AR, 99%) powder/ethanol suspension (3 g of NiO or  $\text{Ni}_2\text{O}_3$  in 5 mL of ethanol, prepared under sonication). A silver wire inserted in an alumina tube filled with 5 g of  $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$  (molar ratio of 43.5:31.5:25.0) and 0.5 mmol  $\text{Ag}_2\text{SO}_4$  (AR, 99.7%) salt was used as the reference electrode [25]. Electrochemical measurements were performed on a CHI1140 electrochemical workstation (Shanghai Chenhua Instrument Co. Ltd., China) in argon atmosphere, and the experimental time was restricted within 1 h at every temperature to minimize the decarbonation of molten salt. Anodic polarization curves were recorded by linear sweep voltammetry (LSV) using a nickel/platinum wire working electrode from the open circuit potential (OCP) to 1.2 V (vs.  $\text{Ag}^+/\text{Ag}$ ) at a sweep rate of 5 mV/s. Cyclic voltammetry (CV) measurements were conducted using the nickel wire electrode, the NiO loaded platinum electrode or  $\text{Ni}_2\text{O}_3$  loaded platinum wire electrode at a potential scan rate of 100 mV/s (650 °C, 750 °C) or 50 mV/s (550 °C), respectively.

### 2.2. Material characterization

The anodic oxidation products of nickel were characterized by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab 250Xi spectrometer, Al  $K\alpha$  X-rays,  $E_{\text{photon}} = 1486.7$  eV), X-ray diffraction spectroscopy (XRD, Shimadzu X-ray 6000 with Cu  $K\alpha 1$  radiation at  $\lambda = 1.5405 \text{ \AA}$ ) and scanning electron microscopy (SEM, FEI Sirion field emission). The samples were prepared by potentiostatic polarization of nickel plates ( $2 \times 4 \text{ cm}^2$ ) at 0.7 V vs.  $\text{Ag}^+/\text{Ag}$ , which is close to the practical operating potential of the anode in MCE process, in the melt at temperatures of 850 °C, 750 °C, 650 °C, 550 °C and 450 °C, respectively. After the electrodes were removed from the melt, they were rinsed with deionized

water to remove the adherent electrolyte and dried in a vacuum oven at 80 °C.

## 3. Results and discussion

### 3.1. Unusual temperature effect on the anodic stability of nickel

Fig. 1b presents the anodic polarization curves of fresh nickel electrodes in molten  $\text{Li}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--Na}_2\text{CO}_3$  at different temperatures. For reference, the polarization curve of a Pt electrode at 750 °C is also shown. As seen, the onset potential for the oxidation of carbonate ions to  $\text{O}_2$  verified by the platinum electrode is approximately 0.4 V vs.  $\text{Ag}^+/\text{Ag}$ . Further, the anodic behaviour of nickel was strongly dependent on temperature, and its corrosion rate was retarded when the temperature increased beyond 575 °C. There exists an activation-passivation transition temperature at 575 °C (Fig. 1b); active dissolution occurs below this temperature, whereas nickel is passivated beyond it.

Visual observation of the electrodes (Fig. 1a) after consecutive anodic polarization tests (Figs. S1–S7, anodic polarization curves conducted repeatedly for 6 times at 450 °C, 500 °C, 550 °C, 575 °C, 600 °C, 650 °C and 750 °C, respectively) at each temperature further confirms the unusual temperature effect on the stability of the nickel anode. No dimensional changes on the nickel electrodes were observed at 575 °C, 600 °C, 650 °C and 750 °C, but serious dissolution happened at the temperature below 550 °C (Fig. 1a). Active dissolution of nickel was observed at 450 °C (Fig. S1) and 500 °C (Fig. S2). The reduced working area resulting from the rapid anodic dissolution of nickel caused the decreasing anodic current in the potential range more positive than 0.4 V with increasing scan numbers, as evidenced in Fig. 1a, in which the exposed wires completely disappeared after 6 polarization cycles. At 550 °C, the anodic current decreased after two polarization tests (Fig. S3) and an oxide film started to form on the nickel electrode (Fig. 1a). However, this film did not provide corrosive protection to the electrode. In contrast, the anodic current became very small before the oxidation of carbonate ions to  $\text{O}_2$  after 6 cycle sweeps at 575 °C, 600 °C, 650 °C and 750 °C (Figs. S4–S7), demonstrating that a protective and electronically conductive film formed on the nickel electrode. As shown in Fig. 1a, the diameters of the nickel electrodes remained almost unchanged but were covered by dark films at the investigated temperatures.

There are two anodic current peaks (a1 and a2) on the nickel electrode prior to the oxidation of carbonate ions to  $\text{O}_2$ , as shown in Fig. 1b. The peak a1 is related to the formation of NiO, whereas a2 is ascribed to trivalent nickel compounds [26]. The current density of a2 at 500 °C is larger than that at 450 °C but smaller than that at 550 °C because of active dissolution of the nickel anode below 500 °C and porous film formation at 550 °C. The anodic current before oxygen evolution continuously decreases with increasing temperature beyond 575 °C, indicating the formation of a protective film at higher temperature. Fig. 1c shows the 5th cycle of the anodic polarization curves at temperatures above 575 °C. As seen, the passivation current in the potential region before oxygen evolution follows the order of 750 °C < 650 °C < 600 °C < 575 °C (inset in Fig. 1c), which demonstrates that the stability of the anodic film increases with increasing temperature in the range from 575 °C to 750 °C.

### 3.2. Mechanism of the temperature-dependent effect

#### 3.2.1. Electrochemical behaviour of Ni(III) and Ni(II) oxides at different temperatures

The chemical composition of an anodic film is crucial to the stability of the nickel anode. Based on the polarization curves shown in Fig. 1b, there exist at least two types of nickel oxidation

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