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Electrochemical performance of Y_2O_3/NiO cathode in the molten $Li_{0.62}/K_{0.38}$ carbonates eutectics

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Abstract

The preparation and subsequent oxidation of Ni cathodes modified by impregnation with yttria were evaluated by surface and bulk analysis. The electrochemical behavior of Y_2O_3/NiO cathodes was also evaluated in a molten 62 mol% Li_2CO_3 + 38 mol% K_2CO_3 eutectic at 650 °C by electrochemical impedance spectroscopy (EIS) as a function of yttria content and immersion time under the standard cathode gas condition (CO_2:O_2 = 67:33%). The stability tests of Y_2O_3/NiO cathodes showed that the yttria additive could dramatically reduce the solubility of NiO in the eutectic molten Li/K carbonates due to the preferential dissolution of yttria. The loss of yttria was confirmed by chemical analysis and X-ray diffraction (XRD). The Y_2O_3/NiO cathodes showed higher catalytic activity for oxygen reduction and lower dissolution of NiO than the pure NiO cathode. The cathode material with 1.0 wt.% of yttria showed the optimum behavior.

Keywords: A. Oxides; C. Impedance spectroscopy; C. X-ray diffraction; D. Catalytic properties

1. Introduction

The molten carbonate fuel cell (MCFC) is believed to be one of the most promising energy conversion devices that convert chemical energy in fossil fuels into electricity in the near future owing to the high energy conversion efficiency, the unparalleled environmental characteristics and the ability to utilize a wide variety of fuels such as hydrogen, natural gas and coal gasified gas. Therefore, it has been gaining attention as a new energy source. The state-of-the-art MCFC nickel cathode, oxidized in situ and lithiated ($Li_xNi_{1-x}O$), has a good electro-conductivity and electrochemical-catalytic activity for the oxygen reduction reaction, but is still insufficient to satisfy the long lifetime of 40,000 h for commercialization of MCFC because NiO presents a relatively high solubility in the electrolyte which can be Li_2CO_3–K_2CO_3, Li_2CO_3–Na_2CO_3 or related alkali molten carbonate eutectics, resulting in short circuit between cathode and anode [1,2].

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Many efforts have been made to solve the NiO dissolution problem [3–7] and several possible approaches have been studied. More basic molten carbonate melts such as Li/Na carbonate eutectic have been used to decrease the Ni dissolution rate in the melt. Alkaline earth metal salts based on Ba or Sr have also been used as additives to increase the basicity of the melt. In addition, several materials like $LiFeO_2$, $LiCoO_2$, Li_2MnO_3 and $La_{1-x}Sr_xCoO_3$ were also investigated as replacement materials for the NiO cathodes because of their extremely low solubility in the carbonate melts [8]. However, the exchange current density for the oxygen reduction reaction on these materials is about two to four orders of magnitude lower than that on NiO. Thus, the slow kinetics of the oxygen reduction reaction limits further improvement of cathodes based on these materials. Recently, new candidate materials such as $LiCoO_2$($LiFeO_2$, $La_{0.8}Sr_{0.2}CoO_3$)-coated NiO have been proposed [9–11].

The most promising way to modify the properties of nickel oxide appeared to be the incorporation of metal oxides into the nickel oxide [12–15]. In this paper, a cathode material has been prepared based on modifying NiO by yttria impregnation, in order to decrease cathode dissolution rate and increase its catalytic activity for oxygen reduction. The present paper is aimed at studying the effect of yttria content on the electrochemical behavior of the new cathode materials in molten carbonates. The study has been conducted using electrochemical impedance spectroscopy (EIS). The phases and microstructures of the cathode materials before and after immersion in molten carbonate were analyzed by X-ray diffraction (XRD). The dissolution of the cathode material in molten carbonates was evaluated using melt analysis.

2. Experimental

2.1. Starting materials

The material system used in this work was based on carbonyl nickel powder, yttria powder, solvent, dispersant, binder and plasticizer. The carbonyl nickel particles (purity: 98%; Shanghai Jinjiang Metal Powder Ltd., China) have a perfect orbicular shape and a narrow size distribution of 2.2–2.8 μm. The Y_2O_3 powder was of an analytical grade (purity: 99.99%; Shanghai Chen. Ltd., China). The solvent system used in this paper consisted of azeotropic mixture of cyclohexanone and butyl alcohol in order to avoid differential evaporation. Glycerol trioleate was used as zwitterionic dispersant. Poly-vinyl-butyl (PVB) and polyethylene glycol (PEG 200) were used as binder and plasticizer, respectively. The PVB binder was supplied as a free flowing fine-grained powder and the PEG plasticizer was obtained in a liquid form. All organic additives were supplied by Shanghai Chem. Ltd., China.

2.2. Preparation of Y_2O_3/NiO cathodes

Porous Y_2O_3/NiO cathodes were prepared by tape casting and subsequently sintering and oxidation process. The slurries for the tape casting process were fabricated by a ball milling method that included two steps. Firstly, 50 g of Ni power containing 0, 0.3, 0.6 and 1.0 wt.% of Y_2O_3 powder (referred to as Ni) was ball-milled in 40 g cyclohexanone/butyl alcohol solvents with 1 g dispersant for 4 h. Secondly, 5 g PVB and 5 g PEG were added to the above system and ball milled for an additional 4 h. After that, the slurry was degassed using a vacuum pump (pressure: 200 mbar absolute) and cast on a casting surface of polyethylene film by a ‘‘doctor-blade’’ method. After the solvent in the tape was completely evaporated, the nickel green tape was obtained. The sintering process of the green tapes was carried out in 75 vol.% H_2/25 vol.% N_2 atmosphere at 850 °C for 1 h. Detailed procedures for cathode preparation and sintering are presented elsewhere [16]. The various nickel plates were then oxidized in the air at 850 °C for 6 h, the porous Y_2O_3/NiO cathodes were thus obtained.

2.3. Electrochemical characterization

The electrochemical characterization of the new cathode materials was performed on the porous electrode/molten carbonates interface by means of EIS. The test cell was an alumina crucible contained in a covered quartz vessel. The cover of vessel had been adapted to accommodate a thermocouple, a gas inlet/outlet and two electrodes. The working electrode was composed of the new cathode material connected to a Pt lead (0.5 mm in diameter) that is shielded from the electrolyte by an alumina tube sealed by ceramic cement at the base of the tube. The counter electrode was identical to the working electrode. Such a configuration allows elimination of the influence of the counter electrode and avoids