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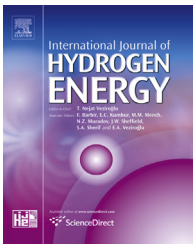

Enhancing Ni anode performance via Gd_2O_3 addition in molten carbonate-type direct carbon fuel cell

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ABSTRACT

Recently, there is a consensus that a limited performance in direct carbon fuel cell (DCFC) using molten carbonate electrolyte is caused by the limited triple phase boundaries (TPB) formation. In order to solve this problem, we added Gd_2O_3, a well-known lanthanide oxide material for the improvement of wettability in the Ni anode. As a result, it was clearly shown that the voltage drop level and charge transfer resistance was decreased, and therefore the peak power density was increased by almost two times that of solely Ni anode to reach up to 106.7 mW/cm^2 with carbon black and 114.1 mW/cm^2 with actual coal fuel. The increased wettability led to the improvement of triple phase boundary (TPB) formation and consequently the enhancement of DCFC performance. While the wettability was increased with oxide content in Ni anode, the proportion of Ni at the surface of anode and the electronic conductivity was gradually decreased. With this reason, the peak power density showed the volcano type change with the amount of Gd_2O_3 addition. Finally, it was revealed that the optimum composition for the anode was Ni:Gd_2O_3 = 1:5 in weight ratio.

Introduction

Recently, new light has been shed on the value of coal as an energy source. Coal is catching on as an energy source that provides higher cost efficiency and more abundant reserves compared to other energy sources. Thus, fuel cell systems that use coal for fuel have also been attracting a great attention. The Direct Coal (or Carbon) Fuel Cell (DCFC) converts the chemical energy of coal as fuel into the electric energy directly with a very high level of fuel utilization [1,2]. The theoretical efficiency of DCFC ($\eta = \triangle G/\triangle H = 1 - T\triangle S/\triangle H$) is slightly over 100%, because unlike general fuel cells, DCFC uses solid fuel, and accordingly, entropy changes in fuel cell reaction have a positive value ($\triangle S = 1.6$ J K^{-1} mol at 600 °C), which in turn, lead to a bigger change in Gibbs free energy ($\triangle G = -395.4$ kJ mol^{-1} at 600 °C) than in enthalpy ($\triangle H = -394.0$ kJ mol^{-1} at 600 °C). In addition, because the fuel, carbon and the product, CO_2, exist in the form of different phases, the chemical potentials (activities) of fuel do not

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change depending on the level of fuel reaction. With this reason, a fuel utilization can be maximized by minimizing Nernst loss, and therefore, DCFC can produce higher efficiency in comparison to other types of fuel cells using gas fuel [2]. Also, DCFC has many advantages, such as a simple structure to allow easy module construction, less air pollution and less noise to allow for urban construction, and a high energy density to allow for a small construction area [2]. Thanks to those advantages, DCFC is considered to be applicable as a next-generation energy source with high efficiency. To date, most of studies on DCFC have mainly concentrated on an technical approach based on Solid Oxide Fuel Cells (SOFC) and Molten Carbonate Fuel Cells (MCFC) [2,3].

In order to improve the performance of DCFC, one of the key issues is developing a highly active anode material for the direct oxidation of carbon. Given that sluggish kinetics in carbon result in a more dominant impact from polarization loss, it is very important to improve the kinetics in the anode so as to achieve a high performance of DCFC [4]. Another major technical issue is related to difficulties in creating an anode reaction zone or triple phase boundaries (TPBs) [5]. To address this issue, various approaches have been recently reported in the literature. Kulkarni et al. proposed mixed ionic electronic conductors (MIEC) that exhibit both ionic and electronic conductions and should be used as an anode material as any use of electrodes having only electronic conductivity put limits in the creation of TPBs between electrolytes and electrodes. When ionic conduction and electronic conduction are simultaneously achieved, the reaction occurs on all surfaces of electrode particles to improve the limited creation of TPBs. Therefore, they intended to improve TPBs by using the MIEC for the anode. Among various MIEC materials, the lanthanum strontium cobalt ferrite (LSCF) was deployed to build button cells. The fuel used was a carbon black (Vulcan XC-72) and the peak power density obtained was 50 mW/cm^2 [5]. Meanwhile, in the research field of MCFC it was widely recognized that the addition of some kinds of oxide materials in the anode could increase the wettability with molten carbonate electrolyte [6–8]. Hong et al. reported that when Al oxide was added by 4 wt% in the Ni anode, the wettability increased from 14.1% to 40%. Also, during a 500-h operation, the anode containing Al oxide was much more stable in comparison to the anode composed of solely Ni, implying that it can also lead to the durability enhancement [9]. Ce oxide has been also considered to be a promising additive for Ni anode. Wee et al. found that the Ce oxide-added anode showed an increase in contact angle, thus improving wettability compared to the Ni electrode. Moreover, through the 200-h durability test it was discovered that the anode with an addition of 3 wt% Ce remained much more stable in comparison to the Ni anodes [10]. Also, Shin et al. added 10 wt% Gd_2O_3, lanthanide material to Ni/MgO anode used for internally reforming catalysts of MCFC and identified a significant increase in catalytic activity and an improvement in the degree of dispersion [11]. In particular, among various lanthanide oxide materials, Gd_2O_3 was found to be the best additive for the anode performance enhancement through the measurement of electron back scattered diffraction (EBSD) [12].

In this study, we attempted to enhance the performance of MCFC-based DCFC by increasing the wettability with the addition of Gd_2O_3 which showed a positive effect to enhanced the performance of MCFC in the previous literature. An anode having various amounts of Gd_2O_3 was prepared in order to identify the effect of the Gd_2O_3 content. The anode performance was examined through I–V and I–P curves, and the electrochemical impedance spectroscopy (EIS) was deployed to measure the charge transfer resistance in the anode.

Experimental

In this study, Gd_2O_3 was added in producing an anode with an aim to improve TPBs creation by the addition of an oxide. In the fabrication of the anode, the Gd_2O_3 (powder, 99.9% trace metals basis, Sigma Aldrich) was added to NiO (nano powder, <50 nm particle size, 99.8% trace metals basis, Sigma Aldrich) with various ratio. Also, for maximizing the reaction area in the electrodes, carbon black (acetylene black, Alfa Aesar) as a fuel was directly added and then the anode was produced in the form of a pellet by hot pressing. For the comparative studies on the effect of fuel type, we additionally tested two actual coals having different volatile matter content, such as the Shenhua coal (containing about 30% of volatile matter) and the Openblue coal (containing about 50% of volatile matter). The prepared anode was thermally treated at the temperature of 700 °C. Molten carbonate (Li_2CO_3–K_2CO_3) was used as an electrolyte. Detailed information on the components of cathodes and matrixes is described in Table 1 below. And component analyses of Shenhua and Openblue coals were conducted using the standard method [13] described below and the results are presented in Table 2.

A button cell type test system as shown in Fig. 1 was employed for this study. After being placed and fixed on a ceramic tube, the components are placed in a furnace where gas can move in and out. The gas flow was controlled by the Mass Flow Controller (MFC). The temperature of the cell in the furnace was initially increased with 5 °C/min to 350 °C in air. The CO_2 gas was firstly provided in order to prevent the electrolyte loss at the temperature zone between 350 °C and 400 °C where the electrolyte melting is begun [2,14]. During the temperature increase, a mixture of 60 mol % air and 40 mol % CO_2, was supplied to the center of the electrode through a tube. The temperature in the furnace was raised by 2 °C/min to 450 °C. The CO_2 gas provision was continued until the temperature reached 700 °C (the temperature of the cell was increased with 5 °C/min to 700 °C).

Table 1 – Specification of components for the button cell type DCFC.

Component		Specification
Anode	Diameter	1.7 cm
	Current collector	Pt mesh
Cathode	Material	NiO
	Diameter	1.9 cm
	Current collector	Pt mesh
Matrix	Material	$LiAlO_2$
	Diameter	2.85 cm
Electrolyte	Material	62 mol%Li_2CO_3–38 mol%K_2CO_3
	Diameter	2.85 cm