Effect of Fe_2O_3 metal oxide on the discharge of a direct lignin SOFC

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Introduction

Biomass, especially lignin, has been attracting attention as a renewable and carbon-neutral energy resource. In this study, we focused on a solid oxide fuel cell (SOFC) that can convert lignin directly into electricity with high efficiency. Generally, when lignin is pyrolyzed at temperatures below 1000 °C, tar and char are easily produced. To use lignin as fuel at 800 °C, the typical operating temperature of SOFCs, it is necessary to accelerate the anode reaction of such difficult-to-decompose products. For this purpose, we investigated the improvement of energy efficiency by adding transition metal oxides to the anode as gasification catalysts and/or pseudo-fuels.

Experimental Procedures

An alumina Tamman tube chamber filled with lignosulfonate and transition metal oxides (MO_x: Fe_2O_3, CuO, CoO, NiO, fixed at 1.26 mmol metal equivalents) was attached to the anode side of a Pt | YSZ | Pt cell to analyze the pyrolysis behavior and anodic reaction activity in the presence and absence of MO_x. The pyrolysis behavior of lignosulfonate was analyzed from room temperature to the operating temperature of 800 °C at a rate of 6.6 °C min^{-1} in an argon (Ar) flow by comparing the cell voltage change with the TG-DTA curve and evolved gas composition (GC). The anodic reaction activity was studied by measuring I-V and V-time at 0.03 A cm^{-2}. The properties of MO_x as a pseudo-fuel were determined by the amount of carbonaceous residue after discharge and the redox state of MO_x using XRD and CV at 5.0 mV s^{-1}. The reaction mechanism in the chamber was investigated using anode-supported Ni-YSZ | YSZ | GDC | LSC-GDC cells, with the impact of the MO_x / Lignosulfonate ratio on the gravimetric energy density at 0.10 A cm^{-2} and the oxidation state of MO_x after discharge.

Results and Discussion

Lignosulfonate gradually pyrolyzed with increasing temperature, residues such as tar, char, and ash amounting for 36% of the charge weigh remained even at 800 °C. The residues had a slow anode reaction rate and could not stably discharge the fuel cell.

As a result of adding various metal oxides (MO_x) to the anode, among them, Fe_2O_3 acted best as a pseudo-fuel and promoted the anode reaction most dramatically. Fe_2O_3 reacts with lignosulfonates to reduce it metallic iron, and then the valence changes to FeO, Fe_3O_4, and then Fe_2O_3 through an anodic reaction, enabling stable discharge over a long period of time (Figure 1). In Contrast, CuO, CoO, and NiO remained reduced to metal, but these metals contributed little to the discharge reaction.

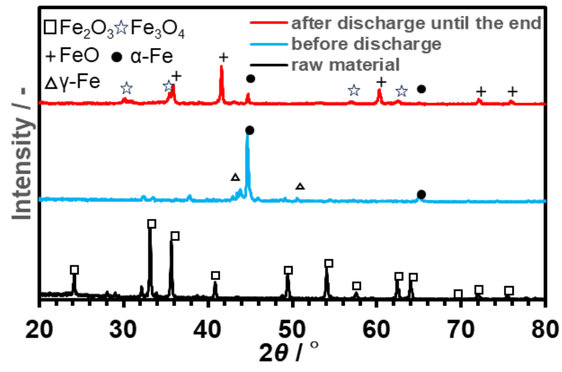

Figure 1 XRD patterns for the lignosulfonate–Fe_2O_3 mixture before and after discharge.

A power density of 0.35 W cm^{-2} was obtained for power generation in the anode-supported SOFC. Interestingly, the gravimetric energy density (Wh g^{-1}) of the lignosulfonate resource increased with increasing resource amount, reaching a maximum value of 0.49 Wh g^{-1} (Figure 2). This was interpreted as being because the Fe_xO_y produced by the discharge acts as a catalyst for the Boudouard reaction [1][2], in which residual carbon reacts with CO_2 to produce CO, thus regenerating Fe metal again, repeating the loop. This energy density value is comparable to 18.3% of the higher heating Value (HHV) of lignosulfonate, 2.68 Wh g^{-1} [3].

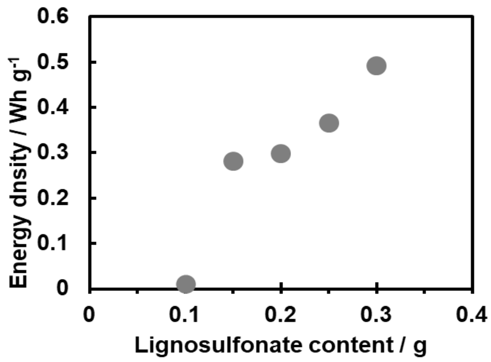

Figure 2 Gravimetric energy density of lignosulfonate.

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