37th Topical Meeting

of the International Society of Electrochemistry

9 - 12 June 2024
Stresa, Italy

Electrochemical energy for a greener and more sustainable future society

PROGRAM

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Solid-solution Driven Metallic Active Sites in Perovskite Anodic Layer for Direct Ethanol Solid Oxide Fuel Cell

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Solid oxide fuel cells (SOFC) running on ethanol are emerging as an attractive power source for different applications such as distributed power and mobility. Bioethanol is a widely available renewable fuel and an interesting alternative carrier for carbon-neutral hydrogen due to easy storage and distribution. Such a liquid fuel has a high energy density and has been considered as possible sustainable fuel for SOFCs. Such features are extended to the new generation of metal-supported SOFC, which have been used in ethanol-fueled prototype electrical vehicles. However, as with any carbon containing fuel, ethanol imposes some challenges for its direct use in SOFC due to possible deactivation of the standard Ni-based cermet anodes. Carbon deposition develops on the Ni nanoparticles if no oxidizing agent (usually, water) is added to the fuel inlet. Stable operation of ethanol SOFC was demonstrated at $T \geq 800$°C by decoupling the electrochemical and catalytic reactions by a catalytic layer deposited over the Ni cermet anode. However, more widespread application of such systems requires lowering the operating temperature to the 600-700°C range. Nevertheless, such range is known to favor carbon formation and, thus, catalytic active anodes are necessary for durable ethanol-SOFC.

As a prototype compound for the anode catalytic layer, the p-type electronic conductor lanthanum chromite $LaCrO_3$ perovskite is compatible with the SOFC components and exhibits high stability in both reducing and oxidizing atmospheres at high temperature. Catalytic activity for the ethanol steam reforming ESR was induced in lanthanum chromite ceramics by Ru species generated from solubilized ionic ruthenium in defective sites of the surface of nanostructured $LaCr_{1-x}Ru_xO_3$ compounds. Single-phase $LaCr_{1-x}Ru_xO_3$ (LCRu) solid solutions with $0.10 \leq x \leq 0.20$ are shown to be stable catalysts for ESR. The effect of reducing conditions of LCRu on the catalytic properties of different ruthenium active species was investigated by spectroscopic techniques such as synchrotron X-rays absorption and X-rays photoelectron spectroscopy. The Ru-doped lanthanum chromite catalyst was applied as catalytic layer for internal ethanol steam reforming in solid oxide fuel cells. The LCRu catalysts were optimized for operating temperatures in the 600-700 °C range to promote stable ethanol reforming. The microstructure of the deposited catalytic layer was controlled using pore formers with low burnout temperature. The performance of the fuel cells was evaluated at 700 °C under hydrogen and dry ethanol. The LCRu catalytic layer had no significant impact on the electrochemical properties of the fuel cells and samples with catalytic layer or without it exhibited similar performance in hydrogen. Nonetheless, ethanol durability tests have shown that the catalytic layer plays a crucial role for the stability of both the anode and the metal supported SOFC. The experimental results indicate that controlling the reduction of the solid solution dispersed ionic species in defective mixed-valence oxide surfaces is an efficient strategy to generate highly active catalytic particles for reactions such as ethanol steam reforming in direct ethanol SOFC.

The support of Nissan and the Brazilian agencies FAPESP, CNPq, and CNEN is acknowledged.