



Gadolinia-Doped Ceria Cathodes for Electrolysis of CO₂

These electrodes have relatively low area-specific resistances.

John H. Glenn Research Center, Cleveland, Ohio

Gadolinia-doped ceria, or GDC, ($Gd_{0.4}Ce_{0.6}O_{2-\delta}$, where the value of δ in this material varies, depending on the temperature and oxygen concentration in the atmosphere in which it is being used) has shown promise as a cathode material for high-temperature electrolysis of carbon dioxide in solid oxide electrolysis cells. The polarization resistance of a GDC electrode is significantly less than that of an otherwise equivalent electrode made of any of several other materials that are now in use or under consideration for use as cathodes for reduction of carbon dioxide. In addition, GDC shows no sign of deterioration under typical temperature and gas-mixture operating conditions of a high-temperature electrolyzer.

Electrolysis of CO₂ is of interest to NASA as a way of generating O₂ from the CO₂ in the Martian atmosphere. On Earth, a combination of electrolysis of CO₂ and electrolysis of H₂O might prove useful as a means of generating synthesis gas (“syngas”) from the exhaust gas of a coal- or natural-gas-fired power plant, thereby reducing the emission of CO₂ into the atmosphere. The syngas — a mixture of CO and H₂ — could be used as a raw material in the manufacture, via the Fisher-Tropsch process, of synthetic fuels, lubrication oils, and other hydrocarbon products.

An electrolysis cell of the type of interest here consists of a solid oxide electrolyte coated on each side with a porous electrode (see Figure 1). A suitable electric potential is applied to the electrodes, causing electrolysis of CO₂ to proceed via overall reaction $CO_2 \rightarrow CO + O$. At the cathode, carbon dioxide is reduced to carbon monoxide and negative oxygen ions in the half-cell reaction $CO_2 + 2e^- \rightarrow CO + O^{2-}$. The carbon monoxide leaves the cell in the carbon dioxide stream. The solid oxide electrolyte conducts the O²⁻ ions (that is to say, the O²⁻ ions diffuse across the solid oxide electrolyte). Upon reaching the anode, the oxygen ions combine to

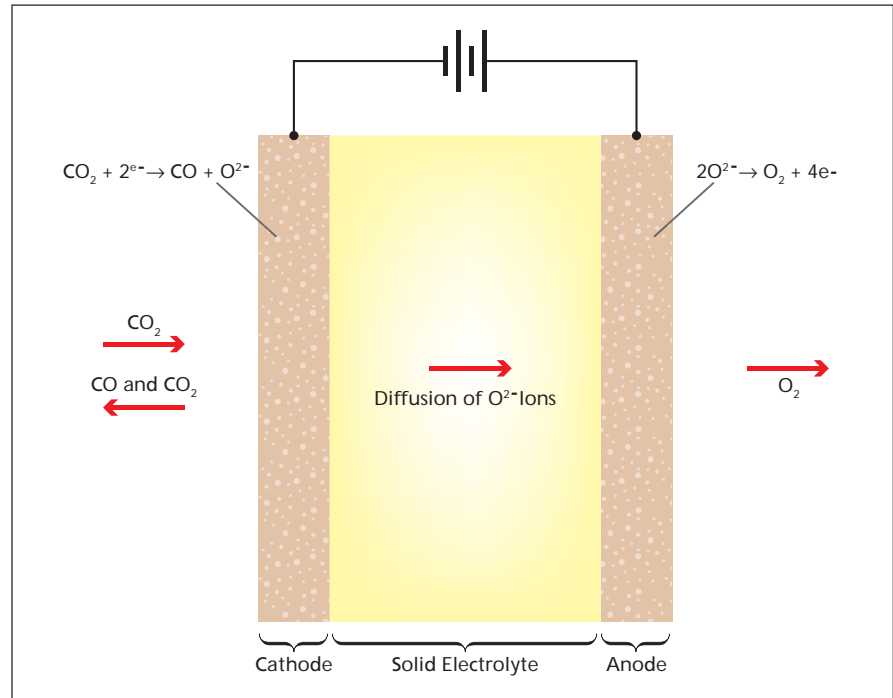


Figure 1. This Schematic Diagram depicts the basic operation of a solid-oxide CO₂-electrolyzer cell.

form oxygen molecules, the overall half-cell reaction sequence being $2O^{2-} \rightarrow 2e^- + O_2$. If the solid oxide electrolyte is made of yttria-stabilized zirconia (YSZ), then it conducts only oxygen ions (but not CO₂ or CO), so that essentially pure oxygen is produced on the anode side.

This process is energy-intensive: The enthalpy of the overall reaction is positive and very large (+283 kJ/mole) — comparable to the enthalpy for the electrolysis of water

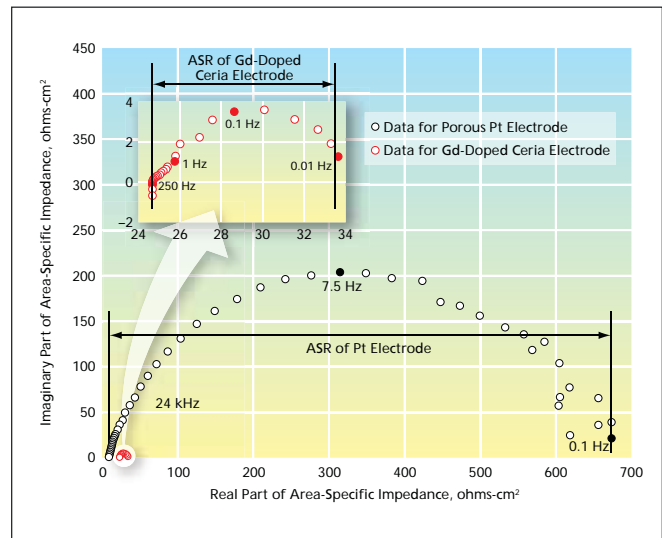


Figure 2. A Nyquist Plot of the AC Impedance Spectra for a GDC and porous Pt electrodes shows measured results on symmetric cells under zero-bias voltage conditions. The measurements were made during operation of the cells at a temperature of 800 °C in a mixture of 5 mole percent of CO and 95 mole percent of CO₂ at a pressure of 1 atm (=0.1 MPa). The ASR of each electrode is the difference between the intersections of its spectral plot with the real axis.

(+286 kJ/mole). In order to make this process economically viable, it is necessary to minimize any irreversible energy losses, notably including those associated with overpotentials and ohmic resistances.

In most of the previous work on electrolysis of CO₂ in cells containing YSZ solid electrolytes, both the cathodes and the anodes have been made of porous Pt. The choice of GDC as the present candidate cathode material was prompted by several considerations:

- GDC is much less expensive (about \$1,200 per kilogram of GDC versus about \$39,000 per kilogram of Pt at 2005 market prices).
- Ceria is known to enhance oxidation of CO when used as a catalyst support in automobile catalytic converters.
- Ceria appears to be an effective an electrocatalyst for oxidation of CO/H₂ mixtures and low molecular weight hydrocarbons (methane) in solid oxide fuel cells.
- GDC acts as a mixed conductor: it conducts both ions and electrons, enabling CO₂-reduction reactions to occur over a larger electrode area and volume than would otherwise be avail-

able for such reactions, thereby reducing the polarization resistance below that of a comparable electrode made of a different material.

Therefore, the performance of GDC as a candidate cathode material, in comparison with the performance of porous Pt as a cathode material, was investigated via electrochemical measurements on symmetric GDC/YSZ/GDC cells and compared with similar measurements on a symmetric Pt/YSZ/Pt cell. Each GDC/YSZ/GDC cell was fabricated by brushing a GDC/organic-binder mixture onto both faces of a thick cylindrical YSZ pellet, then sintering the cell at a temperature of 1,250 °C. The experiments involved several different CO/CO₂ mixtures and temperatures from 700 to 950 °C. In the experiments, electrochemical impedance spectroscopy (EIS) was performed. Area-specific resistance (ASR) values were calculated from the EIS measurements. The ASR values for the cells containing GDC electrodes were found to be substantially lower than that of the cell containing Pt electrodes under identical test conditions, as shown in Figure 2. Lower ASR values are expected to translate to lower

overpotentials and, hence, lower power consumption in electrolyzers.

On the basis of limited published data, it appears that the ASRs of GDC electrodes may also be lower than those of electrodes made of Ni-YSZ, a cermet electrode material commonly used in anodes of state-of-the-art solid-oxide fuel cells. Testing of one of the cells containing GDC electrodes was continued for more than 300 hours, and no degradation of performance was observed; on the contrary, the ASR decreased slightly during the test. In addition, there was no sign of coking (deposition of carbon), which is known to occur in other electrode materials under the gas-mixture and temperature conditions used in the tests.

This work was done by Robert D. Green of Glenn Research Center and Stuart B. Adler of the University of Washington. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18211-1.