V.D.10 Synthesis and Characterization of Mixed-Conducting Corrosion Resistant Oxide Supports

Vijay K. Ramani (Primary Contact), Jai Prakash, Chih-Ping Lo, and Mayandi Ramanathan

Illinois Institute of Technology (IIT)
10 W 33rd Street 127 PH
Chicago, IL 60616
Phone: (312) 567-3064
E-mail: ramani@iit.edu

DOE Managers
HQ: Kathi Epping Martin
Phone: (202) 586-7425
E-mail: Kathi.Epping@ee.doe.gov
GO: Katie Randolph
Phone: (720) 356-1759
E-mail: Katie.Randolph@go.doe.gov

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Fiscal Year (FY) 2011 Objectives

- To develop and optimize innovative non-carbon mixed conducting materials that will serve as corrosion resistant, high surface area supports for anode and cathode electrocatalysts; and
- Concomitantly facilitate the lowering of ionomer loading in the electrode (by virtue of surface proton conductivity of the electrocatalyst support), thereby enhancing performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

Technical Targets

This project addresses the following technical targets:

- <40% electrochemical surface area (ECSA) loss in electrocatalysts using the synthesized supports tested per General Motors (GM) protocol.

- <30 mV electrocatalyst support loss in the synthesized supports after 100 hrs at 1.2 mV; tested per GM protocol.

At the time of writing, the first set of samples prepared have undergone durability testing.

FY 2011 Accomplishments

- Demonstrated that the synthesized RuO_2-SiO_2 catalyst supports possess the following properties: a) high Brunauer-Emmett-Teller (BET) surface areas (260 m^2/g), b) excellent electrical conductivity (up to 24 S/cm), and c) improved electrochemical stability. Start-stop stability tests were performed by cycling electrode potential between 0 V to 1.8 V for 1,000 cycles. The results showed no loss in surface area for the RuO_2-SiO_2 catalyst supports, while a 44% drop in surface area was observed in carbon supports tested as a baseline.
- Synthesized functionalized silica supports with several levels of sulfonic acid functionalization. These materials have demonstrated varying degrees of proton conductivity and electrochemical stability.
- Demonstrated fuel cell performance with a platinum catalyst supported on non-carbon catalyst supports synthesized in this study – Pt/RuO_2-SiO_2.

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Introduction

While Pt supported on carbon is the most commonly used electrocatalyst for polymer electrolyte fuel cells (PEFCs), the carbon support has limitations with respect to its durability at high temperatures and the excursions to high electrode potentials that arise during start-up and shut-down sequences and during fuel starvation. The issue of carbon-carbon corrosion is a major technical barrier. Carbon corrosion facilitates the agglomeration of Pt particles and dissolution of Pt from the support, which leads to a loss in the ECSA of the electrode [1]. To address this issue, the development of non-carbon mixed-conducting catalyst support materials is explored. Desirable properties of these alternative materials include: (i) high surface area; (ii) high electrical conductivity; and (iii) high electrochemical stability. In addition, it is hypothesized that fuel cell performance can be enhanced by utilizing non-carbon catalyst supports that conduct protons on their surface. The addition of sulfonic acid functionalities on the support surface should permit lowering the ionomer content in the electrode, thereby enhancing gas transport to the catalyst site without compromising on the efficacy of ion transport.

Approach

To achieve the first of two objectives discussed above, two approaches have been employed. The first approach involves the development of a core–shell-like RuO_2-SiO_2 structure that serves as the catalyst support. High surface area silica functionalized with sulfonic acid groups (HSO_3-) was used as core matrix. This matrix was further functionalized with a shell layer of RuO_2 to introduce electronic conductivity; the final material was calcined at temperatures ranging from 100–450°C. The electrochemical stability of RuO_2-SiO_2, Pt/RuO_2-SiO_2, and HSO_3-SiO_2 were measured and compared with that of commercial Pt/C and XC-72R carbon. The electrical and proton conductivities and BET surface areas of materials prepared with different extents of functionalization were also measured.

The second approach involved the synthesis of sulfonic acid functionalized silica with a bimodal pore-structure. The intent of this approach was for RuO_2 to be selectively impregnated in the mesopores of the bimodal structure, while leaving the macropores free for reactant and product transport.

Results

BET Surface Area and Electrical Conductivity

A series of core-shell-like structures of RuO_2-SiO_2, have been synthesized and characterized in terms of electrochemical stability, electrical conductivity, and BET surface area values. The BET surface areas of supports with 0, 9, 33, 50, and 60 mol% of RuO_2 were measured to be 1,100, 470, 420, 260 and 220 m^2/g, respectively. These values show considerable improvement over the values obtained with the co-condensation approach reported in our earlier work [2]. The electrical conductivity of the supports was estimated using a 2-point probe by linear-sweep voltammetry. As shown in Figure 1a, the electronic conductivity was significantly higher for the support materials calcined at 450°C than for those calcined at 100°C. X-ray diffraction (XRD) analysis confirmed that the difference was due to the extent of crystallinity of the material that was enhanced while annealing at higher temperatures. Additionally, the increase in conductivity with RuO_2 loading is very sharp up to a loading of 40%, following which the rate of increase of conductivity is less rapid. This difference in the rate of increase of conductivity with loading is attributed to the amount of RuO_2 particles needed for creating optimal pathways (i.e. percolated network) to conduct electrons. Above 40 mol% of RuO_2, there is a sufficient amount of RuO_2 particles available for electron conductivity. The electrical conductivity of the sample with 33 mol% RuO_2 loading is 3 S/cm, a value that is adequate for fuel cell operation. These results suggest that RuO_2-SiO_2 is indeed a viable high surface area catalyst support with adequate electrical conductivity. Given that the BET surface area is drastically lowered as the amount of RuO_2 in the sample is increased,
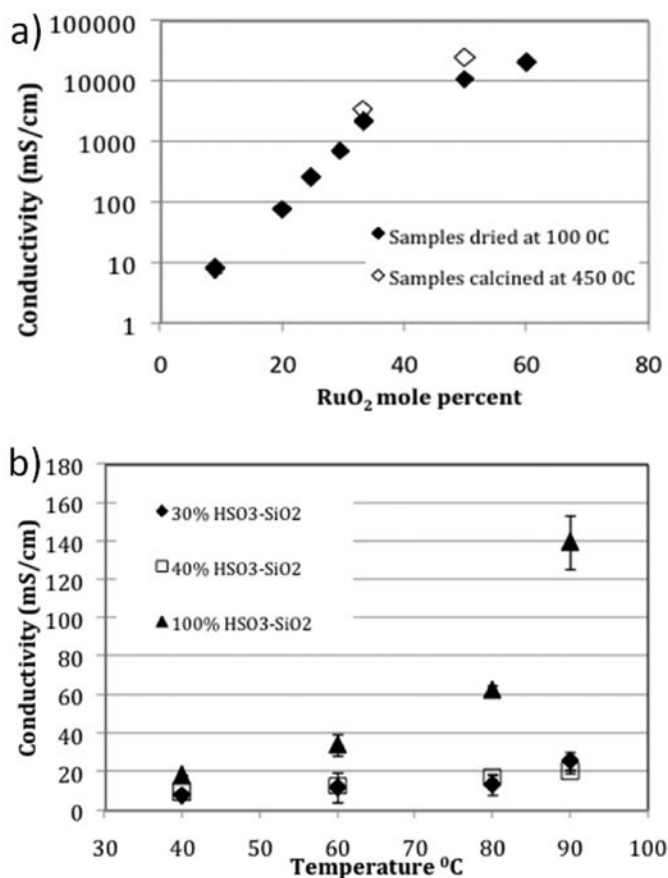

FIGURE 1. (a). Electrical conductivity of RuO_2 functionalized silica. All measurements were obtained at room temperature. (b). Proton conductivity of sulfonic acid functionalized silica at various temperatures. All measurements were obtained at 100% relative humidity (RH).

future research will focus on lowering the RuO_2 content while maintaining or enhancing the electrical conductivity by tuning the distribution of RuO_2 in the silica matrix. To accomplish this task, work has been initiated on the second approach stated above, namely the synthesis of silica with a bimodal pore-structure, wherein the ruthenium oxide can be selectively impregnated in the mesopores, leaving the macropores free for reactant and product transport.

Stability of Catalyst Supports

The stability of the different RuO_2 functionalized silica supports was evaluated by potential cycling using a rotating disk electrode (RDE) setup. The support samples were coated on a glassy carbon (GC) disk electrode and the cycling experiment was carried out in a N_2 saturated 0.1M $HClO_4$ solution. The catalyst support loading was controlled at 200 µg/cm^2 for all experiments. The supports were cycled between 0 to 1.8 V vs. reference hydrogen electrode (RHE) at a scan rate of 1 V/s for up to 1,000 cycles, and cyclic voltammograms (CVs) were recorded at periodic intervals at a scan rate of 10 mV/s. The CVs recorded were analyzed

to assess the double-layer charge (Q_{DL}) of the supports. This metric was employed as a preliminary estimate of support surface area and stability. The stability data obtained using the RuO_2-SiO_2, HSO_3-SiO_2 and XC-72R carbon samples upon potential cycling are shown in Figure 2. Both RuO_2-SiO_2 supports exhibited excellent stability in contrast to carbon, while still showing Q_{DL} values similar to that of carbon. Carbon showed a 44% drop in Q_{DL} after 1,000 cycles due to loss in surface area, while the RuO_2-SiO_2 supports did not show any loss in Q_{DL}. HSO_3-SiO_2 did not show a change in Q_{DL} during potential cycling, but it had a much lower Q_{DL} compared to carbon. The samples tested here have been shipped to NTCNA for further stability evaluation using prescribed protocols. These tests are underway.

Ion Exchange Capacity (IEC)

The IEC of the silica supports functionalized with varying amounts of sulfonic acid groups was measured by titration. The surface area of the functionalized silica was determined by the BET method. The presence of HSO_3 in these samples was confirmed by IEC measurements, which revealed that the samples had an IEC ranging from 1.7-2.1 meq/g. The IEC did not change substantially with extent of functionalization, but was much higher than the near-zero IEC obtained for unfunctionalized silica samples. The BET surface areas of the 20%, 30%, and 40% functionalized HSO_3-SiO_2 samples were 650, 520, and 450 m^2/g, respectively. The BET surface area decreased as the extent of functionalization was increased; however, the values obtained are in excess of requirements even at high levels of functionalization.

Proton Conductivity

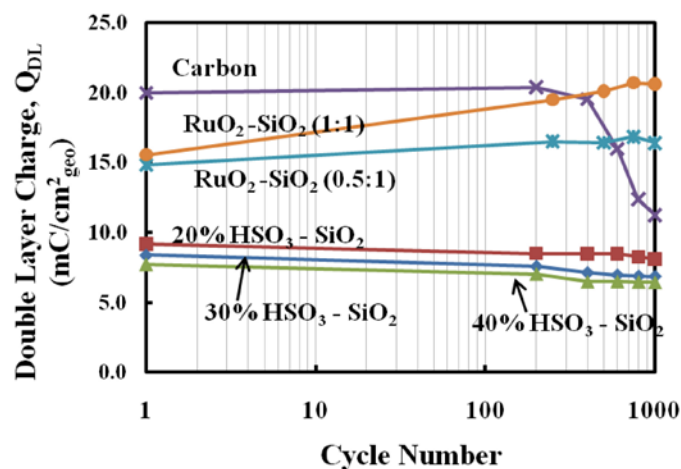Preliminary proton conductivity measurements were performed at 40, 60, 80 and 90°C at 100% RH for samples with 30, 40 and 100% extents of functionalization (data shown in Figure 1b). Proton conductivity measurements were performed with a two-point conductivity cell using electrochemical impedance spectroscopy. A maximum proton conductivity of 140 mS/cm was obtained for 100% HSO_3-SiO_2, while 30 and 40% HSO_3-SiO_2 had much lower proton conductivities in the range of 7-25 mS/cm. In line with expectations, high levels of functionalization of SiO_2 allowed for more efficient proton conduction. However, the 100% functionalized HSO_3-SiO_2 was not thermally stable and decomposed around 100°C. One approach to solve this issue that is currently being pursued is to employ and functionalize templates with greater thermal stability, such as polyhedral oligomeric silsesquioxanes.

Stability of Catalyst

Platinum was deposited on selected non-carbon supports using conventional deposition methods. The stability of the Pt on RuO_2-SiO_2 supports was again characterized by potential cycling using a RDE. The catalyst loading on the GC disk was controlled to 50 μg/cm^2 of Pt and 200 μg/cm^2 of RuO_2-SiO_2 support for all stability experiments. The supports were cycled between 0 to 1.2 V vs. RHE at a scan rate of 1 V/s for up to 10,000 cycles, and CVs were recorded at intermediate points (at 10 mV/s) to determine the ECSA of the Pt.

ECSA was calculated from the difference between the total charge involved in the hydrogen desorption and the double-layer charge using the specific H_{upd} charge of 210 μC/cm^2. The ECSA values for 20% Pt deposited on RuO_2-SiO_2 and 57% Pt/C are shown in Figure 3. The 20% Pt/RuO_2-SiO_2 exhibited consistently high ECSA (>100 m^2/g_{Pt}) and showed high stability for up to 10,000 cycles. The 57% Pt/C showed deterioration of ECSA under this potential cycling test.
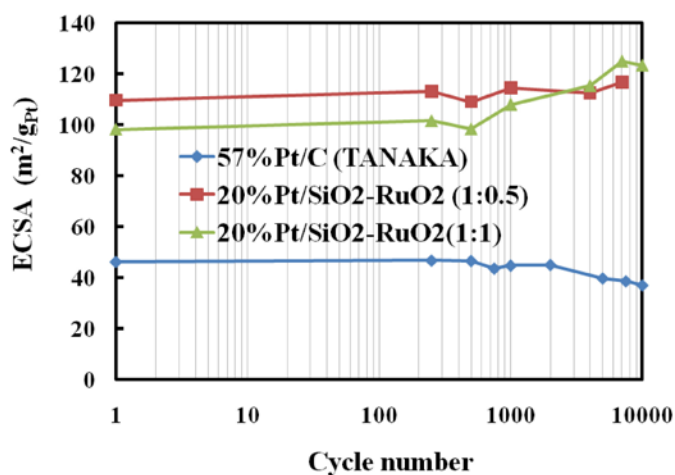

FIGURE 2. Double layer charge obtained from synthesized RuO_2-SiO_2, sulfonic acid functionalized silica, and Vulcan XC-72R carbon during potential cycling between 0 to 1.8 V vs. RHE.

FIGURE 3. ECSA of Pt supported on RuO_2-SiO_2 and Pt/C (57%, TKK) after 10,000 potential cycles between 0 to 1.2 V vs. RHE.

Ex situ benchmarking of various Pt-based catalysts with different carbon supports has been completed at NTCNA. Start-stop cycling and load cycling durability tests have been performed by cycling electrode potential between 1.0 V to 1.5 V (triangular wave form) and between 0.6 V to 1.0 V (rectangular wave form). The results of these tests show that NTCNA has acquired a very good understanding of the interplay between Pt and its support on durability of the catalyst. NTCNA is also performing ex situ benchmarking of various un-catalyzed carbon supports for their durability using the start-stop cycling protocol. These tests are expected to provide a more in-depth understanding of the support material's stability, which will help benchmarking the non-carbon supports being developed under this project. Finally, NTCNA is currently working to evaluate the durability of non-carbon supports developed at IIT using the above protocols. The results obtained at NTCNA will be further described in the forthcoming quarterly report.

Fuel Cell Performance

Preliminary fuel cell performance has been demonstrated with the non-carbon support catalyst. Figure 4 shows the polarization curves of a PEFC employing Pt/RuO_2-SiO_2 at the anode and cathode. The current density at 0.6 V was 750 mA/cm^2, and the maximum power density obtained was 570 mW/cm^2 under H$_2$/O$_2$. Further analysis of polarization data is in progress.
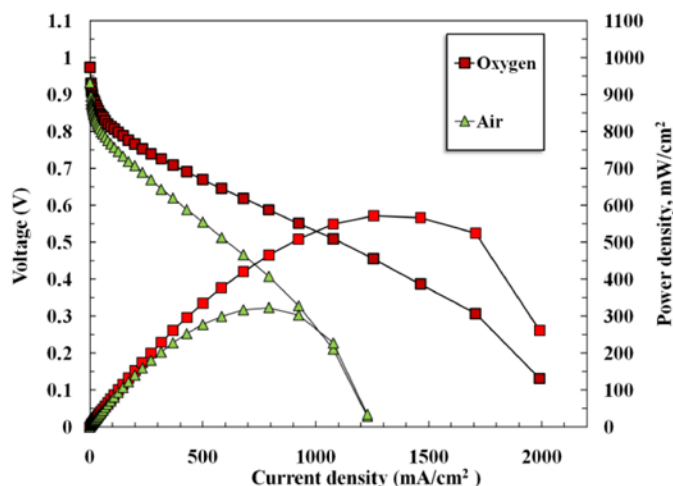

FIGURE 4. Polarization curves obtained from a PEFC membrane electrode assembly prepared using Pt/RuO_2-SiO_2 electrocatalysts at both electrodes. Measurements were conducted at 80°C with 75% RH. Reactant flow rates were set at two times the stoichiometric requirement for both H$_2$ and O$_2$/air. Pt loading was controlled at 0.4 mg/cm^2 at the cathode and 0.2 mg/cm^2 at the anode.

Conclusions and Future Directions

- Highly durable RuO_2-SiO_2 catalyst supports with a core–shell-like structure were synthesized with high BET surface areas and electron conductivities.
- Both RuO_2-SiO_2 and Pt/RuO_2-SiO_2 materials exhibited superior electrochemical stability in comparison to carbon catalyst supports under potential cycling tests.
- Several samples of sulfonic acid functionalized silica have been prepared, and they demonstrate excellent proton conductivity.
- Promising preliminary fuel cell performance with H$_2$/O$_2$ has been obtained with Pt/ RuO_2-SiO_2 electrodes.
- Future efforts will be focused on refining microstructure-property relationships in the ruthenium oxide-silica composite system in terms of extent of functionalization, pore-structure of silica/functionalized silica employed, and platinum loading. Efforts are underway to synthesize a stand-alone mixed conducting support by combining the methods described herein. Work will be performed collaboratively with NTCNA to subject the supports synthesized to a more diverse set of stability testing protocols.

References

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2. Lo, C.-P., Kumar, A., and Ramani, V., ECS Transactions, Vol. 33, PP. 493 – 505, 2010.