doi:10.1017/S143192761006191X
Microsc. Microanal. 16 (Suppl 2), 2010

Characterization of the Ternary Compound $Pd_5Pt_3Ni_2$ for PEMFC Cathode Electrocatalysts

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Research on proton exchange membrane fuel cells (PEMFC) has increased over the last decade due to an increasing demand for alternative energy solutions. Most PEMFCs use Pt on carbon support as electrocatalysts for oxygen reduction reactions (ORR) [1]. Due to the high cost of Pt, there is a strong drive to develop less expensive catalysts that meet or exceed the performance of Pt. Binary and ternary Pt alloys with less expensive metals are a possible route [1]. In this work, a ternary alloy with composition $Pd_5Pt_3Ni_2$ was studied as a potential cathode material. Preliminary results showed similar catalytic performance to pure Pt in single-cell tests. However, to enhance its performance, it is necessary to understand how this ternary catalyst behaves during fuel cell operation. Various electron microscopy techniques were used to characterize the ternary $Pd_5Pt_3Ni_2$ catalysts within the membrane-electrode assembly (MEA) both before and after fuel cell operation.

Thin sections of two MEA's (composed of the ternary $Pd_5Pt_3Ni_2$ as the cathode, Nafion as the membrane, and Pt as the anode) were microtomed. One of the MEAs was observed before fuel cell operation, and the other was examined after 180 hours of operation. The sections were characterized in a JEOL 2010F TEM using bright-field TEM and energy-dispersive x-ray spectroscopy (EDS), and also in an aberration-corrected JEOL 2200FS STEM/TEM, using high-angle annular dark-field techniques (HAADF/STEM) and EDS with a Bruker-AXS silicon-drift detector (SDD).

Figures 1a and 1b show a cross section of the cathode before and after testing. The nanoparticles at the cathode are highly agglomerated and unevenly dispersed both before and after operation. The anode shows smaller particles more evenly distributed and some large agglomerates before and after operation. EDS analysis showed that the ratio of Pd/Pt in the cathode dropped from 1.4 to 1.1 after operation, while the anode contained a small amount of Pd after operation (see Table 1). In the membrane, there was a clear change after fuel cell operation, during which a 3.5μm-wide strip of particles was formed (see Fig. 2). EDS revealed that these particles were about 90% Pd and 10% Pt. Furthermore, Pd-rich particles were found in the membrane near the cathode/membrane interface (see Fig. 3). In addition to Pd, Ni was found within the membrane, while at the cathode Ni dropped significantly. Kelly et al. [2] have shown that Ni ions can exchange with hydrogen ions in the sulfonic acid groups of Nafion. Thus, it seems that both Ni and Pd dissolve from the ternary catalyst during fuel cell operation. However, unlike Pd, Ni does not precipitate out in the membrane [3].

References

[1] H. Liu and A. Manthiram, *Energy and Environmental Science* 2 (2009) 124.
[2] M.J. Kelly, et al., *Solid State Ionics* 176 (2005) 2111.
[3] This work was supported in part by the Office of Naval Research MURI grant # N00014-07-1-0758; microscopy at Oak Ridge National Laboratory's High Temperature Materials Laboratory was sponsored by the U. S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Vehicle Technologies Program.

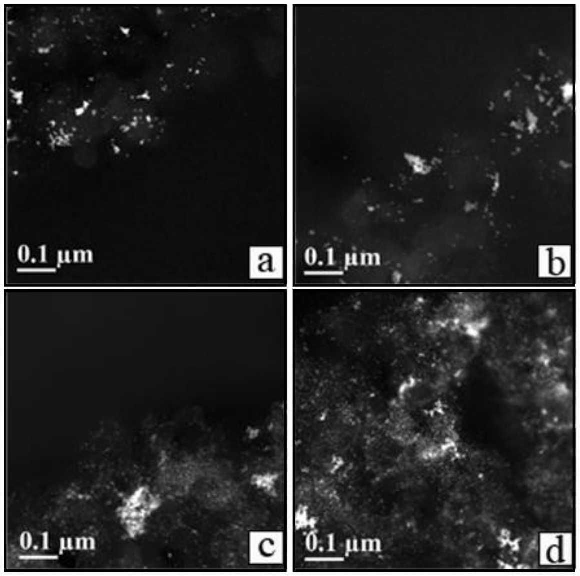

FIG. 1. HAADF/STEM images of the cathode before operation (a) and after operation (b) and the anode before operation (c) anode after operation (d).

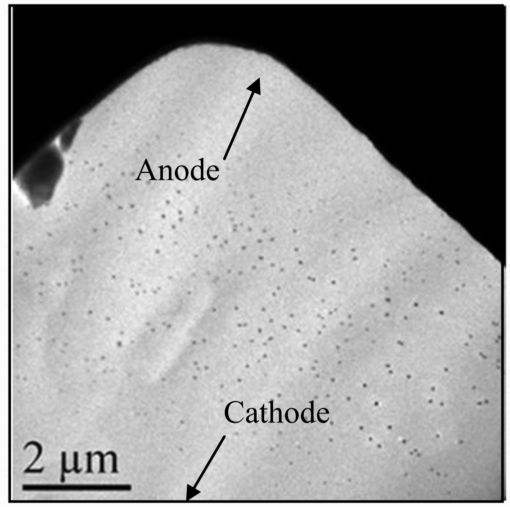

FIG. 2. BF TEM image of the Nafion membrane after operation. The arrows indicate the directions to the anode and cathode electrodes. The black region is the copper grid.

Table 1. Semi-quantitative EDS analysis across MEA.

Location	Pd (at %)	Pt (at %)	Ni (at %)	F (at %)*
Cathode (BO)**	49	35	16	0
Cathode (AO)	52	47	<1%	0
Anode (BO)	0	100	0	0
Anode (AO)	6	94	0	0
Membrane (BO)	0	0	0	100
Membrane (AO)	0	0	0.5	99.5

* F is normalized to Ni. The membrane is composed of F, S, O and H.
** BO is before operation and AO is after operation.

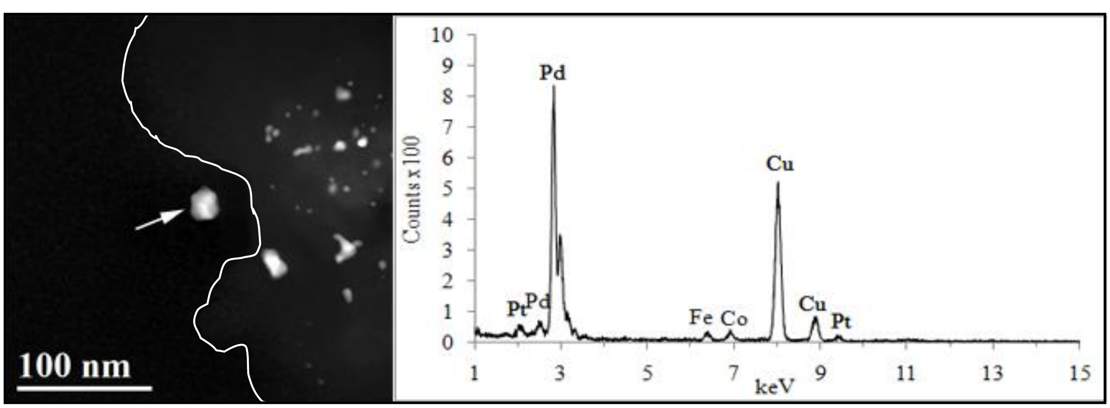

FIG. 3. HAADF/STEM image of the cathode after operation and corresponding EDS spectrum from the particle indicated by the arrow. The cathode/membrane interface is outlined in white. The Fe and Co peaks in the spectrum are artifacts from the 2200FS pole piece.

https://doi.org/10.1017/S143192761006191X Published online by Cambridge University Press