

Ways to Improve Alcohol Oxidation in Fuel Cells

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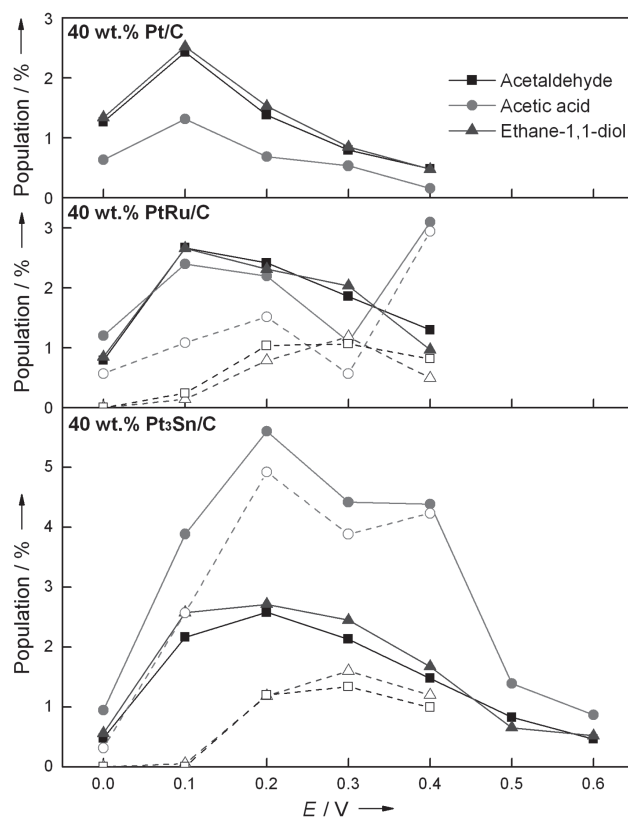
Fuel cells are expected as an option for power sources of small electronic devices as well as for vehicles, and residential power generators because they exhibit high efficiency, generate constant power output and are environmentally benign. Direct methanol fuel cell (DMFC) and polymer electrolyte fuel cell (PEMFC) are two most widely studied types. Despite these advantages, fuel cells in general need to overcome not only technical, but also economic barriers for wide applications. Main barriers are the cost of materials such as platinum used in catalysts for both electrodes, proton conducting polymer in membranes, and bipolar plates for flow pattern and current collection. Catalysts are the core material for fuel cell operation and many attempts have been made to find out the most active, efficient and durable formulae for ORR and alcohol oxidation. Oxidation of methanol requires a series of steps to result in CO₂ and water, and it needs a high oxidation barrier. Also, ethanol oxidation(DEFEC) has additional merits over methanol as a fuel. However, the C-C bond in ethanol leads to more complicated reaction intermediates and products during oxidation, [1] and catalysts must be able to activate C-C bond scission for complete oxidation to CO₂.

In this presentation, various ways to improve the oxidation of alcohol in fuel cells. They are mechanistic study of alcohol oxidation, preparation of catalysts, proper utilization of carbon supports.

The ¹³C liquid-state NMR experiments were performed on DEFECs to identify and quantify the reaction products present in the liquid anode exhaust of DEFECs that were operated with three different anode catalysts at various potentials. [2] All catalysts were prepared by a polyol method with 40 wt% Pt/C, PtRu/C, or Pt₃Sn/C anode catalysts. Figure shows the relative quantities of the major organic chemicals in the anode exhaust of the DEFECs with different anode catalysts at different potentials.

High performing catalysts are especially welcome for alcohol oxidation. In order to reduce the material cost, many attempts have been tried, especially to reduce the amount of precious metal used as catalyst. In this respect, low loading Pt-Ru electrodes were prepared by using galvanostatic pulse technique to show advantages of the electrochemical deposition for high utilization of catalysts in fuel cells. [3] They exhibited uniformly prepared and well dispersed catalysts for high performance despite the fact that the amount of metal is much smaller than normal preparation methods. From TEM images, particle size of PtRu was estimated mainly as 3~4 nm regardless of concentrations of Ru precursor. In CO stripping voltammograms, the onset and peak potential of PtRu deposited from 20 mM Pt and 30 mM Ru precursors have similar tendency and unit cell performance of electrodeposited PtRu is better than those of 40 wt.% PtRu E-TEK.

Graphene nanosheet is also very exciting materials being investigated recently, because it has unique electronic,



Population of the reaction products in the anode exhaust vs. operating potential of fuel cells containing Pt/C, PtRu/C, or Pt₃Sn/C anode catalyst. The dotted lines indicate the populations of the reaction products after subtracting the values of the fuel cell with Pt/C anode catalyst.

thermal, mechanical, and chemical properties arising from its strictly 2D structure. [4] Particularly, these remarkable characteristics can be utilized for fuel cell application. However, constructing graphene support with nano size metal particles that show a high electrochemical active surface area remains a great challenge. [5] Also, we prepared graphene with Vulcan carbon composites to improve the mass transport by introducing necessary channels in the support. Graphene layers tended to form agglomerates when used in fuel cells, so a nano-sized spacer could separate some fraction of agglomerated graphene layers. So, Vulcan carbon was added as to enhance electrocatalytic activities of PtRu catalysts for methanol oxidation and thereby overall fuel cell performance. Experimental results showed that Vulcan carbon is effectively placed between graphene sheets, resulting in more triple-phase boundaries available for electrochemical reaction and better mass transport in the catalyst layer. We believe that this work could be one of the interesting concepts helpful for developing new supporting material in fuel cell application. Experimental details and results will be discussed.

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