Role of Oxygen Permeation in Direct Ethanol Fuel Cells with Noble Metals Anodes

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When various fuels for low temperature polymer electrolyte membrane fuel cells are considered, ethanol has several advantages, which make it an attractive alternative to hydrogen or methanol. These advantages include low cost of production, convenience of storage and transport, low toxicity and high theoretical efficiency. However, the activity of anode catalysts is still far from making direct ethanol fuel cell (DEFC) economically viable. Additionally, the commonly used Nafion membranes are permeable to both fuel and oxidizer, resulting in phenomena called "mixed potential", where processes supposed to occur exclusively on one electrode are in fact occurring to a different degree on both, resulting in lower voltage and overall poor efficiency of working fuel cell. Thus more research is needed to understand the electrochemical oxidation of ethanol and other processes occurring in working fuel cell.

Obviously oxidation of ethanol molecule to different products releases different number of electrons (2, 4 and 12 for acetaldehyde, acetic acid and carbon dioxide, respectively). The degree of completeness of ethanol oxidation reaction, or how the operating conditions influence the different routes of ethanol electrooxidation, is routinely determined from the observed amounts of different products in the anode stream of working fuel cell.

We have recently shown that oxygen molecules, permeating from cathode to anode compartment, are able to chemically oxidize ethanol at anode catalyst's surface. Such parasitic process influences the distribution of ethanol electrooxidation products, observed at anode outlet of DEFC [1-3]. This process does not only render the analysis of product of electrooxidation of ethanol in working fuel cell not reliable, but also severely influence the practical efficiency of working fuel cell.

We have determined, that the oxygen permeation distorts the observed distribution of products, not only qualitatively, but also quantitatively, which is most pronounced in case of pure Pt anode. It is often reported, that acetic acid is observed at fuel cell anode as a product of electrooxidation of ethanol. Our data suggest, that at relatively high cell voltage (low anode potential) the whole amount of acetic acid observed should be rather attributed to chemical oxidation of ethanol by oxygen permeating from cathode. This is in agreement with ex-situ, spectroscopic data[4,5], and overall the mechanism of ethanol electrooxidation on Pt, but has not been presented for working DEFC before.

Overall the unbiased product distribution data for electrooxidation of ethanol on numerous anode catalysts, in particular on pure Pt, Pt-Ru, Pt-Sn and Pt-Pd alloys let us to comment on the possible mechanism of electrooxidation of ethanol in DEFC on different anode catalysts. The use of the currently most active anode materials, Pt-Sn and Pt-Ru nanoparticles, let us to determine the actual reason for their high activity, which is the preferential oxidation of ethanol to acetic acid, most pronounced for Pt-Sn. As the acetic acid cannot be further oxidized at the conditions of working DEFC, this is effectively a dead end of ethanol oxidation and should be avoided. This stresses the need for different materials, able to oxidize ethanol to a higher degree, in order to further advance the development of DEFC.

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