Ethanol Oxidation in Direct Ethanol Fuel Cells

B.B.L. Reeb[1,2], N. Kluy[1], O. Schneider[1], U. Stimming[1,2]
[1] Technische Universität München, Department of Physics E19, James-Franck-Str. 1, D-85748 Garching, Germany
[2] TUM CREATE Centre for Electromobility Singapore, 1 CREATE Way, #10-02 CREATE Tower, SG 138602, Singapore

Ulrich.Stimming@tum-create.edu.sg

Introduction:

Over the last decades, fuel cells have attracted much attention due to their independence of the Carnot limitation of thermodynamics, which sets an upper limit for the energy conversion efficiency of the widespread internal combustion engines. Hence, higher efficiencies are possible and consequently the worldwide increasing demand for both finite fossil and emerging renewable fuel sources will be eased [1]. As a possible renewable energy source, ethanol is very attractive as it is non-toxic, it has a high energy density comparable to gasoline and it can be produced from ubiquitary available biomass sources, like lignocellulose. Considering this, the direct ethanol fuel cell (DEFC) combines both advantages of renewability and high efficiency. From studies with the DEFC it is well known, that for operating it with high efficiency, the cell temperature has to be in the intermediate temperature region between 200 and 400 °C to enhance C-C bond breaking, which is thermally activated and the rate determining step during ethanol oxidation [2-4]. Without thermal activation, partial oxidation products are mainly produced, in particular acetic acid and acetaldehyde [3]. Associated with the elevated operation temperatures, the loading with noble metal catalyst, which is a major hindrance for mass production of fuel cells, can be lower - even operation without precious catalysts could be envisaged.

Electrolytes

For building a DEFC, Nafion® cannot be used as electrolyte because of the high fuel permeation across the membrane [5]. In addition to that, the upper operation temperature limit of Nafion® is the glass transition point of ≈ 110°C, which lies below the necessary intermediate temperature region. Here, a promising alternative proton conductor for temperatures above 100°C can be ammonium polyphosphate (APP). APP is a commercially available inorganic salt of ammonia and polyphosphoric acid. Pure APP is not stable at temperatures above 240°C, but its stability can be improved by a thermal reaction with inorganic oxides (e.g. SiO_2, TiO_2) [5, 6]. To obtain a fuel cell membrane, composites of APP and metal oxides can be imbedded in a polymer matrix, as was recently shown by Kluy et al. [8].

Catalyst supports

In real fuel cell systems, noble metal catalysts are often supported on carbon based materials. Carbon is used, as it cheap, has a reasonable electronic conductivity and a high surface area. The latter one is necessary, as it mitigates Ostwald ripening of the dispersed catalytic nanoparticles. Nevertheless, carbon based supports are prone to corrosion during both fuel cell operation and start up conditions, even at temperatures below 100°C. Alternative promising support materials for intermediate temperatures are metal oxide based (e.g. SnO_2, TiO_2), which become electronically conductive by either doping with a second metal (e.g. $Sn_{0.98}Nb_{0.05}O_2$), or by forming solid solutions with carbides ($TiO_{2-x}C_y$) [9, 10]. The latter one is carbothermally reduced titania, which can be obtained during a thermal process from anatase in an acetylene atmosphere [11].

Catalysts

For the oxidation of ethanol, mainly Pt and bimetallic Pt catalysts (e.g. PtSn, PtRu) are used. As results from Rao. et al. have shown, PtSn catalysts have a superior CO_2 efficiency at a similar faradaic current compared to PtRu. The lower CO_2 efficiency is due to the fact that PtRu favors the formation of partial oxidation products acetaldehyde and acetic acid. Compared to unsupported Pt, PtSn has a lower faradaic current, but a higher CO_2 efficiency at considerably lower noble metal content [3].

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