Plurimetallic Electrocatalysts for Direct Alcohol Fuel Cells.

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For various applications topics, fuel cells are widely recognized as very attractive devices to obtain directly electric energy from a chemical product. Low temperature fuel cells, generally conceived around a proton electrolyte membrane, seem able to be used for various applications in a large range of power. However, the final choice of the fuel is still difficult and depends greatly on the field of application. If hydrogen or hydrogen-rich gas obtained by reforming is clearly the best choice for stationary applications, the problem related to its storage leads to the necessity to propose alternative fuels to use directly in fuel cells. The direct use organic fuels have been often considered despite their rather low activity in comparison to hydrogen. Methanol is widely proposed as the best choice for mobile applications such a electric vehicles[1,2]. This is due mainly to its availability and to the easiness of its storage as a liquid. It is possible to improve its electroreactivity by using platinum-based electrocatalysts.

However, the question of the toxicity of methanol becomes crucial. Methanol is considered since a long time as a toxic product (mainly neurotoxic), in addition to its possible environmental problems in relation to its large miscibility to water. From this observation, the use of other alcohols presenting a negligible or very low chemical toxicity is necessary, at least for some applications. Ethanol appears to be an interesting alternative fuel for a wide utilization, even if its price appears actually too high. Its low toxicity added with its availability (from biomass) is an important positive point for its use as an alternative to methanol even if its reactivity is slightly lower. But methanol remains a very attractive fuel, even if it is necessary to be cautious. As examples, for uses in mobile electronic devices (laptop, cellular phones…), methanol can be used if technical solutions involving tight and/or disposable reservoirs.

As pointed above, the use of alcohols as fuels needs to have efficient electrocatalysts for their oxidation. However, it is necessary, in addition, to overcome the problem of the cross-over of the fuel, due to the properties of the protonic membrane. The finding of cathodic electrocatalysts non sensitive to organic fuel is crucial.

Preparation of such catalysts is then of great importance. For the oxidation of alcohols, platinum-based catalysts are necessary, typically Pt-Ru for methanol, but with a optimized composition. The preparation of nanoparticles of bimetallic system is necessary, with a narrow dispersion in size and with a given composition.

Different way can be used to prepare small particles. Impregnation followed by reduction step is a convenient and versatile way. An other simple process proposed several years ago seems well-adapted to prepare chemically plurimetallic electrocatalysts. This soft chemistry method consists in the synthesis of colloïdal precursors which prevent the formation of large metallic particles. Such a technique can be used for the preparation of unsupported as well as carbon-supported electrocatalysts suitable for fuel cell electrodes. Moreover, this technique can be developed with a wide range of metals.

As an example, it was possible to vary the composition of a platinum-ruthenium system in order to determine the optimum composition for the methanol electrooxidation. In fact, if a composition of 50-50 at% is widely considered as the optimum, and is commercially available for fuel cell electrodes, systematic experiments confirmed that, even for the case of nanoparticles (typically 1.5 to 2 nm diameter), the optimum composition is in the range 20 to 30 at% of ruthenium.

In the case of the electrooxidation of ethanol, Pt-Ru particles give interesting results (better than pure platinum nanoparticles), but the bimetallic system platinum-tin appears as the most active one. However, the optimum composition is still an open question and problems related to the stability of such bimetallic compounds still exist.

This route of preparation of nanophase materials from colloïdal precursor can be also used for the synthesis of platinum-based electrodes for the oxygen (or air) reduction. These cathodic electrocatalysts should be less sensitive or even insensitive to the presence of organic fuels coming from the anodic compartment by the cross-over process though the membrane. Modification of platinum by chromium or cobalt give interesting results.

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References

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