

DURAMET

IMPROVED DURABILITY AND COST-EFFECTIVE COMPONENTS FOR NEW GENERATION SOLID POLYMER ELECTROLYTE DIRECT METHANOL FUEL CELLS

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| Application Area: | Early market | | |
| Project type: | Research and technological development | | |
| Topic: | SP1-JTI-FCH.2010.4.4: Components with advanced durability for Direct Methanol Fuel Cells | | |
| Contract type: | Collaborative Project | | |
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| Coordinator: | Dr. Antonino Salvatore Arico' CONSIGLIO NAZIONALE DELLE RICERCHE E-mail: arico@itae.cnr.it | | |

ACHIEVEMENTS TO DATE

The project deals with Direct Methanol Fuel Cells (DMFCs). These systems are promising candidates for portable electric power sources and auxiliary-power-units (APU) because of their high energy density, lightweight, compactness, simplicity as well as easy and fast recharging. Nevertheless, before this technology can reach large scale diffusion, specific problems related to the high cost of fuel cell components and the low performance must be solved.

In the framework of the DURAMET project, specifications and protocols for assessing direct methanol fuel cells components and devices such as membranes, catalysts, MEAs and stacks have been delivered. These are available to the public through the project web-site (<http://www.duramet.eu>).

Cost-effective hydrocarbon membranes for low temperature operation with improved conductivity and reduced methanol cross-over have been developed. Interesting results have been achieved with sulfonated polysulfone-based membranes in DMFCs operating under passive mode (room temperature, no auxiliaries, air breathing operation). These devices are of specific interest for portable fuel cells due to the significantly higher energy density of methanol compared to conventional batteries. The cost-effective sulfonated polysulfone hydrocarbon membrane showed conductivity characteristics approaching Nafion (world-reference proton exchange membrane) with much lower methanol permeation i.e. an equivalent current density for cross-over (causing methanol loss and cathode poisoning) ten-times lower than Nafion in the presence of the same thickness and lower water uptake at similar levels of conductivity. Sulfonated polysulfone-based DMFC monopolar mini-stacks developed in the DURAMET project provided an average cell power density larger than 30 mW cm⁻² under passive mode operation (room temperature, air breathing, natural diffusion of methanol from the tank to the anode) with 5 M methanol. Thus, this polymer electrolyte combining low cross-over and reasonable conductivity represents a cost-effective alternative to Nafion in direct methanol fuel cells for portable applications.

For the high temperature range, mixed functionality membranes based on PFSA polymer (sulfonic acid polymer-bound) and molecular bound phosphonic acids have been developed. These membranes have provided a proton conductivity of $\sim 40 \text{ mS cm}^{-1}$ at $120 \text{ }^\circ\text{C}$ with 50% R.H.. Cross-linked highly phosphoric acid doped PBI with conductivity better than 100 mS cm^{-1} at $120 \text{ }^\circ\text{C}$ under dry conditions have been obtained. At temperatures higher than $150 \text{ }^\circ\text{C}$, highly phosphoric acid doped and cross-linked membranes have provided, under the same operation conditions, DMFC performance better than commercial membranes for high temperature operation. Performances better than 100 mW cm^{-2} have been achieved at high temperatures using a high methanol concentration in the anode stream and a vapour-feed mode (10-17 M methanol). The achieved results are promising for APU applications.

Non-carbonaceous and carbonaceous supports alternative to conventional carbon blacks (e.g. Vulcan, Ketjenblack) have been prepared and investigated in terms of surface area, morphology, conductivity and stability. Novel synthesis procedures were developed including colloidal approaches and methodologies leading to spherical and fibrous support morphologies. The developed supports showed excellent corrosion resistance (at least one order of magnitude better than a benchmark carbon black), proper surface area ($100\text{-}250 \text{ m}^2/\text{g}$) and capability to favour a high dispersion of the active noble metal phase.

Regarding the DMFC anodes, the focus of the project was concerning the reduction of the total noble metal loading to less than 1 mg cm^{-2} . To enhance the performance in the presence of low noble metal loading, a composite electrocatalyst consisting of a high surface area TiO_2 nanoparticles and nanosized PtRu/C was developed. The composite electrocatalyst produced a relevant increase of active surface area (more than twice) with regard to a baseline PtRu. An increase of performance of about 20-30 % for the cell equipped with this filler at the anode, under different conditions, versus a baseline DMFC cell was recorded. This was due to the enhanced kinetics of methanol oxidation promoted by the presence of TiO_2 and the increase of PtRu interface area.

For the DMFC cathodes, electrocatalysts based on 50 wt.% Pt-Co/C with mean particle size of about 3 nm and nominal alloy composition Pt_3Co_1 (at.) have been developed. The electro-catalyst showing primitive cubic structure (as evident from the presence of the superlattice reflections) and obtained by a high temperature treatment has allowed to achieve a maximum power density better than 110 mW cm^{-2} in low temperature DMFCs in the presence of a baseline PtRu at the anode. To decrease the Pt content at the cathode, an alternative PdCo cathode catalyst decorated with Pt was developed; this allowed to get reasonable performances. Both Pt_3Co_1 and Pt-decorated PdCo have shown appropriate stability in accelerated stress tests (1000 cycles between 0.6-0.9 V vs. RHE at high temperature) with essentially no loss in performance.

An explorative study has been undertaken to replace Pt with cheap electrocatalyst formulations at the cathode. Promising results have been obtained with valve-metal oxide catalysts in terms of oxygen reduction activity and methanol tolerance.

The new developed DMFC components will be validated in short stacks in the next phase to further assess their performance and durability under practical operation conditions.