

## Particle Size and Structural Effects of TiO<sub>2</sub> - Filler in a Composite Membrane-based Direct Methanol Fuel Cell

V. Baglio<sup>1</sup>, A. Di Blasi<sup>1</sup>, A. S. Arico<sup>1</sup>,  
V. Antonucci<sup>1</sup>, P. L. Antonucci<sup>2</sup>, F. Serraino Fiory<sup>3</sup>,  
S. Licoccia<sup>3</sup>, E. Traversa<sup>3</sup>

<sup>1</sup>CNR-TAE Institute, via Salita S. Lucia sopra Contesse  
98126 Messina, Italy

<sup>2</sup>University of Reggio Calabria, Località Feo Di Vito,  
89100 Reggio Calabria, Italy

<sup>3</sup>University "Tor Vergata" of Rome, via della Ricerca  
Scientifica, 00133 Roma, Italy

Liquid-fuelled Solid-Polymer-Electrolyte Fuel Cells represent a promising alternative to hydrogen based devices as electrochemical power sources for application in portable technology and in electric cars, due to their simplicity of design. However, despite the practical system benefits, the power density and the efficiency of Direct Methanol Fuel Cells (DMFCs) are lower compared to Polymer Electrolyte Fuel Cells (PEFCs). This is mainly due to the slow oxidation kinetics of methanol and the methanol cross-over through the electrolyte membrane. An increase in the operation temperature is highly desirable to enhance the kinetics of methanol oxidation. Various approaches have been proposed to allow the operation of liquid-feed solid polymer electrolyte fuel cells at temperatures higher than 120°C. Recently, the use of recast Nafion membranes containing finely dispersed nanocrystalline ceramic oxide powders (SiO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>) has been proposed [1,2]. The role of the ceramic filler is to improve the water retention characteristics, allowing fuel cell operation at a temperature close to 150°C with the oxidant humidifier and fuel conditioner maintained at 85°C. Yet, at the present, limited attention has been devoted to the investigation of surface structural and morphological properties of these oxides in relation to their use in composite membranes.

In the present work, the electrochemical behaviour of composite TiO<sub>2</sub>-Nafion membranes has been studied, in order to understand the role of the above properties on the performance of a DMFC. An investigation of the influence of TiO<sub>2</sub> crystallographic phase transition (from anatase to rutile) and particle size on the electrochemical behaviour of a composite membrane for high temperature operation has been carried out.

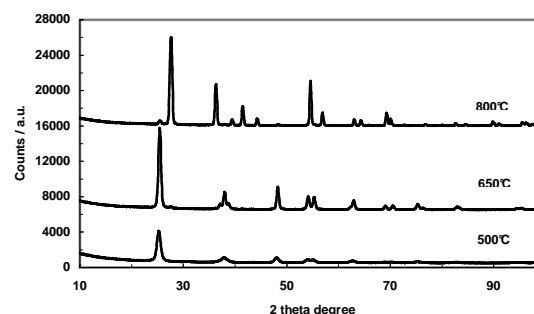
In this regard, TiO<sub>2</sub> nanometric powders were synthesized via a sol-gel procedure and calcined at various temperatures in order to obtain different particle size and different crystalline phases. XRD patterns of TiO<sub>2</sub> powder have shown the crystallographic structure of anatase with a particle size of 12 and 22 nm for the powders calcined at 500°C and 650°C, respectively; whereas the presence of rutile with a particle size of about 51 nm was observed for the powder calcined at 800°C (Fig. 1).

The membranes were prepared by using a recast procedure. The thickness of the membranes was about 100 µm. Fuel cell tests were carried out in a 5 cm<sup>2</sup> single cell (GlobeTech, Inc.). The catalyst employed for methanol oxidation was 60% PtRu (1:1)/Vulcan (E-TEK), whereas a 30% Pt/Vulcan (E-TEK) was used for oxygen reduction. The platinum loading for all the electrodes used in the experiments was 2 mg cm<sup>-2</sup>.

Preliminary DMFC investigation of such membranes at

high temperature reveals a significant influence of the ceramic oxide surface area on the electrochemical behaviour. This indicates that the water retention properties are strictly related to the number of adsorbing sites. Further enhancement of such properties may be achieved through a proper tailoring of the crystalline phase and morphology.

TiO<sub>2</sub>-based recast Nafion membranes may be suitable candidate to replace the present commercial membranes for high temperature operation in polymer electrolyte fuel cells.



**Fig. 1.** X-ray diffraction patterns of TiO<sub>2</sub> calcined at different temperatures.

### References:

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