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Microscopic methods for ceramic fuel cell studies

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ABSTRACT

Ceramic fuel cells, such as solid oxide fuel cells (SOFCs) are devices that convert chemical energy directly to electricity [1]. Since ceramic fuel cells have complex nanostructures, advanced microscopic techniques are required to examine fundamental mechanisms behind the cell performance. In this paper, we review the microscopic methods that have been applied for ceramic fuel cell studies, beginning from 2D methods (SEM, TEM) [2] and proceeding to 3D techniques (FIB-SEM, X-ray nanotomography) [3]. Advantages and limitations of each technique will be discussed. Finally, we briefly discuss about possibilities to go beyond current state of the art with new experimental configures.

I. INTRODUCTION

Limiting global warming due to greenhouse gas emissions to an acceptable level requires new, clean energy sources to replace fossil fuel based power plants. Fuel cells that convert chemical energy of the fuel directly to electricity with high efficiency are promising alternatives for future electricity generation.
Ceramic nanocomposite fuel cells, including solid oxide fuel cells (SOFCs) are under intensive research. These devices consist of two porous electrodes (anode and cathode) which conduct both electrons and ions, and a dense electrolyte, which is ionic conductor and electronic insulator, wrapped between the electrodes (Fig. 1a). SOFCs have many advantages, including fuel flexibility and high efficiency, but also challenges to be solved for commercial success, such as lowering the operational temperature and improving stability.
Since the components of ceramic fuel cells are complex nanoscale structures, microscopic techniques are crucial to understand what happens inside a fuel cell during its operation. 2D methods, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) can be used to study the microstructure of a fuel cell [2]. Focused ion beam – scanning electron microscopy (FIB-SEM) and X-ray nanotomography allow making 3D reconstructions of fuel cell components [3], revealing important information of 3D parameters.

II. 2D STATE OF THE ART

SEM is a commonly used electron microscopy technique that observes secondary and backscattered electrons (Fig. 1b). With SEM, it is possible to study the cross section and surface morphology [2] of the sample. Also analyzing the elemental composition by using energy-dispersive X-ray spectroscopy (EDX) is possible [2]. Although SEM can be used to obtain important information about the sample with rather simple sample preparation and operation procedures, it has several limitations, most importantly the depth of electron penetration: since SEM is observing secondary and backscattered electrons generated near the sample surface, it can provide information only from near the surface of the sample. An example of a SEM image is presented in Fig. 1c.

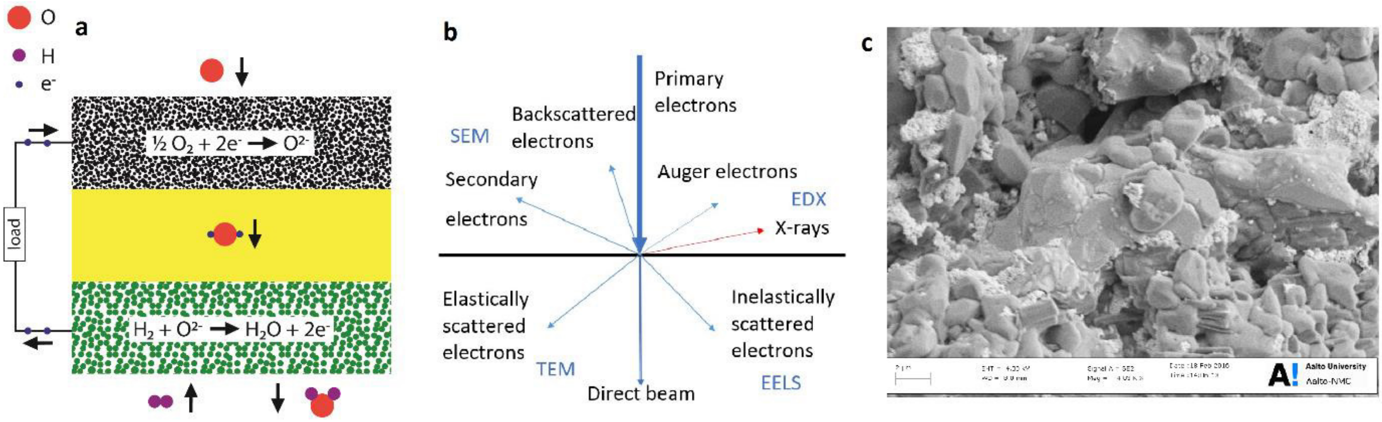

Figure 1 Components and operation principle of a SOFC (a), interactions between incident electron and sample (b), SEM image of ceramic fuel cell electrolyte showing oxide (white dots) and carbonate (stone-like structures) (c).

TEM has ultra-high (even sub-nm) resolution, but to be able to use TEM, sample has to be thin enough for electron transparency (Fig. 1b). This limit the possibilities for using TEM to analyze fuel cells, but it is still useful tool for certain purposes, such as characterizing fuel cell powder [2] or the grain size and crystalline orientation of a fuel cell electrolyte [4]. Elemental analysis can be done with TEM by electron energy loss spectroscopy (EELS).

III. TOWARDS 3D

The motivation to use 3D microscopic methods in fuel cell studies is that the 2D projections imaged by SEM or TEM are often not enough to determine accurately microscopic parameters related to 3D structure. These parameters include porosity (volume fraction of pores), tortuosity (the length the gas molecule has to travel in porous structure vs. the thickness of the structure) and triple phase boundary (TPB) density (density of areas where pore, electronic conductor and ionic conductor meet, allowing electrode reaction to take place). There are two main 3D tomography technologies that have been used in fuel cell studies: FIB-SEM and X-ray nanotomography. These methods have been shown to be consequent with each other [5].

When using FIB-SEM, the sample surface is imaged by SEM and then cut off by FIB. The new surface is again imaged etc. The original 3D structure can be reconstructed from the series of 2D SEM images. This method has high resolution, but it destroys the sample.

In X-ray nanotomography, the 3D reconstruction is based on a series (from few dozen to few hundred) of X-ray images taken from different angles. Unlike FIB-SEM, this method is non-destructive, allowing to image same sample multiple times (e.g. reconstructing fresh and aged sample for degradation studies), although the resolution is lower than with FIB-SEM.

IV. BEYOND STATE OF THE ART

Today, most of the microscopic experiments are done *ex-situ*, i.e. the image obtained shows only the outcome and does not reveal when the observed phenomena actually has happened. To link a certain phenomenon to a certain step, *in-situ* measurements are required: e.g. Cheng et al. [6] showed by *in-situ* Raman spectroscopy that the sulfur poisoning of their anodes resulted from reactions between bulk Ni and H2S during the cooling of the cell.

For microscopic techniques, interesting in-situ experimental setups have been reported, including environmental TEM to study redox stability of a SOFC anode [7] and imaging SOFC cathode at realistic operational conditions by X-ray nanotomography [8].

Besides going *in-situ*, also combining different measurement techniques allows to expand further the possibilities to characterize ceramic fuel cells. E.g. combining *in-situ* microscopy with Raman spectroscopy can be an interesting addition to standard measurement procedures.

V. SUMMARY AND CONCLUSIONS

This extended abstract introduces ceramic fuel cells and existing microscopic techniques to characterize them. The importance of performing microscopic experiments in order to understand the macroscopic behavior of a ceramic fuel cell is highlighted. The advantages and limitations of both 2D (SEM, TEM) and 3D (FIB-SEM, X-ray nanotomography) microscopic techniques are discussed. Finally, ideas for future development of ceramic fuel cell analysis are presented.

VI. REFERENCES

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