FA2-MS10-O1

Electron Microscopy Techniques for the Detailed Study of Fuel Cell Electrodes and Components.
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Transport processes play a significant role for the proper operation of polymer electrolyte membrane fuel cells (PEMFC). In PEMFCs the reactant gases must have access to the catalytically active sites, protons and electrons must be conducted through the electrode and the reaction product water must be removed from the pore system to avoid blocking of the gas diffusion paths. In the current standard electrode design each transport process is realized by a different component. Since the various components influence each other and therefore the electrode properties in a nonconstructive manner, optimization of the electrode structure is far from being trivial.
Porosity and the distribution of the polymer electrolyte appear to be the key parameters for the electrode performance. For the detailed investigation of these parameters transmission electron microscopy (TEM) has been chosen as a suitable tool. However, the sample preparation is crucial to the success of the experiment: the membrane-electrode assembly (MEA) is embedded in an epoxy resin and cut into thin sections by ultramicrotomy using a diamond knife. Details of the procedure can be found in [1] and references therein.
For the analysis of the polymer electrolyte distribution, infiltration of the sample with an epoxy resin has a significant drawback. Since the polymer electrolyte and the embedding resin have almost identical scattering contrast, the polymer electrolyte cannot be distinguished directly. As pores in the electrode structure may be filled by the polymer electrolyte or the embedding resin, it is also not possible to distinguish between open and closed pores (i.e. those filled by the polymer electrolyte). In this paper, we present different approaches to solve the contrast problem and suggest methods to characterize the polymer electrolyte distribution and electrode porosity.
A new imaging routine has been developed in order to avoid significant beam damage of the sensitive sample. By this technique 200 x 200 nm sized parts of the electrode can be imaged and the polymer electrolyte distribution analyzed with the help of the F signal in energy filtered transmission electron microscopy (EFTEM). This approach was very successful in contrast to staining techniques used earlier, and respective results for different MEAs before and after operation will be presented. In addition, first results applying a novel technique using Wood's alloy will be reported, which will help us to image both MEA and gas diffusion layer (GDL) at once in the future.

[1] Scheiba F., Benker, N., Kunz, U., Roth, C:, Fuess, H., *J. Power Sources.* 177, **2008**, 273.

Keywords: fuel cell electrode; TEM; EF-TEM

FA2-MS10-O2

Transmission Electron Microscopy of Electronic Ceramics.
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Electronic ceramics based on strontium titanate, $SrTiO_3$, and zinc oxide, ZnO, doped with small amounts of other oxide materials are of commercial interest as capacitors and varistors. Such materials are also ideal for fundamental studies on grain boundaries in ceramics because they have relatively simple crystal structures. Transmission electron microscopy (TEM) is a powerful tool for investigating the dopant distribution and, in principle, the space charge at grain boundaries in these materials. It can also provide detailed information through electron diffraction of both grain boundary crystallography and the nature of any second phase particles located at grain boundaries arising as a consequence of doping of the pure materials. This is particularly true for zinc oxide varistor materials where dopant levels of 1−2 wt% of other oxides such as vanadium pentoxide and manganese oxide produce second phase particles which cannot necessarily be identified unambiguously through X-ray powder diffraction. In this paper I will demonstrate using examples from work on these two electronic ceramics how the use of TEM at different length scales and a knowledge of crystallography are together indispensible tools for characterising the grain boundary microstructure of such materials.

Keywords: grain boundary engineering; precipitation phase formation; transmission electron microscopy

FA2-MS10-O3

Transmission electron microscopy of BNT-BT-KNN.
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Lead-free piezoelectric ceramics $(1\text{-}x\text{-}y)Bi_{0.5}Na_{0.5}TiO_3\text{-}xBaTiO_3\text{-}yK_{0.5}Na_{0.5}NbO_3$ ($0.05 \leq x \leq 0.07$ and $0.01 \leq y \leq 0.03$) have been prepared by a solid state sintering method [1]. Preliminary electromechanical measurements revealed a giant strain of 0.45 % at an electric field of 8 kV/mm for composition 0.92BNT-0.06BT-0.02KNN [2].
Therefore the main focus of the following TEM study was directed on this composition. No domain structures, as commonly seen in lead zirconate titanate, were observed in TEM experiments on lead-free ceramics [2]. Only a lamellar contrast was visible within the grains. Selected area electron diffraction revealed no spot splitting but superstructure reflections and satellites due to octahedral tilting and cation ordering. Streaking of reflections in distinct directions

has been observed by tilting experiments. Further TEM investigations within the composition range given above are in progress. Findings will be correlated with X-ray and neutron diffraction experiments.

[1] Zhang S.-T-, Kounga A.B., Aulbach E., Ehrenberg H., Rödel J., *J. Appl. Phys.*, **2007**, 91, 112906. [2] Zhang S.-T-, Kounga A.B., Aulbach E., Granzow T., Jo W., Kleebe H.-J., Rödel J., *J. Appl. Phys.*, **2008**, 103, 034107.

Keywords: diffraction; piezoelectric ceramics; TEM

FA2-MS10-O4

Exaggerated Grain Growth Triggered by Intrinsic Defects; A TEM Study. Stefan Lauterbach[a], Hans-Joachim Kleebe[a]. [a]*Institute for Applied Geosciences, Geomaterial Science, Technische Universität Darmstadt, Darmstadt, Germany.*
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Three different oxides, namely bixbyite, $(Mn,Fe)_2O_3$, boron suboxide B_6O and spinel, $MgAl_2O_4$, were investigated by transmission electron microscopy in order to determine the origin of exaggerated grain growth observed in each of these systems.
Bixbyite revealed the presence of planar defects that were identified as thin braunite lamellae present as a 3D-network within the host crystal.
In boron suboxide, doped with excess silica, numerous enlarged grains were observed within the otherwise rather fine-grained matrix. Those grains contained, similar to bixbyite, planar defects enriched in Si.
Spinel polycrystals, doped with LiF, also showed pronounced grain growth at intermediate sintering temperatures. The grains that revealed considerable grain growth contained F (and Li), which as a consequence causes the formation of oxygen vacancies.
Based on the above examples, a model is presented that explains the observed exaggerated growth of individual grains by the presence of intrinsic defects within the host crystal. One example will be shown that allows the utilization of such a correlation to tailor the overall microstructure of polycrystalline ceramics.

Keywords: grain growth; defects; transmission electron microscopy

FA2-MS10-O5

Investigation of Precipitation of β-Cr_2N in Duplex Stainless Steel SAF 3207HD Using Transmission Electron Microscopy (TEM). Ping Liu. *Department of physical metallurgy, R and D Centre, Sandvik Materials Technology, 811 81 Sandviken Sweden.*
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The critical pitting temperature (CPT) of welded SAF 3207 HD was found to be lower than what was expected based on the pitting resistance equivalent (PRE). So is the welded SAF 3207 HD. In order to understand and eventually find a way to circumvent this problem a detailed microstructural study was carried out using high resolution field emission scanning electron microscopy (SEM) and analytical transmission electron microscopy (TEM).

β-Cr_2N ($P\bar{3}1m$ (No.162) a=4.8113 and c=4.4841 Å) was found in 1200°C/5 min with cooling rate of 339 °C/s sample. No intermetallic phase such σ-phase ($P4_2/mnm$ (136) a=8.790 and c=4.544 Å) or β-Cr_2N was observed in sample heat treated at 1120°C/15 min-1000°C/16 min with cooling rate of 25 °C/s. σ-phase was observed in sample heat treated at 1120°C/15 min-700°C/32min. It was found that the size and volume fraction of β-Cr_2N was a function of solution temperature and cooling rate after solution treatment.

The diffusion of nitrogen is the dominant fact which controls the precipitation of β-Cr_2N. This in term is interpreted as solubility and diffusivity of N in ferrite.

As a result of this investigation it is recommended that in order to keep duplex phase structure and to avoid the precipitation either β-Cr_2N or σ-phase, low solution temperature (1000 °C-1100 °C) and slow cooling after solution treatment (or welding) is recommended down to temperature above which formation σ-phase would take place.

Key words: TEM; stainless steel; intermetallic phase