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In Situ Transmission Electron Microscopy in Materials Science – Possibilities and Prospects

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Introduction

Electron microscopy is an integrated part of materials science and has been since the dawn of electron microscopy. In order to link the microscopic structure to materials properties it is beneficial to perform this otherwise passive characterization technique *in situ*. In other words, characterize the materials under various forms of stimuli such as heating, gas exposure, light exposure, liquid exposure, electrical bias, magnetic fields, mechanical stress, indentation, etc. Here, gas exposure and heating will be in focus, and limitations and prospects of *in situ* electron microscopy will be discussed.

Scattering of the primary electron beam on gas molecules results in loss of coherence of the incoming electron wave and thereby influence the performance of the electron microscope, mainly in terms of loss of resolution. In order to maintain the highest performance of the microscope while the sample is exposed to gas, the gas has to be confined around the sample. In general, this criteria has been fulfilled by two different routes:

1. The controlled gas atmosphere is confined near the sample by means of pressure limiting apertures securing a sufficient pressure drop to the remaining column by a differential pumping scheme. The pressure limiting apertures placed in the objective lens in close proximity to the sample ensures the high-pressure zone less than 1 cm thick. The concept known as differential pumping was described by Boyes and Gai [1] and further exploited on microscopes from various vendors [3-6]. A schematic drawing of the differential pumping approach in environmental transmission electron microscope (ETEM) is shown in Figure 1. This approach limits the obtainable pressure to ca. 10^3 Pa in the sample area. However, no solid material is interfering with the electron beam on its path to and from the sample. The controlled gas atmosphere is supplied by either injection through the objective lens resulting in a uniform pressure between the pole pieces or direct injection onto the sample via a nozzle in close proximity to the sample.

2. The gas is confined by solid electron transparent membranes allowing higher pressures in the vicinity of the sample compared to the differential pumping scheme without compromising the requirement of UHV near the electron gun. Placing two membranes, typically fabricated from silicon nitride or oxide, in a holder with a spacing of less than 100 μm , pressures exceeding atmospheric pressure in a closed cell can be obtained while preserving atomic resolution [7, 8].

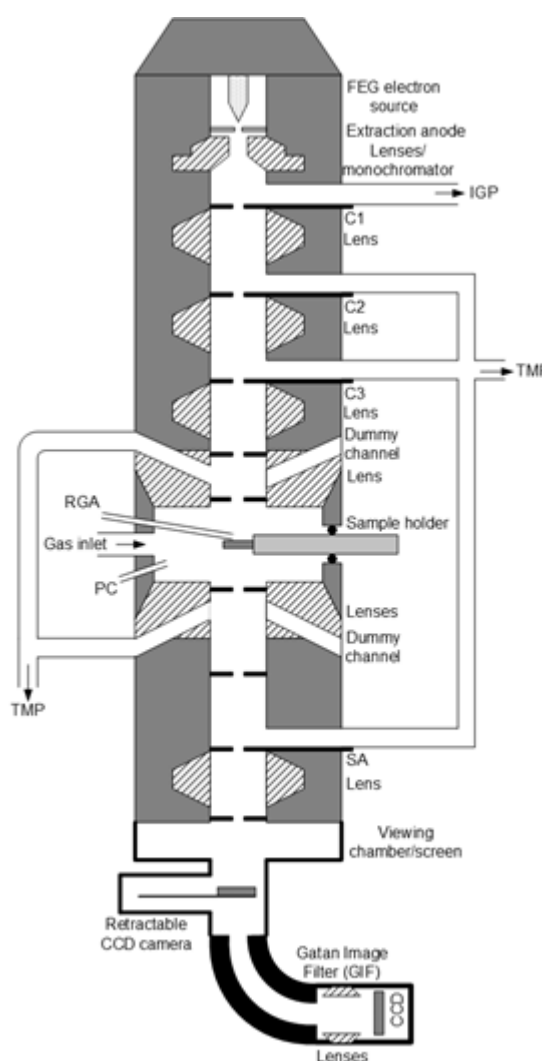


Figure 1. Sketch of differentially pumped ETEM

Experimental Procedures

The experiments and results presented in this abstract are mainly based on characterization performed using a FEI Titan 80-300 ETEM operated at 300 kV following the differential pumping scheme [2]. The pressure of the

controlled atmosphere varies from 0.1 Pa to 1000 Pa depending on the actual experiment. The sample is directly dispersed onto commercially available MEMS-based heating chips, capable of heating the sample to more than 1000 °C.

Results and Discussion

Towards quantitative ETEM – Understanding the gas-electron interaction

Ever since the proposal and first attempts of *in situ* electron microscopy involving non-vacuum imaging in the early days of electron microscopy, addressing the influence of the gas on the fast electron pathway has been crucial. The higher the pressure and the longer gas path the fast electrons have to pass, the larger is the probability of scattering events between electrons and gas species.

Scattering on gas molecules results in a significant loss of electrons (intensity) on the viewing screen depending on the gas species, total pressure and energy of the primary electrons. Furthermore, the spatial resolution will decrease both for Scanning Transmission Electron Microscopy and for broad beam electron microscopy (Figure 2). The unusual scattering geometry to be considered in the high-pressure region of differentially pumped ETEMs leads to the resolution being dependent on the total beam current during acquisition even at constant beam current density. The contrast in the resulting images might be influenced as well depending on the scattering power of the gas molecules.

In addition to the loss of spatial resolution and contrast of the acquired micrographs due to the electron-gas interaction, the observations will also be influenced indirectly by ionization of gas species, which can lead to more reactive gas species and charge transfer effects. For example, the ionized gas species can be used for charge compensation, since ionized gas species act as charge carriers compensating for charging of the sample during electron beam irradiation.

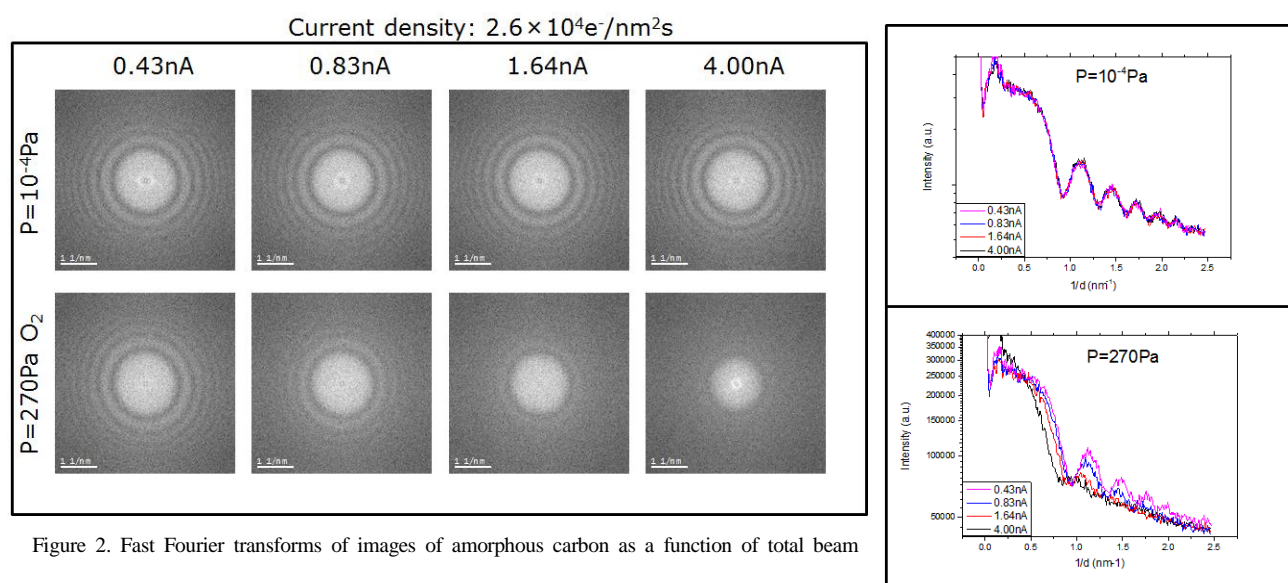


Figure 2. Fast Fourier transforms of images of amorphous carbon as a function of total beam current. The damping of the information transferred to the image is highly dependent on the total electron beam current in the presence of gas. The resolution of the images acquired in conventional vacuum mode do not show the same dependency.

In order to take the next step towards quantitative TEM in the presence of gas, a more

descriptive picture of the propagation of electron waves throughout the high-pressure zone of the TEM has to be developed. The strong magnetic fields of the objective lens are affecting not only the primary beam of electrons, but also secondary electrons and ionized gas molecules making the description of the various phenomena a rather complex task [9].

In situ TEM on operating model solid oxide fuel cells

The necessity of going towards a sustainable production and storage of energy requires alternative solutions. The implementation of solid oxide cells (SOCs) represents an important milestone to fulfil. In the last years, several studies were addressing the understanding of degradation effects in SOCs, mostly implementing post mortem analyses for the characterization of solid oxide fuel and electrolysis cells [10, 11]. Here, we present *in situ*

characterization within a TEM allowing the observation in real time of degradation effects in a model cell during exposure to reactive gasses, elevated temperatures and electrical potential. We prepared a symmetric model SOC by depositing two thin layers of lanthanum strontium cobaltite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC), as electrodes, and one layer of yttria stabilized zirconia ZrO_2 : 8% mol Y_2O_3 (YSZ) as electrolyte, on a single crystal of 1% Nb doped strontium titanate (STO) by pulse laser deposition (PLD).

The sample was exposed to different conditions in the microscope. At first, the stability of the sample was investigated during in-situ heating in high vacuum. A high mobility of electrode cations was observed when the temperature exceeded 600 °C [12]. At 900°C heavy depletion of Sr and Co were observed leading to an irreversible degradation of the cathodes. Electrodes for standard bulk SOC are porous and sintered above 1000 °C [13] and a similar degradation effect at these temperatures is not observed in literature. It is hypothesised that Sr and Co depletion takes place by surface migration due to the small dimension of the sample.

In situ heating in oxygen ($P(\text{O}_2) = 200$ Pa), revealed faster grain growth within the electrode layers in comparison with heating in vacuum. Moreover, STEM-EELS showed a higher amount of oxygen at the interface between LSC and YSZ. Cobalt white lines ratio calculations showed a transition to a higher average oxidation state already at 500 °C.

Finally, in order to study the effect of the electric biasing on the symmetric model SOC, we have prepared experiments that involve current together with heat and oxygen gas. These experiments require the implementation of a TEM heating and biasing Protochip™ chips and a special FIB procedure for sample preparation of the TEM lamella (Figure 3). I-V measurements have been performed in the temperature range that goes from 25°C to 700°C in the presence of 200 Pa of oxygen.

***In situ* growth of Single-Wall Carbon Nanotubes**

A deep understanding of the formation mechanisms of low-dimensional nanostructures from bottom-up processes is of great importance in order to exploit the controllability of the nanostructures and their applications in photovoltaics, electronics, sensors, etc. on an industrial scale.

A well-established nanostructure formation process, which is based on thermally driven growth of a solid from a gas source, is the growth of carbon nanotubes (CNTs). Single-wall CNTs (SWCNTs) show either metallic or semiconducting behavior depending on the exact geometry of the rolled-up single carbon layer. In order to facilitate large scale production of CNTs with specific properties, a better understanding of the initial growth from the catalyst particles is essential. The growth of individual SWCNTs is monitored by ETEM allowing for direct determination of growth rates, catalyst-CNT structure relationship, etc. [14].

Figure 4 shows a TEM image sequence of a transition from gaseous carbon to solid carbon to form a CNT. The elongation process of a SWCNT is shown by a series of images extracted from a movie, acquired during exposure of a Co/MgO sample to a mixture of CO and H_2 at elevated temperature [15]. The diameter and thereby the chirality of the SWCNTs strongly depends on the access to carbon atoms, which can be incorporated into the tube securing growth. Changes in the amount of accessible carbon either by changes in the carbon source supply (gas pressure of CO) or by changes in the catalytic cracking of CO to free carbon atoms, strongly influence the growth and can be a limiting step for the CNT growth. External forces such as stress will also lead to growth termination, because in this case, the incorporation rate of active carbon atoms into the tube is limited. However, we observe that the same catalyst particle stayed active in terms of nucleating additional solid carbon structures after the growth termination of the first SWCNT. These observations elucidate the importance of an in-depth understanding of the role of catalysts and carbon sources in the continued growth of SWCNTs.

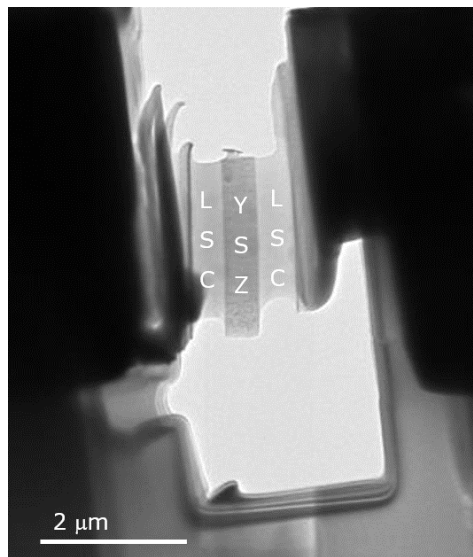


Figure 3. LSC-YSZ-LSC model cell mounted on electrothermal chip for in situ TEM characterization allowing both heating and biasing.

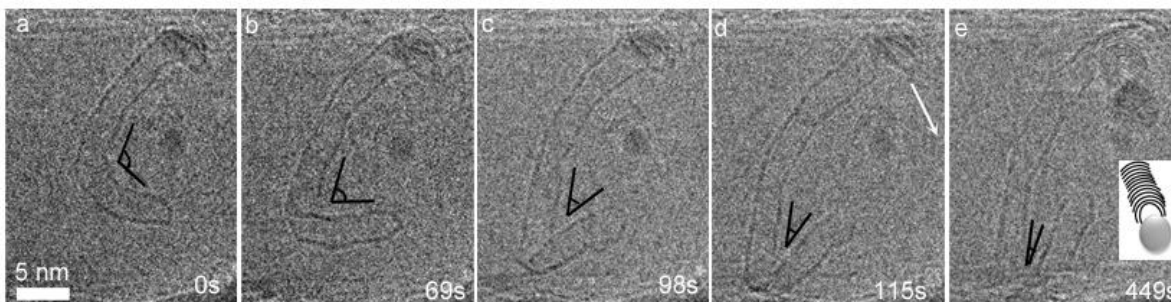


Figure 4: Co/MgO sample exposed to a mixture of CO and H₂ precursor gas (5:2 in mole ratio, totally 760 Pa) at 700°C resulting in the formation of a SWCNT and its growth termination [15].

The above examples of ETEM illustrate the possibilities and prospects of the technique within materials research. The dynamics of nanostructures when exposed to stimuli such as heat and gas are monitored and thereby give direct evidence for phenomena hinted at with other techniques. The understanding and insight into these phenomena at the sub micrometer and atomic scale ultimately leads to development of the next generation functional materials.

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