In-situ SEM electrochemistry and radiolysis - DTU Orbit (03/11/2019)

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Electron microscopy is a ubiquitous technique to see effects which are too small to see with traditional optical microscopes. Recently it has become possible to also image liquid samples by encapsulating them from the vacuum of the microscope and a natural evolution from that has been to include microelectrodes on the windows to enable studies of electrochemical processes. In this way it is possible to perform in-situ electrochemical experiments such as electroplating and charge and discharge analysis of battery electrodes.

In a typical liquid cell, electrons are accelerated to sufficiently high energies to traverse a thin window made by a silicon nitride membrane, and interact with the sample immersed in liquid. In transmission electron microscopy (TEM) the majority of the electrons continue through the sample to form an image. In scanning electron microscopy (SEM) a fraction of the electrons are backscattered and an image is reconstructed by the microscope. But the high energy electrons are a form of ionising radiation which can significantly affect the chemistry in liquid experiments. Ionising radiation can split water, produce radicals, reduce dissolved metal ions to metal particles, and more. It is therefore essential to understand and control the radiolytic processes that results from in-situ electron microscopy experiments.

Although radiolysis has been studied extensively in connection with the advent of e.g. nuclear reactors the information obtained for that purpose often has to be extrapolated many orders of magnitude to reach the radiation conditions of the extremely focused beam of typical electron microscopes. To date there is a distinct lack of direct measurements and quantification of the radiolytic conditions for in in-situ liquid cells.

In this thesis an electrochemical in-situ SEM cell is used to study the radiolytic effects of the electron beam. Potentiometric measurements in-situ demonstrate that the electrolyte contains hydrogen upon irradiation, and that the ratio of H_2O_2 to H_2 is only 1:2.5, much less than the predicted ratio of 1:1.1. Electrochemical impedance spectroscopy (EIS) measurements between two electrodes when irradiating at an average intensity of 6 M Gy/s indicate that the conductivity may be at least 200 μS/cm, two orders of magnitude higher than what would be expected from H⁺ alone. Finally, the radiolytic yield of copper is measured by gradually increasing the radiation intensity until copper precipitated. Based on the amount of backscattered electrons it has been possible to quantify the amount of reduced copper, resulting in an average radiolytic yield per 100 eV of deposited energy (g-value) of 0.05, lower than the value of 4.4 seen in pulse radiolysis experiments. During the course of these studies it has also been possible to improve on the EC-SEM system. This has resulted in pyrolysed carbon electrodes, which offer the benefit of stability at 0.75 V higher potentials than traditional gold thin-film electrodes.

With the quantitative insight into the radiolytic conditions in liquid electron microscopy cells that this thesis provides it may be possible to design and analyse experiments where such effects are correctly accounted for. The results are therefore of high value for the in-situ community who until now have had to rely on only limited experimental data in combination with theoretical predictions that have been extrapolated several orders of magnitude.