

## Monitoring electrode reactions by in situ ESEM

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### Introduction

Monitoring electrode reactions by *in situ* methods is a useful tool for direct investigation of processes occurring at the electrodes. In situ Dilatometry is used in order to quantify volume changes due to lithium intercalation / de-intercalation [1], [2]. *In situ* Raman [2], [3], scanning tunneling microscopy (STM) [3], mass spectrometry [1], [4], [6] FTIR [4], and XRD measurements [4] are performed to investigate the electrode / electrolyte interfacial behavior during cycling. *In situ* optical microscopy [5] and *in situ* atomic force microscopy (AFM) [3] have been the first attempt to make electrochemical reactions visible. Our aim was the construction of a cell for simultaneous realization of ESEM (Environmental Scanning Electron Microscopy) and electrochemical experiments.

### Experimental

Unlike standard SEM technology a separated specimen chamber Fig 1) with lower vacuum ( $< 10$  Torr) allows the use of wet samples (electrodes). An imaging gas ( $N_2$ , Ar...) is introduced to the specimen chamber via a separate dedicated vacuum pump. The highly energetic primary electron beam penetrates the imaging gas with little apparent scatter, scanning across the surface of the sample. Secondary electrons are released from the surface of the sample, as they are in normal SEM, but they encounter imaging gas molecules once they exit the surface. The gas molecules, when they are struck by the secondary electrons, produce secondary electrons themselves, which in turn produce secondary electrons from adjacent gas molecules. Thus the gas functions as a cascade amplifier, amplifying the original secondary electron signal from the sample. The amplified secondary electron signal is collected at the GSED (gaseous secondary electron detector).

The low pressure and the fact that the gas inside the sample chamber plays an important role in the imaging process impacts on the design of the electrochemical cell. The working electrode must be free accessible by the electron beam which excludes a complete sealing of the cell. Otherwise strong electrolyte evaporation must be prevented to hinder drying up the cell and impurify the imaging gas by the electrolyte solvent. Hence we use carbonate solvents with high boiling point and low vapor pressure, for example ethylene carbonate (EC) and propylene carbonate (PC), and minimized the uncovered cell area (Fig. 2). Small evaporation of the electrolyte solvent will be balanced by the electrolyte reservoir.

Our contribution will show the monitoring of surface modifications at anode materials for lithium - ion batteries in dependence on the applied potential.

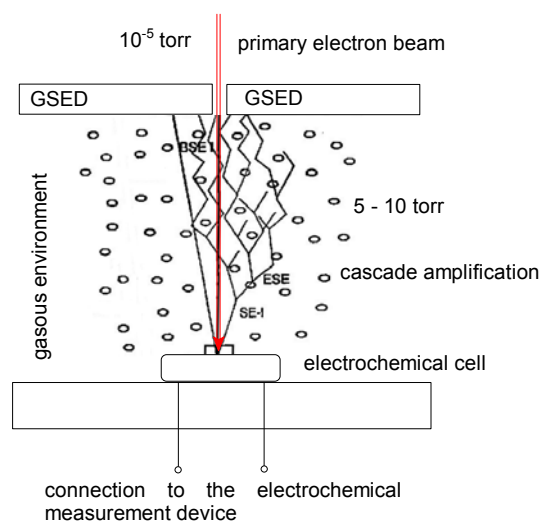


Fig. 1: Principle of in situ ESEM

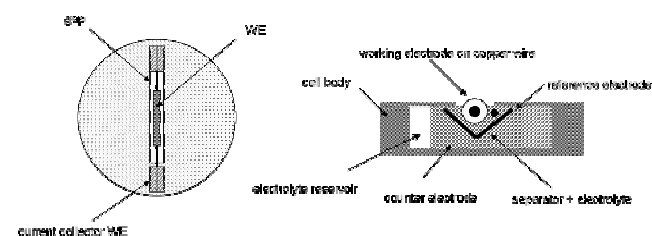


Fig. 2: Schematic figure of the ESEM cell

### References

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