

# In-situ visualization of Li-ion intercalation and formation of the solid electrolyte interphase on TiO<sub>2</sub> based paste electrodes using scanning electrochemical microscopy

## Supporting Information

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### Experimental

#### *1. Material and electrode preparation.*

Anatase TiO<sub>2</sub> nanoparticles (Sachtleben Chemie, Germany) with a specific surface area of ca. 10 m<sup>2</sup>g<sup>-1</sup> (particle size of about 150 nm) were used as active material. Paste electrodes were prepared following a standard method [1]. TiO<sub>2</sub> nanoparticles were mixed with C65 carbon black (Timcal, Switzerland) and polyvinylene difluoride binder (Solef S5130, Solvay) in N-methylpyrrolidone (Aldrich, Germany) in the weight ratio of 75:15:10 using an ultra-turrax disperser (Ika, Germany) at 200 rpm for 30 min. The mixture was cast onto aluminum foil (Schlenk, Germany) using the Doctor-Blade technique. The solvent was first evaporated at 60°C for a few hours and then the paste electrodes were dried at 110°C under vacuum (Büchi, Germany) overnight to remove traces of solvent. The mass loading and thickness of the paste electrodes were approximately 3 mg cm<sup>-2</sup> and 25 μm, respectively. The geometric electrode area exposed to the solution was 0.78 cm<sup>2</sup>.

#### *2. Electrochemical characterization.*

SECM measurements were performed using a customized instrument (Sensolytics, Germany) integrated into a Ar-filled glove box (Jacomex, France) on a vibration damped table enabling SECM experiments rigorously excluding O<sub>2</sub> and H<sub>2</sub>O (below 1 ppm). Because of the dry atmosphere inside the glove-box, special positioner motors (OWIS, Germany) were employed and the bi-potentiostat (Jaissle PG-100, Germany) was placed outside of the glove box. Bi-potentiostat, AD/DA converter (Measurement Computing Corporation, USA) piezo controller (Physik Instrumente, Germany) and computer (outside the glove box) were connected with the SECM setup (inside the glove box) through BNC connectors inserted in the roof of the glove box. The SECM was controlled by home-made software. Prior to all SECM measurements, the surface tilt was corrected.

A scheme of the home-made four-electrode open cell employed in this study is shown in Figure S1. The main body of the cell consists of polyether ether ketone (PEEK). During the cell assembly, the substrate (working electrode 2) is placed at the bottom. Then, the cell is filled with electrolyte solution, and the SECM tip (working electrode 1), counter electrode and reference electrode are immersed into the solution from the top.  $\text{TiO}_2$  paste electrode was used as the substrate. The area of  $\text{TiO}_2$  paste electrode exposed to the electrolyte solution was limited to a diameter of 5 mm. A  $10\ \mu\text{m}$  Pt microelectrode sealed in glass was employed as SECM tip or working electrode 2. A large cylindrical mesh of steel (Alfa Aesar, USA) covered with carbon nanotubes was used as counter electrode. A metallic lithium ribbon in propylene carbonate (PC) 1 M  $\text{LiClO}_4$  separated by a frit from the electrolyte in the cell was used as reference electrode. The electrolyte consisted of propylene carbonate (PC, battery grade Sigma Aldrich, Germany) and ethylene carbonate (EC, battery grade Sigma Aldrich, Germany) (1:1 by wt.) containing 0.5 M  $\text{LiClO}_4$  (battery grade Sigma Aldrich, Germany) and 10 mM ferrocene (98% Sigma-Aldrich, Germany). Since the sample is polarized between 3.0 and 0.5 V vs.  $\text{Li/Li}^+$  during the experiment, Fc is not oxidized at the sample.

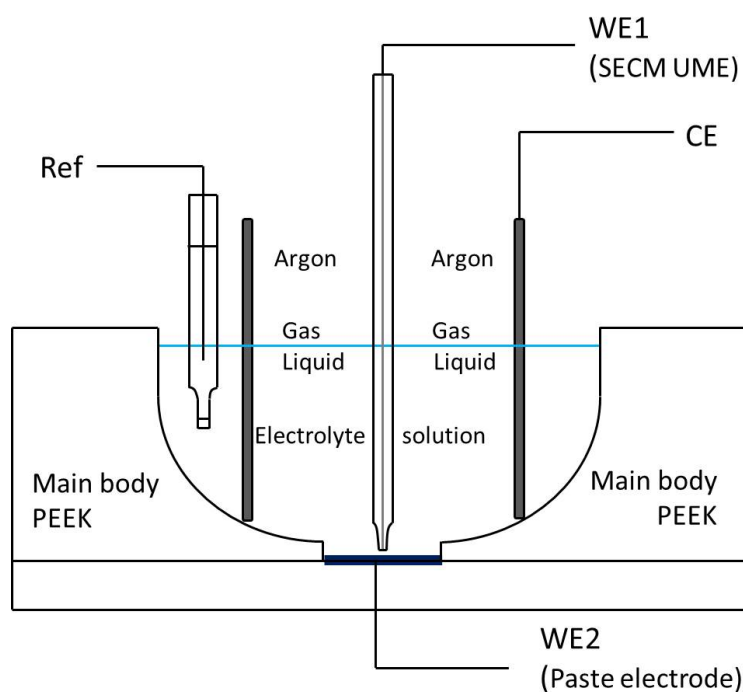


Figure S1. Scheme of the SECM open cell cross-section.