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Combined detection of electrochemical reactions and topographical effects - imaging with scanning ohmic microscopy

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ABSTRACT

The ohmic principle for the detection of local current densities with capillary-based microreference electrodes was used for reactivity imaging. Specifically, reactions of adlayers and ion-intercalation and ion deintercalation reactions were imaged that are not directly visible to other electrochemical imaging methods such as scanning electrochemical microscopy. The microreference electrodes were inclined by 45° vs. the surface normal. During the scanning process, cyclic voltammograms (CVs) were performed at each grid point of the image while the voltage between the two reference electrodes was recorded and processed by a lock-in-amplifier. Images of specific electrochemical reaction rates were generated by integration of the corresponding data segments within the CVs. The setup was coupled with a shear force distance control to correlate the electrochemical reactivity with topographical data. The results clearly show that processes like adsorption and intercalation reactions, invisible to SECM, can be imaged by scanning ohmic microscopy with a resolution in the low micrometer range.

1. Introduction

The local electrochemical characterization of interfacial reactivity is of considerable importance with respect to many different applications because inhomogeneous distribution of interfacial reaction rates influence the product quality (e.g. from galvanic processes) or the overall performance and life time of reactors. This includes fuel cells, batteries, corroding systems, sensor arrays or composite electrodes within technical electrochemical reactors. Therefore, various scanning probe techniques have been adapted for the use at electrochemical interfaces almost since the inception of modern scanning probe techniques [1,2]. While electrochemical scanning tunneling microscopy (ECSTM) and electrochemical scanning force microscopy (ECSFM) provide high resolution images of electrodes, they may provide reactivity information only, if this is associated with a change in topography [3,4]. Scanning electrochemical microscopy (SECM) has become an essential method for direct imaging of local heterogeneous reaction rates at different samples [5–9]. The SECM signal is typically generated by a forced electron transfer reaction at an amperometric microelectrode (ME). The compound electrolyzed at the ME is either added deliberately to the working solution (mediator) or it is released from the sample surface. Since the SECM response depends on the distance and the surface reactivity of the sample, a very vivid development is continuing for combining SECM (for detecting local reactivity) with topography-sensitive techniques because complex samples often require complementary and spatially correlated data for a complete image interpretation [10–14]. Increasing lateral resolution also mandates a distance regulation scheme to maintain a constant working distance. Such combinations with SECM comprise ECSFM [15,16], ECSTM [17], integration of a shear-force based detection scheme [10,11,18–21], exploitation of intermittant contact [22], use of overlaid AC currents [14–24] or scanning ion-conductance microscopy [25,26]. However, the addition of a redox mediator may change the native environment of the sample and can be a critical issue for certain applications [27]. Furthermore, ion-transfer reactions at the sample can only be visualized under very special circumstances [28].

As early as 1938, Thornhill and Evans [29,30] measured the potential drop above a freely corroding sample by a Luggin capillary moved close to the surface and reference electrode far from the surface. From the measured equipotential lines, the primary current distribution at the surface could be calculated. 1974 Jaffe and Nuccitelli [31] demonstrated the measurement of currents by the voltage drop between two reference electrodes placed along the current path in a resistive electrolyte solution. They also introduced the enhancement of the signal-to-noise (S/N)

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ratio by probe position modulation. According to Ohm's law, a voltage difference between two points in solution ΔU depends on the solution current density j, the specific solution resistance ρ and the distance l between the two locations [32] from which the local current density at the sample surface can be obtained [33].

$$\Delta U = j\rho l \quad (1)$$

These general principles have later been adopted in a large variety of related techniques such as scanning reference electrode technique (SRET) [32], scanning vibrating electrode technique (SVET) [32], localized impedance spectroscopy (LEIS) [34,35] and ohmic microscopy (OM) [36,37].

We are interested in reactivity mapping with micrometer resolution for composite electrodes in energy conversion devices such as intercalation/deintercalation of redox-inactive ions into

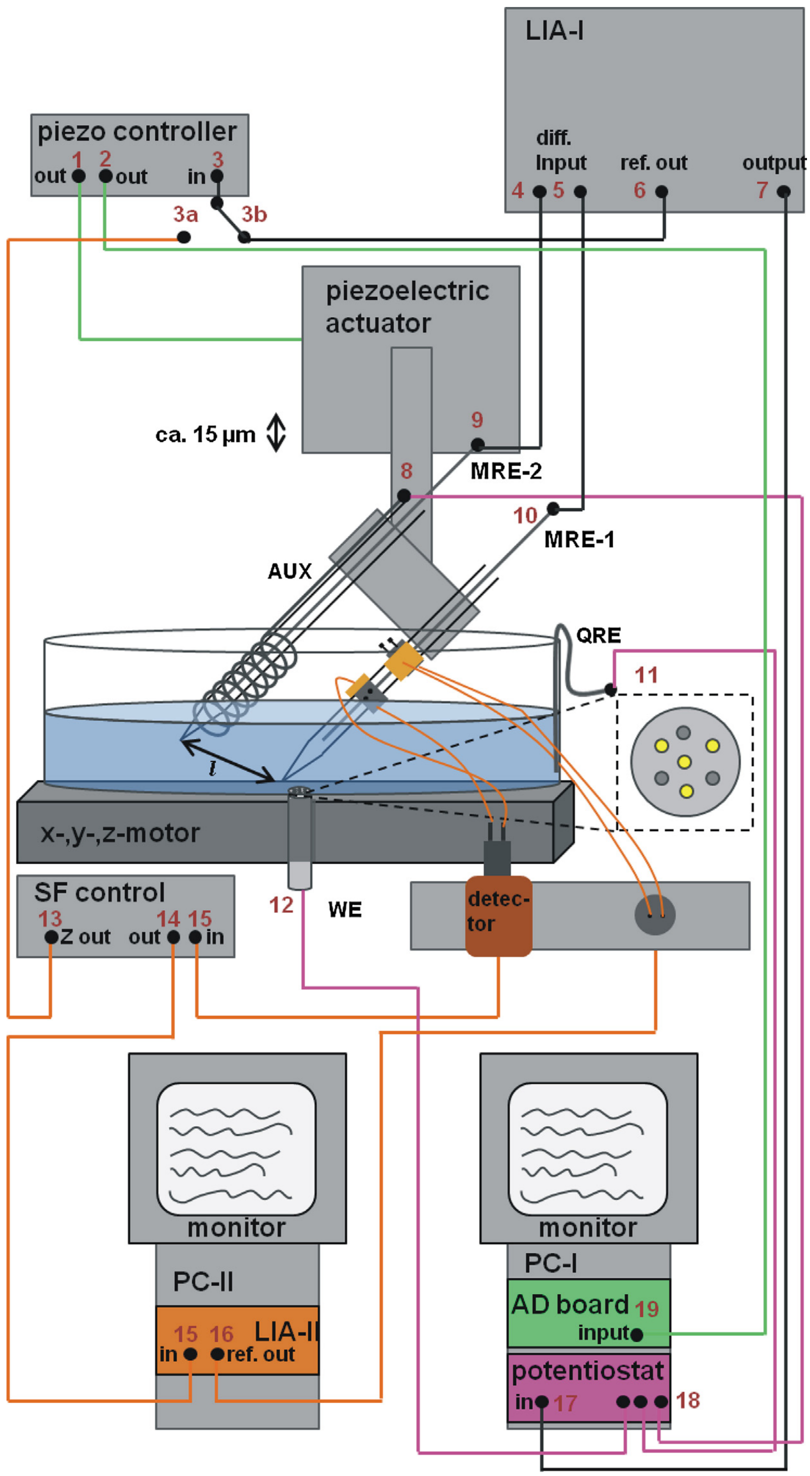

Fig. 1. SOM setup with shear-force distance control. Personal computer PC-I was used to control the SOM experiment, the AD board and the digital potentiostat. Lock-in amplifier LIA-I was used to enhance the voltage between the two MREs. The shear-force distance control was applied to MRE-1 via two piezoelectric plates twisted by 90° against each other; the upper one was used for excitation, the lower for detection of the vibration.