DEVELOPMENT OF A MICROELECTRODE FOR HIGH RESOLUTION INVESTIGATIONS OF REDOXPOTENTIALS AND IMPEDANCE SPECTROSCOPY IN CORROSION SCIENCE

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INTRODUCTION

The use of microelectrodes in electrochemical characterisation methods allows new achievements in the investigation of electrochemical processes. Fundamental research refers to the scaling down of corrosion reactions taking place in the µm range.

EXPERIMENTAL

The microelectrodes were prepared from a 100µm Pt and 100µm Pt/Ir (80:20) wire. The wire was etched in a two step process. In the first step a sinusoidal voltage of 20V (RMS) with 50 Hz in a 1:1 mixture of 1M KCl and 1 M KNO_3 was applied. The current at the beginning is 70 mA and drops down to zero. The etching process was stopped when the current reached 10mA.. In the second step in a solution of 1 M H_2SO_4 a rectangular voltage [10V (RMS) for 40 µs and –0,5V (RMS) for 200µs] is applied for 120 seconds. Tip radii varied between 1µm and 5µm. Fig.1. depicts a SEM picture of such a typical tip.
Different methods for insulation of the tips were investigated: The best way seemed to be dipping the tips for several time in baking varnish and heating it. Investigating the tips by galvanic deposition of copper shows a porous insulation. The tips were then etched first and afterwards molten into a glass capillary. With this method the active surface could be held very small. The tips where characterised by optical microscopy, SEM, cyclic voltammetry and limiting current measurement. generated during the galvanostatic treatments. A typical cyclic voltammogramm is shown in Fig.2.

Redox processes on macroscopic electrodes were characterized by scanning such a microelectrode in different distances above a working electrode (100 µm diameter platinum wire embedded in epoxy; iodide was oxidised at this electrode at a constant potential of 600mV vs. sat Ag/AgCl). A three dimensional plot of the redox potential was recorded and transferred into a concentration profile.
In another approach the electrolyte resistance depending on the distance between the working and the microelectrode was recorded via impedance measurements (Two point measurement).
First results of the spatially resolved measurements of the redox process leave the impression that this method could become by further development a way to investigate metal dissolution process without any influence on it.

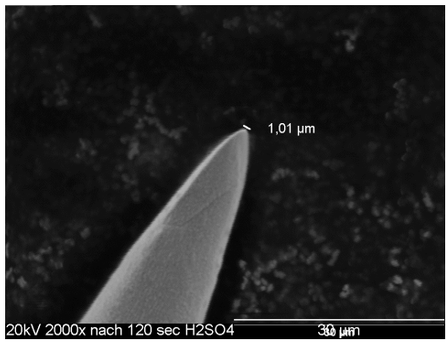

Fig. 1: SEM picture of a tip prepared using the two step etching process (magnification 2000 x).

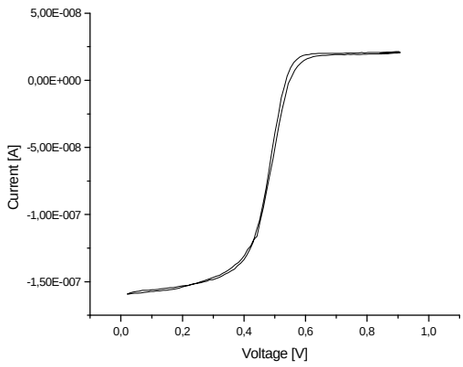

Fig.2: Cyclic voltammogramm of a Pt-microelectrode in Fe(II)/Fe(III) 0.01 M/1 M KCl solution;reference electrode: SCE; scan rate: 5 mV/sec.

Acknowledgement: This work is supported by the Kplus program of the Austrian Government.