Simulations of Transient Signals in Micro-Galvanic Processes G.Fafilek¹, J.O.Besenhard², H.Kronberger¹, G.E.Nauer³ ECHEM Center of Competence in Applied Electrochemistry, A-2700 Wr.Neustadt; Austria ¹ Institute of Chemical Technology and Analytics, TU-Vienna, A-1060 Vienna, Austria ² Institute for Chemical Technology of Inorganic Compounds, TU Graz, A-8010 Graz, Austria. ³ Institute of Physical Chemistry, University Vienna, A-1090 Wien, Austria

The structuring of surfaces in the micrometer and nanometer range is of great importance for micro system technology. Several electrochemical techniques exist which may be divided into different categories: mask or maskless processes, etching or machining processes, electroless or plating techniques and so on.

An overview of the possibilities of localization of galvanic processes as a function of solution resistance and resistance of the interface between substrate and solution is given in [1]. In this paper an EMT number has been defined which is the ratio between the polarization resistance RP and the electrolyte solution resistance REL: EMT = RP/ REL. It has been claimed that a localization of the electrical field is only possible, if the resistance of the electrolyte solution exceeds that of the electrode. Attempts have been made to produce micro- or even nanostructures by maskless methods. For this purpose microelectrodes have been used to confine the electrochemical process. Some experiments have been made to realize microstructures either via metal deposition [2] or electrochemical machining [3,4]. In [4] the machining process for the direct current (dc) case and for pulse currents with very short pulse interval has been described by a simple electrical equivalent circuit model. With short pulses the double layer capacity at closer distances to the working tool is charged with a higher voltage in the first moment. The Faraday current depends exponentially on the potential at the interface and therefore the dissolution rate will decay quickly with distance from the electrode. This is somewhat contrary to the rules given by the EMT number in [1] but these where defined only for the dc case. It is therefore possible to manufacture well shaped micro- or nanostructures even in well conducting solutions (and thus higher EMT numbers) if the pulse time is short enough.

The quasi 3-dimensional simulation of the transient current distribution of such a micro-galvanic process using short pulse current or voltage stimuli may highlight the transient electrochemical processes and the necessary conditions for well confined structuring. The simulation has been performed on the basis of a 2-dimensional electrical network. The quasi 3-dimensionality was achived by transformation of the 3-dimensional geometry of the considered working tool-substrate arrangement, having a radial symmetry, into two spatial dimensions.

Since there was no Pspice[®] model available for us for the electrochemical charge transfer reaction (the Butler-Volmer relation), we have constructed the current voltage characteristic by an approximation circuit with elements for which Pspice[®] models exist. For this purpose a diode model can be used. By adjusting the model parameters of the diode, the exponential region the Tafel region - of the Butler-Volmer equation can be fitted for a given anodic reaction. The same can be done for the cathodic section when another diode is connected antiparallel to the first one. The linear part at low polarization was taken into account with a resistor Rp connected in parallel. With such a circuit it is possible to approximate the complete Butler-Volmer equation. For the capacity of the double layer, Cdl was connected in parallel (Fig.1). Fig.2 shows that deviations are small between model and calculation for the current/voltage relation.



Fig.1: Equivalent circuit for the approximation of the Butler-Volmer equation. I_F is the Faraday current responsible for a deposition/dissolution process.



Fig.2: Comparison of the calculated current/voltage relation (line) with the approximation (circles). Relative difference between the two curves: dashed line (right axis).

The electrolyte solution was modeled by a resistor grid network taking into account the electrodesubstrate arrangement (Fig.3). The interfacial properties of the substrate were introduced as shown in Fig.3. A voltage pulse source was connected to a node of this grid. Current distribution was obtained by running the PSpice® transient simulation and evaluation of the Faraday currents in the individual branches.



Fig.3: Electrical network for simulation of the Faradic current distribution

References

^[1] J.W.Schultze, A.Bressel, Electrochimica Acta **47** (2001) 3

^[2] A. Jannsson, G.Thornell, S.Johannsson, Journal of the Electrochemical Society, **147** (5) (2000) 1810

^[3] M.Kock, V.Kirchner, R.Schuster, Electrochimica Acta, **48** (2003) 3213

^[4] R.Schuster, V.Kirchner, P.Allongue, G.Ertl, Science, **289** (2000) 98