CONTROL APPROACH FOR MEASUREMENT OF ELECTROCHEMICAL IMPEDANCE

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ABSTRACT

The paper presents appropriate control approach of a local scanning system for measurement of electrochemical impedance. Suitable piezoactuators with high dynamics are used for realization of scanning motion of the measured electrode. Because of the high velocity and high dynamics of piezoactuators they can receive a lot of information for a short time and thereby the quality of obtained results is increased.

KEYWORDS Piezo actuated mechatronic system, electrochemical impedance measurement

1. INTRODUCTION

Electrochemistry is the study of the chemical response of a system to an electrical stimulation. Its application is in domain of oxidation (the loss of electrons) and reduction (the gain of electrons)[1, 2, 3]. These reactions are known like redox reactions and they can supply information about concentration, kinetics, reaction mechanisms, chemical status and other behavior of a species in solution. Similar information can be obtained concerning the electrode surface. Electrochemical techniques can be used to investigate many things – from neurotransmitter behavior in biological situations to brightener concentrations in plating baths to initiator behavior in polymerizations to the speciation of cadmium ions in natural waters. The electrochemistry offers a perspective different from spectroscopy and the other approaches because it investigates different phenomenon than others, investigated with spectroscopy.

In electrochemistry it's possible to measure one or more of four parameters – potential (E), current (i), charge (Q), and time (t). The system response depends on which parameter is used as the excitation signal. By plotting different parameters in different ways it's possible to obtain a wealth of information.

The electrochemical measurements are made in electrochemical cell, which is composed, from three electrodes – working electrode, reference electrode and counter electrode – immersed into an electrolyte. They are connected to a potentiostat (an instrument, which controls the potential of the working electrode) and measures the resulting current which is obtained by application of a potential to the working electrode or it's possible to vary the potential with appropriate frequency. The resulting current is necessary for calculation of the electrochemical impedance that presents the ability of the electrochemical circuit to resist of the current flow.

During the investigation of electrochemical systems, the electrochemical impedance spectroscopy (EIS) can give you accurate, error-free kinetic and mechanistic information using a variety of techniques and output formats. For this reason EIS is becoming a powerful tool in the study of corrosion, semiconductors, batteries, electroplating, and electro-organic synthesis. One of the companies, working at this domain is Princton Applied Research – USA.

Its device LEIS270 [4] Is composed of three step motors with 1000 steps per revolution, scanning range in X, Y, Z axes is 70x70x20 mm, resolution - 1µm, frequency range - 10 µHz – 50 кHz. The system positions the electrode on the investigated surface and measures the resulting current. A scanning reference electrode approach is used that enables the measurement of the local current near corrosion surfaces in see water.

Other achievement in domain of EIS is SVP100 SRET scanning system. A technique with vibrating scanning electrode is used that measures electric field generated above the surface of an electrochemically active sample. A piezo-ceramic displacement device allowing vibration amplitudes from 1-60 µm controls the probe vibration (perpendicular to the sample surface). It is an ac technique; thus, high system sensitivity can be achieved via a differential electrometer in conjunction with a lock-in amplifier.

The aim of this paper is a development of a control approach for local scanning system and investigation of granular structures in micro range. This application needs of piezo actuators with maximal range of 8 µm, suitable for dynamic applications because of their high velocity and possibility of preload until 1000N.

2. PROBLEM STATEMENT

The known electrochemical scanning approaches don't allow surface scanning in submicron range because the measurement is made at static mode and the resolution of the scanning systems is very high.

The approach, discussed at this paper, allows local scanning motion of the measured electrode on the investigated surface in micro and nano range.

Inconvenience at this approach is the calibration of the scanning system because of the maximal range of the piezo elements (8µm).

The other problem is the high dynamics of the chemical reactions that prevents the achievement of the system stability for a long time.

The linearization of the hysteresis of the used piezo elements also is a problem that has to be resolved.

3. MECHATRONIC SYSTEM FOR LOCAL SURFACE SCANNING

The investigations are made into an electrochemical cell that is composed of three electrodes, immersed in electrolyte. Between two of the static electrodes is created an electric field while a small sinusoidal voltage perturbation is applied from a PC. The investigated surface is placed on the one of the static electrodes. The used scanning electrode is from wolfram. It's connected to a potentiostat that control the voltage between the static electrodes and measures the local current that flow into the electrolyte. A convenient mechatronic system is developed (fig. 1) that enables scanning motion of the Wolfram electrode. This system is composed from three degrees of freedom necessary for one translation in Z direction for fine probe positioning and two scanning motions among the X, Y directions on the surface of measurement.

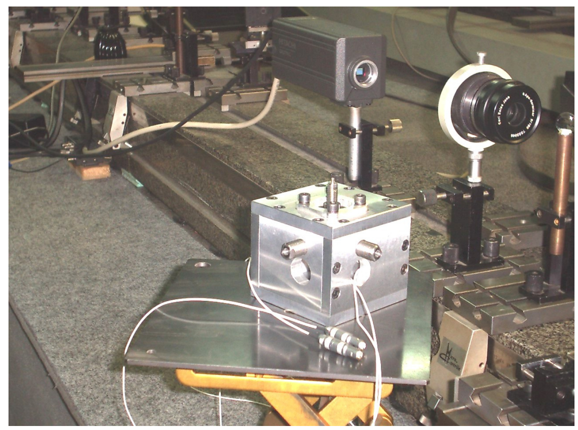

Fig. 1 Photo of the developed local scanning mechatronic system.

The synthesised kinematic scheme is shown on Fig. 2.

The stick that carries the measured electrode is mounted on axe Z and piezoactuators respectively on axes X, Y, Z. The sick is heavy connected with joint P3 (type Point-Line) that has one translation on Z and two rotations on X, Y. On the scheme each piezo actuator is modeled with one prismatic joint P5. Piezo actuators are connected to the based stick with spherical joints P3 and to the fixed base with spherical joints P4. The stress mechanism exists at the opposite part of the X, Y-axes. It's composed of a lever with disk springs parallel situated to him. Each lever is fixed to the based stick with spherical joint P3 and to the base with joint P3 (type Point-line). The stress mechanisms reduce the backlash during dynamic motion in nanometer range.

The degrees of freedom (DOF) of the system are presented by the following equation:

$$h = 6 * n - 5 * p^5 - 4 * p^4 - 3 * p^3 \qquad (1)$$

Where: n – number of mobile links, P3, P4, P5 – number of different joints.
The system presented on the figure 2 with n=9; P3=8; P4=3; P5=3 has h=3 DOF.

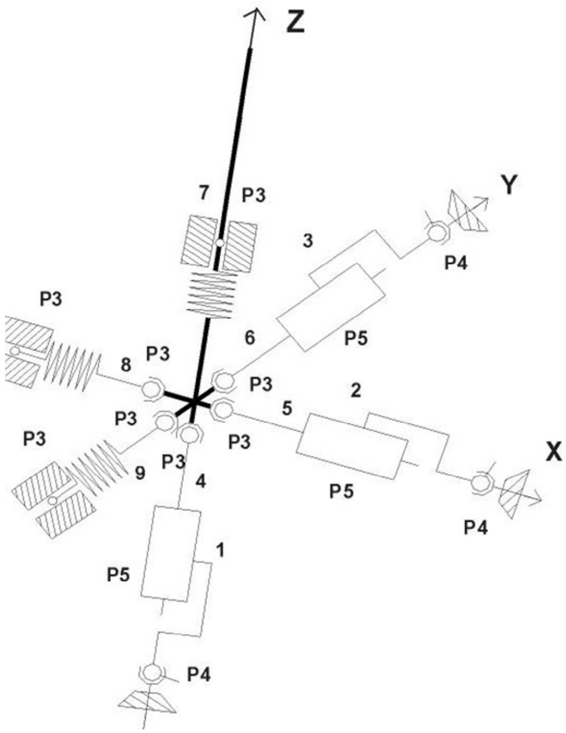

Fig. 2 Cinematic scheme of mechatronic system for local electrochemical impedance scanning.

The joint P3 in the link 7 between a stick and fixed base is an elastic plate (fig. 3). It realizes joint motions and stress of the piezo actuator on Z axes.The stiffness of the plate is defined with simulation software Ansys that calculates axial stress of the plate versus displacement and presents graphically the obtained results (fig. 4).
The plate with thickness of 1 mm has stiffness 110.558 N/mm.
The piezo ceramic elements (PA 8/12) [5] from the company Piezojena – Germany are a modulus realizing the scanning motion of the developed system. They are with maximal range 8µm and resolution open loop 0.01 nm. These features allow local scanning of surfaces in nano range. The PA series of actuators are internally pre-loaded by a mechanical spring, making them ideal for dynamic applications. The ability to generate a large force and be subjected to High Mass loading make them particularly useful for machine tools and dynamic scanning systems. The motion of actuators is made with a three-channel high voltage card (NV C1 PC –10V till 150V) from Piezosystem Jena – Germany. In it's dimensions this is a normal PC-card with full length. It needs an 8bit slot of an IBM compatible computer.

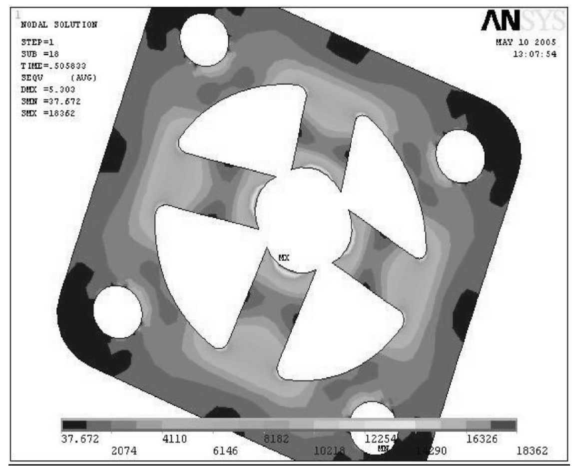

Fig.3 Type of the elastic plate and corresponding measurements of axial stress

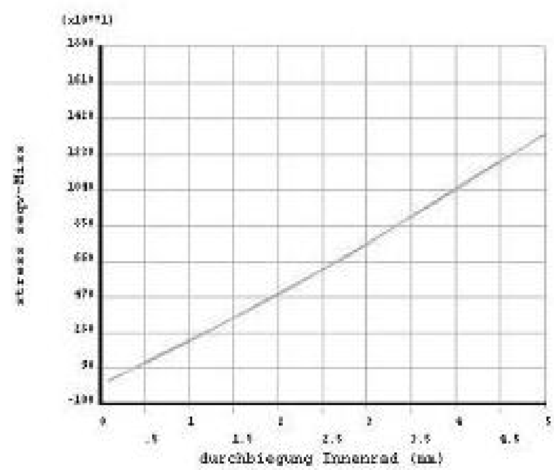

Fig. 4 Displacement and eqv. Von Misses Stress.

Three channels can be directed by software program. With an output noise of 3mV it is excellent suited for positioning in the sub-micron and nanometer range. A high stability of the output voltage makes the PC-card NV C1 ideally suited for positioning problems with highest precision. The resolution of 14 bit

makes it possible to operate in the nm-range. A microscope Zeiss Jena and connected digital camera Hitachi F110 are used for reading the position and orientation of the scanning element.
Joystick and keyboard is used for development of a telemanipulated system. The joystick is connected to PC into the game port. The relation between all system modulus is made by suitable software developed on C++ Builder. On this way the mechatronic system is more comfortable and easier to use from human.

4. MODELLING AND SIMULATION OF THE LOCAL SCANNING SYSTEM

Solid Dynamics 2004+ combines the physical motion simulation technology and 3D modeling, visualization and data translation capabilities available in one product [6]. The work with speed, acceleration and reliability in Solid Dynamics are comfortable and comprehensive to use. Kinematic and Dynamic Simulations can then be performed to optimize the mechanical motion of the assembly in a virtual environment before building a single physical prototype. A scanning system (fig. 5) is modeled using Solid Dynamics 2004+ that is composed from based, actuated and stressed chains.
The based chain (fig. 6) is composed of case (3), axial element (1) to which is mounted wolfram electrode. Into the actuated chain (fig. 7) three piezo actuators with stiffness of 120 N/µm are modeled. The stressed chain (fig. 8) is composed of two disk springs with appropriate stiffness and stress forces. All chains are strongly connected each other with appropriate spherical joints and they form a mechanical closed loop. For simulation of the prototype each piezo actuator receives a suitable law of motion and disk springs and elastic plate are stressed. Figure 9 presents graphically the motions of piezo actuators versus time. The range of piezo elements is 8 µm, disk springs are stressed to 3 mm and elastic plate – 2 mm with coefficient of elasticity 110.558 N/mm.

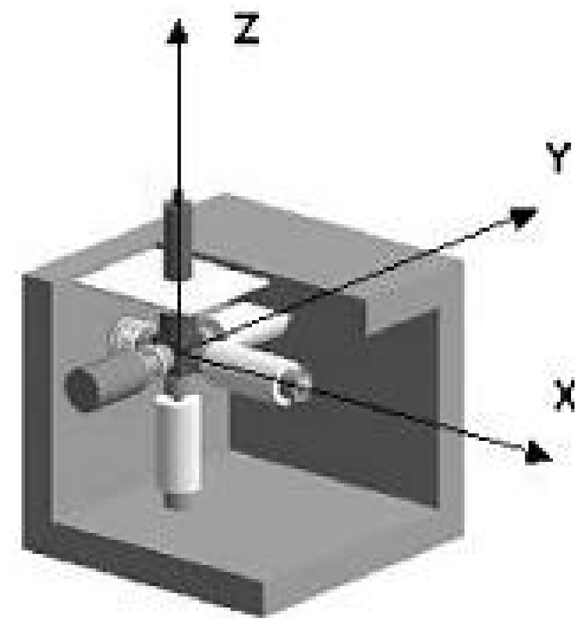

Fig. 5 Structural scheme of mechatronic system for local surface scanning

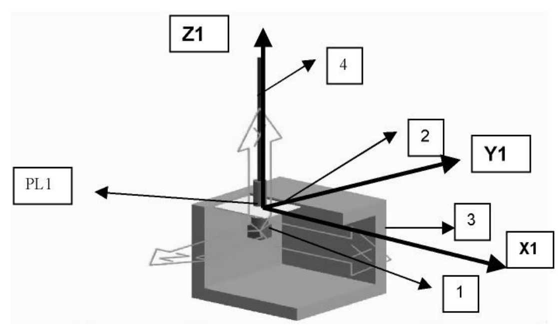

Fig. 6. Base circuit modelled in Solid Dynamics

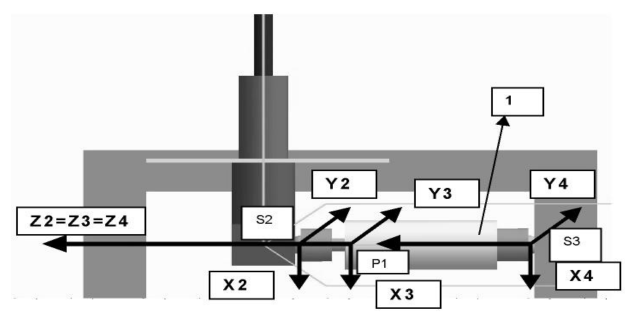

Fig. 7 Motion circuit modelled in Solid Dynamics

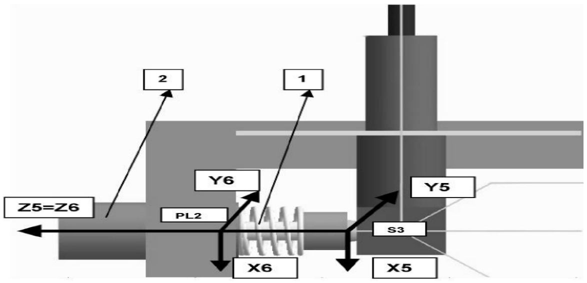

Fig. 8 Regulated circuit modelled in Solid Dynamics

Figure 10 presents the motion of the measuring electrode mounted on top of the stick with length 10mm. The resolution of piezo actuators is 0.01 nm and because of the high voltage card it becomes 0.5nm.

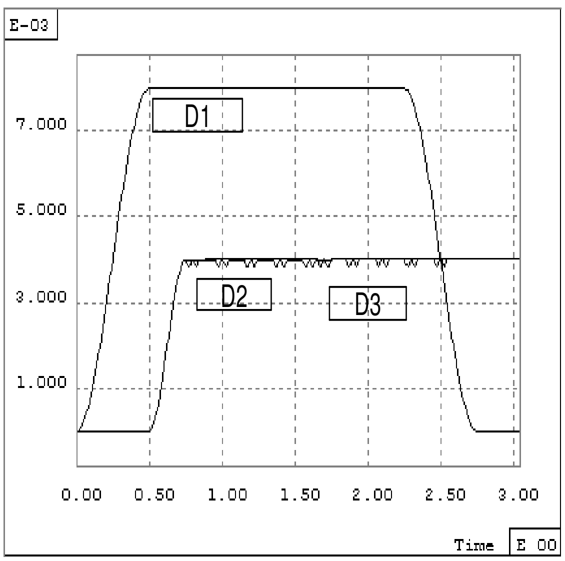

Fig. 9 D1 – piezo actuator axis z 8 µm D2, D3 – piezo actuators axes X, Y 4 µm with amplitude of the signal 9 nm

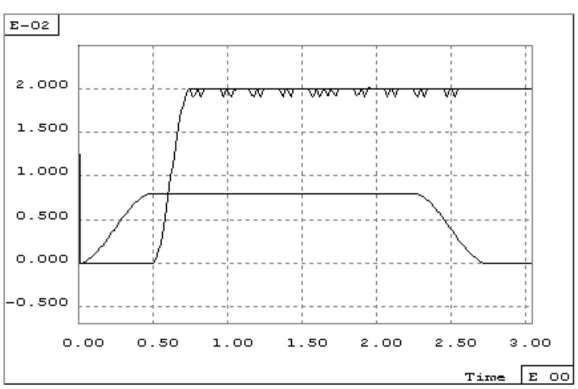

Fig. 10 Motion of the measuring electrode

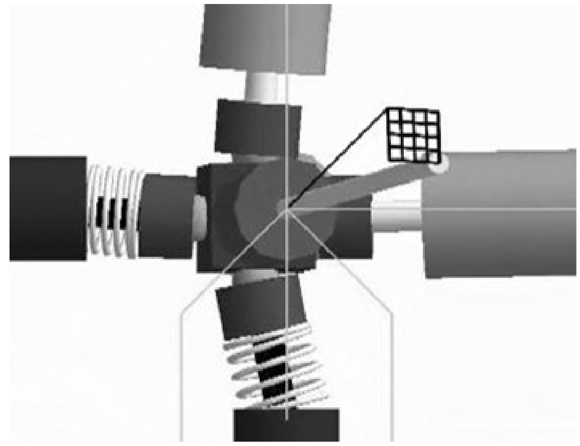

Fig. 11 Trajectory of the measuring electrode and SDS system model.

The length of the stick defines the final resolution of the whole scanning system equal to 2.5nm. The trajectory (Fig. 11) of motion of the measured electrode presents a grille with dimensions of 9x9nm and step between each scanning line equal to 3 nm.

So it's possible to make local surface scanning in nanometer range. The aim of the stress of the disk springs and elastic plate is reduction of backlashes of the mechanic scanning modulus.

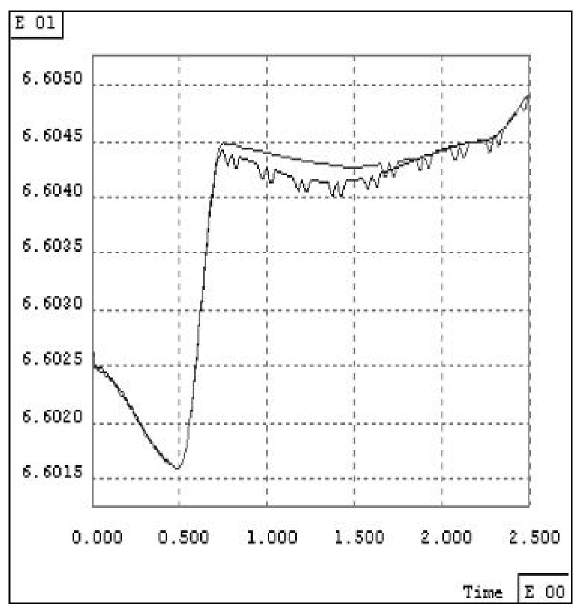

Fig. 12 Driving forces of piezo actuators.

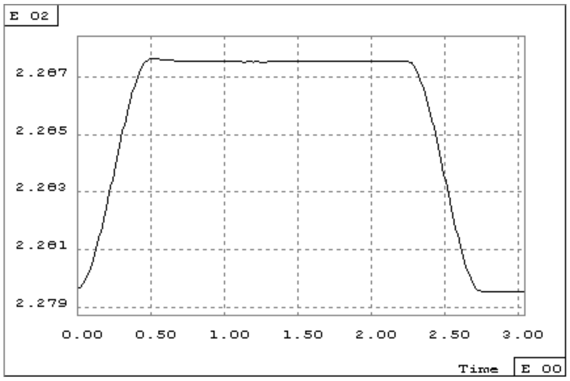

Fig. 13 Force change on Z-axis

Figure 12 presents the modification of forces versus time, generated by stress of piezo actuators with 3mm and application of its own stiffness 120 N/µm. They remain almost consants during the scanning motion and they are arised because of the home position of the piezo actuator on Z axes.
The Fig. 13 presents the change of the force on axis versus time. At the end of the positionning the value of the force decreases a little because of the start of the other piezoactuators. At the beginning the resulting forces on axes X, Y decrease because of positioning of the piezo actuator on Z axis. The force arises till 60 N/mm because of positioning of piezoelements on axes X and Y

5. CONCLUSION

At the paper was presented one scanning mechanic modulus for measurement of electrochemical impedance. A suitable kinetic scheme was synthesized with three degrees of freedom. Elastic joint is developed that eliminates backlashes in kinematic chain. Usually they are bigger than working range of the output part of mechanic system. A technique for scanning motion is developed enabling the application for granular surface scanning in nanometer range.

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REFERENCES

[1] ∗∗∗ Princton *Applied Research, Catalogue, A review of techniques for electrochemical analysis,* http://www.princetonappliedresearch.com, 11p.
[2] ∗∗∗ Www.gamry.com
[3] Vladikova D., *The technique of the differential impedance analysis*, Proc.of the Int. Workshop “Adv. Techn. for Energy Sources Inv. and Testing” 4 – 9 Sept. 2004, Sofia, Bulgaria, 28p.
[4] ∗∗∗ Princton Applied Research, LEIS270 Localized Electrochemical Impedance Spectroscopy, http://www.princetonappliedresearch.com, 6p.
[5] www.piezojena.com
[6] ∗∗∗ Solid Dynamics, Poweful 3D mechanical simulation software, Manual, 2004, 112p.

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