

## Mirjana Metikoš-Huković – *Curriculum Vitae*

**P**ROFESSOR MIRJANA METIKOŠ-HUKOVIĆ was born in Mostar in 1937. She received a BSc in Chemistry from the Faculty of Science, University of Sarajevo in 1961. Under the supervision of Professor Branko Lovreček, she received an MSc degree in 1965, and a PhD in 1974 in Physical Chemistry/Electrochemistry from the Faculty of Chemical Engineering and Technology (FCET) (former Faculty of Technology), University of Zagreb, Croatia.

Prof. Metikoš-Huković started her academic career at the Institute of Chemistry and Technology, Faculty of Technology, University of Zagreb in 1971. Two years later she became a permanent staff member in the Department of Electrochemistry, FCET. She started as a Teaching Assistant in 1971, and then rose through the ranks (Assistant Professor in 1975, Associate Professor in 1984, Full Professor in Physical Chemistry and Electrochemistry in 1992) to become a permanent Full Professor in 1999, and then Professor Emerita in 2008.

During her PhD studies (1967–1970) she worked with the research group headed by Prof. Ewald Heitz at the Dechema Institute, Department of Electrochemistry in Frankfurt am Main, Germany acquiring state-of-the-art expertise in the fields of electrochemistry, corrosion, and materials' protection.

She was a Visiting Fellow for an academic year at the Fritz Haber Institute at the Max Planck Society, Department of Electrochemistry, in Berlin, Germany from 1977 to 1978. She was working in the research group established by Prof. Heinz Gerischer and Dr. Karl Doblhofer, conducting research in the electrochemistry, and photochemistry of semiconducting materials.

Between 1993 and 1994, Prof. Metikoš-Huković was a Visiting Professor at Forschungszentrum Jülich, Jülich, Germany where she collaborated with Prof. Ulrich Stimming on the application of bimetallic catalyst materials for electrocatalysis and energy conversion.

Prof. Metikoš-Huković is a distinguished and internationally recognized scientist. She was a lead investigator in

nine international and numerous domestic projects, which resulted in numerous high quality scientific output.

Prof. Metikoš-Huković published over 130 scientific papers, all indexed in *Current Contents*, along with numerous papers in other journals, which have been cited more than 3800 times (h index 35). She co-authored one book, and wrote five chapters on chemistry, and electrochemistry.

### Research interests and scientific work

Prof. Mirjana Metikoš-Huković started her scientific career in collaboration with Prof. Branko Lovreček. Under his supervision, she received her MSc degree specializing in iron passivity and corrosion, and also her PhD degree researching the electrochemistry of semiconducting oxide films on valve metals.

*Photoelectrochemistry of Semiconductors.* The new scientific field of the electrochemistry of semiconductors emerged in the second half of the twentieth century and scientists were developing theory and experimental research concerning problems related to solid-state physics of semiconductors. Initially, germanium represented the model for semiconducting electrode properties. Research then extended into new semiconducting materials, such as transition metal oxides and sulfides, and organic semiconductors. It became clear that oxide and sulfide films on the surface of metals and alloys possess semiconducting properties. Prof. Lovreček and Prof. Metikoš-Huković were among the first researchers in the world who applied the fundamental relations developed for high purity monocrystal semiconductor materials to the new types of semiconductors. The principal role of passive oxide films in materials' corrosion protection is closely related to their semiconducting properties. Using the simple yet brilliant idea from Prof. Heinz Gerischer—that at the semiconductor|electrolyte interface the Schottky diode is formed (analog to p-n junction), which then generates photo-potential upon illumination—, the method of photoelectric polarization is

introduced (enabling *in situ* studies of the conductivity type for semiconducting films).

Prof. Metikoš-Huković and her colleagues (Dr. Mihajlo Ceraj-Cerić, MSc Slavko Ferina, Prof. Sasha Omanovic, Prof. Zoran Grubač) studied the photo-electrochemical and semiconducting properties of numerous semiconducting films (e.g., p-CuIn<sub>2</sub>Se<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, CdS, Bi<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, TiO<sub>2</sub>, etc.). The main goal of this research was to investigate how to apply semiconducting films' in photo-electrochemical cells in order to convert solar energy into electric energy (analog to photovoltaic cells). Although photo-electrochemical cells have not fulfilled expectations, and achieved wide technological application due to their corrosion problems, this research gave a strong impetus to the development of surface electrochemistry, and investigations of the passivity of metals.

*Passivity of Metals (Point Defect Model)*. Fundamental and practical aspects of passivity and passivity of metals and alloys have been a permanent research focus of Prof. Metikoš-Huković and her colleagues (Prof. Ranko Babić, Prof. Sasha Omanovic, Prof. Slobodan Brinić, Dr. Željka Petrović and Dr. Jozefina Katić), because a vast number of technological applications of metals depend on their passivity. Thin (measured in nanometers) oxide coatings reduce the chemical reactivity of metals in contact with the environment by several orders of magnitude transforming the metals' passive states. Prof. Metikoš-Huković and her colleagues studied the passivity of numerous metals and alloys with polycrystalline or amorphous structures (metal glasses). The goals of this research project were (i) to contribute to the theory of passivity, based on the *Point Defect Model*, and (ii) to design corrosion-resistant alloys for application in engineering and biomedicine.

*Role of Alloying Elements in the Designing of Corrosion Resistant Materials*. Her study of different aluminum alloys with physicists from the Ruđer Bošković Institute, Zagreb (Dr. Nikola Radić) expanded the fundamental knowledge about the role of alloying elements in the design of materials resistant to *pitting corrosion*. These studies examined amorphous alloys, Al-Mo and Al-W, so-called Al-steels with different Mo and W atomic content, in high-concentration chloride solutions (Prof. Zoran Grubač). The findings show that the key factor in pitting corrosion occurrence is the flux of mobile cation vacancies across the oxide film that are formed at the film | solution interface after the chloride ions adsorption. According to the solid-state reactions, the ions of the alloying component, such as Mo<sup>6+</sup> ions, are segregated in the formally negatively charged cation vacancies of the oxide film. The formation of a neutral complex between mobile cation vacancy and immobile metal ion leads to a decrease in ionic, and an increase in electronic conductivity of surface film, and consequently to enhanced corrosion resistance of the material.

In collaboration with Prof. Ingrid Milošev, Prof. Metikoš-Huković designed and studied *Cu-Ni alloys* with different Ni contents (10–40 wt. %). Based on the electronic structure of passive film on copper, exhibiting the p-type semiconducting behavior, the authors discussed the influence of the alloying component Ni, and its concentration in the alloy, on the corrosion properties of these materials, which are crucial in naval technology.

*Semiconducting Properties of Passive Films*. Prof. Metikoš-Huković studied the semiconducting properties of passive oxide films of various alloys (Ti, Co, Cu, Fe, Al, ...) and sole alloy's components (Cr, Mo, Ni, V, Nb, ...) *in situ* under conditions in which the electronic conductivity of film prevails, that is, when the Schottky barrier is formed at the film|electrolyte interface. Using the Mott-Schottky analysis, Prof. Metikoš-Huković determined the type of conductivity for the semiconducting film (n-type or p-type), the concentration of charge carriers, and the flat-band potential. These semiconducting characteristics enable the prediction of electronic and ionic charge transfer reactions at the film|electrolyte interface in the photocatalytic reactions of energy conversion, as well as in waste-water treatment technologies.

*Biocompatible Metallic Materials*. Prof. Metikoš-Huković also studied *biocompatible metallic materials* that are most frequently used as implant materials: titanium alloys, cobalt alloys, and high-alloyed steels. The alloy film's properties determine the level of biocompatibility and bioactivity on the surface of the implant and, therefore, the corrosion resistivity of the underlying alloy in body fluid. In collaboration with Prof. Ranko Babić, Prof. Ingrid Milošev, Prof. Zora Pilić, Dr. Ana Kwokal and Dr. Jozefina Katić, she studied the effect of alloying components (Ni in Ti-Ni alloys, V and Nb in TiAlV(Nb) and Cr and Mo in CoCrMo alloys and high-alloy steels) on their corrosion properties in simulated physiological solutions. The investigations have showed that in traditional titanium alloys (TiAlV), widely used in the commercial production of implants, the vanadium content should be replaced by niobium because a significantly higher corrosion resistance and biocompatibility is achieved for the TiAlNb alloy. In an aggressive body fluids environment, toxic V<sup>4+</sup> ions are released from a TiAlV alloy and are deposited in vital organs of the human body.

*Electrochemistry of Interfaces and Thin Films*. Prof. Metikoš-Huković has also had particular research interests in *electrified solid|liquid interfaces*, and the *modification-functionalization of surfaces by thin films*. After Rudolph A. Marcus won the Nobel Prize in Chemistry in 1992 for the theory of charge transfer, including electrochemical transfer reactions, a new discipline, the *electrochemistry of interfaces*, started to develop rapidly.

The fundamental objective of Prof. Metikoš-Huković's (and her colleagues') studies conducted in this field was to

find ways of modifying inorganic and metallic materials by using highly-effective catalytic, thin, organic or semiconducting films. Knowledge and correlation of their physical and electrochemical properties is important for understanding the usage of functional materials in sustainable technologies, based on the electrochemical concept of materials science.

*Electrocatalysis of Bimetallic Catalytic Coatings.* Prof. Metikoš-Huković and her associates (Prof. Sasha Omanovic, Prof. Zoran Grubač, Prof. Ante Jukić, and MSc Roberta Horvat) have significantly contributed to the development of synthesis methods for thin efficient catalytic films, which are used for oxidation of small organic molecules in fuel cells and for hydrogen evolution reaction in hydrogen generators.

In this research program, electrodeposited Pt-bimetallic coatings with different stoichiometric ratios of Sn and Ru showed high catalytic activity for methanol oxidation as well as a long-term stability in the presence of carbon monoxide—a catalytic poison—in the fuel. According to the bifunctional mechanism, Sn and Ru atoms in bimetallic catalysts enable the oxidation of carbon monoxide molecules, and the adsorption of oxygen species at the significantly lower potentials in comparison to the pure Pt. The Pt70-Ru30 coating exhibited the highest catalytic efficiency, thus supporting the theoretical predictions.

Prof. Metikoš-Huković has also focused on the intrinsic nature of *hydrogen evolution reaction (her)* as well as on the composition, electronic structure and chemical properties of catalysts.

One of the main goals of these studies has been the development of *highly efficient Ni-based catalysts for her*, as the alternative to expensive Pt catalysts. Thin films of Ni-alloys were prepared by electrodeposition (polycrystalline Ni), sputter-deposition (nanostructured Ni) or very fast melts solidification (metal glasses). The design of Ni-bimetallic catalysts was based on the correlation of electrocatalytic activity of intermetallic phases with *d*-electron density states. Prepared by sputter-deposition, each of the investigated catalyst materials—Ni-Zr, Ni-W and Ni-Mo—with different atomic ratios of Zr, W and Mo, has shown enhanced catalytic properties for *her* in comparison to polycrystalline Ni itself. The highest catalytic activity correlated with the density of Ni-3d electron states on Fermi level, and the rapid change in magnetic properties. The investigations also revealed that the catalytic activity depended on the nanoparticle dimensions as well as the structure of interparticle space.

*Self-assembled Monolayer (SAM) Formation on Conducting Substrates.* As part of research into thin functional films on conductive substrates, Prof. Metikoš-Huković, together with Dr. Željka Petrović, Dr. Jozefina Katić, and Prof. Zoran Grubač, also studied thin organic films with

applications in electronics, biochemistry, and biomedicine. Extensive investigations have focused on the modification of metallic surfaces by thin films, especially by self-assembled monolayers (SAM) of long-chained organic molecules. As it is possible to control the film's thickness and structure, as well as their surface properties, SAMs are ideal systems to study the fundamental principles of surface chemistry and surface phenomena. The studies explored a large number of systems, such as long-chained and aromatic (alkane)thiols assembled on Au and Cu, carboxylic and phosphonic acids on biodegradable Mg alloys, and phosphonic acids and their derivatives on Ti alloys, trying to optimize the surface properties for various technological applications. The SAMs have generated massive interest because of their potential applications in different technological fields (*e.g.*, sensors, corrosion protection, catalysis, microelectronics, biotechnology, molecular and biomolecular recognition).

*Corrosion and Materials' Corrosion Protection.* Prof. Metikoš-Huković and colleagues also studied, *in situ* in real environments, the mechanisms and the kinetics of corrosion processes of a large number of technologically important metals and alloys (Fe, Cu, Al, Pb, austenite and martensite steels, Cu-Ni, Al-alloys, Pb-Sb, *etc.*). Considering that the corrosion processes are of electrochemical nature, the application of electrochemical pulse, potentiodynamic techniques, and electrochemical impedance spectroscopy in these studies resulted in a parametrization of the corrosion variables. The objective of this research program was to extend fundamental knowledge of the mechanics of corrosion processes, with the purpose of designing new engineering materials and corrosion inhibitors that would result in more efficient, and yet ecologically acceptable corrosion protection procedures. This research systematically studied: benzotriazole and its derivatives as inhibitors for Cu and Cu-alloys corrosion (with Prof. Ranko Babić and Dr. Mirjana Lončar), amines and N-arylpipyrrols as inhibitors for Al and Al-alloys corrosion (with Prof. Ema Stupnišek-Lisac), thiourea and tannins (Prof. Slobodan Brinić) as inhibitors for Fe and low-alloyed steels.

## Scholastic work and education of scientists

Throughout her career, Prof. Metikoš-Huković has been a dedicated teacher and mentor of many scientists-to-be. She established new education plans and programs of study in the Faculty of Chemical Engineering and Technology (FCET) (former Faculty of Technology), University of Zagreb (UniZg), Croatia. She co-founded the course *Applied Chemistry*, available at both undergraduate and graduate levels (FCET, UniZg). She also established and coordinated the postgraduate doctoral course *Engineering Chemistry* (FCET, UniZg). Establishing this doctoral course enabled

FCET to award students a doctoral degree in the field of Natural Sciences. The degree acquired upon the completion of these studies is Doctor of Natural Sciences, area: Chemistry (*Doctor scientiarum naturalium ad chemiam pertinentium*, Dr. Sc.). The right to award the Dr. Sc. degree was an important accomplishment for FCET as it has enabled the continuation of undergraduate and postgraduate courses in *Applied Chemistry*, and the preservation of the longstanding tradition of teaching chemistry at FCET, which first started in 1919.

Although now officially retired, Prof. Metikoš-Huković, as Professor Emerita, is still active as a University Professor for postgraduate doctoral courses at FCET, and for the Faculty of Science, Department of Chemistry, UniZg where she is also a member of the Doctorate Course Study Council.

Prof. Metikoš-Huković taught the core course *Electrochemistry* in the Department of Electrochemistry, FCET, and is the author of the internal textbook *Electrochemistry*. She also introduced the following courses and laboratory seminars for undergraduate and graduate programs: *Electrochemistry of Semiconductors*, *Selected Chapters on Materials Electrochemistry*, *Corrosion Protection Methods*, *Electrochemical Corrosion of Materials*, *Semiconducting Materials*, *Fuel Cells*, and *Chemical-Technological Laboratory*. For all of these courses, she wrote internal course materials.

She has always firmly supported conceptually sound, and state-of-the-art studies and teaching, emphasizing the acquisition of fundamental—rather than descriptive—knowledge while enhancing the students' research skills through experimental practice. This pedagogical approach has informed her teaching work. She has been a dedicated, fair, and nurturing professor. She has always tried to consistently reach out to students. In addition to keeping regular office hours, she has always made herself available to students for conversations about course materials, research projects, exams, job searches, career interests, or any other student concerns.

Students consistently praised her lectures for being concise, systematic, and always incorporating the newest content from scientific literature. Considering her scientific excellence and the exemplary student care that she was offering, it is not surprising that numerous undergraduate and postgraduate students wanted Prof. Metikoš-Huković to be their advisor. Using the funds secured from scientific projects, and collaborations with fellow expert researchers, she meticulously equipped her laboratory. Through her personal dedication and collaborations, she provided the FCET students with opportunities to use modern research techniques and investigation methods at the Ruđer Bošković Institute, the Institute of Physics, and at the Institute for Medical Research and Occupational Health.

In addition to educating and nurturing young scientists-to-be, she worked tirelessly to raise the practical relevance of students' work at FCET, and to forge close ties between FCET and Croatian industry. She helped many students to obtain degree-suitable jobs with Nikola Tesla-Ericsson, Končar, Ina, Pliva, and other companies. She also encouraged students to maintain contacts with FCET after graduation, and to continue to pursue further study in Croatia and abroad.

Prof. Metikoš-Huković supervised 12 doctoral, 27 M.Sc. and 51 B.Sc. thesis. Many of her students were awarded the Rector's Award for their projects.

Prof. Metikoš-Huković also taught abroad. While at the Dechema Institute (Frankfurt, Germany), she led an engineering course for industry students, and for young teachers. She was the principal lecturer for *Electrochemistry Corrosion* at the Department of Chemistry, Faculty of Science, University of Sarajevo, Bosnia and Herzegovina. She co-mentored MSc and doctoral candidates at the Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia. As a Visiting Professor at Forschungszentrum (Jülich, Germany), she participated in postgraduate doctoral courses.

The scientific projects that Prof. Metikoš-Huković secured and managed have been especially important for the education and development of successive generations of young scientists. Many of Prof. Metikoš-Huković's student protégés have become reputable University Professors, and successful scientists who themselves continue educating the younger generations of scientists in Croatia and abroad. Her former students include, among others, Prof. Sasha Omanovic at McGill University (Canada), Prof. Ingrid Milošev at the Jožef Stefan Institute (Slovenia), Prof. Zoran Grubač and Prof. Slobodan Brinić at the University of Split, Prof. Marijan Šeruga and Prof. Vlatka Gvozdić at the University of Osijek, Dr. Željka Petrović at the Ruđer Bošković Institute, Prof. Nushe Lajci at the University of Prishtina (Kosovo), Prof. Emir Turkušić at the University of Sarajevo (Bosnia and Herzegovina), and Prof. Zora Pilić at the University of Mostar (Bosnia and Herzegovina).

### Academic citizenship and administrative work

Prof. Mirjana Metikoš-Huković has been actively involved in multiple aspects of scientific and administrative work at the University of Zagreb. She diligently served on a number of committees. These include: (i) the National Committee for Natural Sciences (area: Chemistry), at the Croatian Rector's Conference for Higher Education Institutions, (ii) the Regional Scientific Council for Natural Sciences at the National Council for Science, Higher Education and Technological Development of the Republic of Croatia, and (iii) the Committee for Science and International Cooperation at the University of Zagreb.

As a key member of these, and numerous other committees and councils, Prof. Metikoš-Huković has always worked for the benefit of FCET, and her discipline. Through relentless effort and personal engagement, she made sure that *Applied Chemistry* was introduced into the university curriculum in *Chemistry*, which was important and significant for researchers in this field at FCET.

Having served numerous mandates since 1982 as the Head of the Department of Electrochemistry at FCET, UniZg, Prof. Metikoš-Huković has consistently and passionately cared about advancing the educational processes and conditions at FCET, including the constant improvements of the laboratory practicum, and maintaining high standards in the work place, and in the student laboratories. Due to these efforts, undergraduate and graduate programs are still offered at FCET, preserving the longstanding educational content developed through the scientific and educational work of multiple generations of her older colleagues. The continuation of these undergraduate programs has had a long-term positive impact on FCET, its employees, its students, and its research.

Together with Professor Osman Muftić, the first Croatian Minister of Science, Technology and Informatics, and Professor Jure Radić, she served on the Committee for Science and Higher Education at the Croatian Ministry of Science and Education. This committee established and introduced the *Model of Scientific Novices (Junior Researchers)* into Croatian higher education in 1991. This model has supported the systematic employment of the best undergraduate students in Croatia, leading them into science and curbing brain drain from the Republic of Croatia.

Prof. Metikoš-Huković was a member of the Editorial Board, and Associate Editor of the *Croatica Chemica Acta* journal. She served as the National Secretary for the *International Society of Electrochemistry* from 1991 to 1994, and as the President of the *Organization Committee for the 11<sup>th</sup> Yugoslav Symposium on Electrochemistry* in 1989.

Prof. Metikoš-Huković is also a member of the following organizations: the *International Society of Electrochemistry (ISE)*, the *Electrochemical Society*, the *International Korrosion Gesellschaft*, the *Croatian Chemical Society (CCS)*, and the *Croatian Society of Chemical Engineers (CSCE)*.

She is also a regular reviewer for leading scientific journals such as the *Journal of Electroanalytical Chemistry*, the *Journal of Applied Electrochemistry*, *Electrochimica Acta*, the *Journal of Hydrogen Energy*, the *Journal of Electrochemical Society*, *Corrosion Science*, *Biomaterials*, *Materials Chemistry and Physics*.

For more than forty years, Prof. Metikoš-Huković has worked tirelessly to build her scientific reputation and, during that process, to contribute to building the scientific reputation of FCET. Throughout her academic career, she has ceaselessly and wholeheartedly worked on promoting the FCET, and the fields of physical chemistry and electrochemistry, on national and international levels. It is therefore entirely fitting that a special issue of *Croatica Chemica Acta* should mark her eightieth birthday due to her teaching, research, and institutional efforts in, and contributions to the scientific fields of physical chemistry and electrochemistry.

*Dr. Jozefina Katić  
Prof. Ingrid Milošev*