# Zdravko Stoynov - the scientist who turns curiosity into multidisciplinarity

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It is not easy to write about the scientist Zdravko Stoynov, about his achievements and contributions, which stem from his vivid and unconventional personality, about his original way of thinking – sometimes too avant-garde for its time, or as they say today – innovative, and thus not at all easy to understand and accept. It is not easy, however, it is downright challenging.

While trying to systemize his activities, I realized that nearly everything Zdravko Stoynov has set his mind on doing has turned into an achievement on the cutting edge of science.... since the beginning of his career at the age of 25, i.e. 55 years ago, when he developed the first analog computer to calculate systems of differential equations to the twelfth order after the decimal point for his thesis at the Technical University of Sofia. That took place in 1960 and now – 56 years later he continues to introduce new methodological algorithms and solutions which, when integrated into his nonstandard equipment, register significant unexplored phenomena in electrochemical power sources - the latest area of his professional interests.

Prof. Stoynov's scientific achievements are not only numerous and significant, but also cross between different disciplines to redefine problems outside normal boundaries and reach solutions based on a new understanding of complex processes - a novel approach in modern science which usually involves different teams of scientists from diverse backgrounds and fields. Zdravko Stoynov's research marries electrochemistry with engineering, mathematics, computer sciences... he suits the equipment he creates to his experimental goals - from the development of unique hardware and software to original methods for data analysis. For example, he measured the underpotential prenucleation of Ag on dislocation free surface of single crystal face by constructing an ultra-sensitive potentiostat with a voltage range of 10 mV and sensitive current measurements. His precision equipment and methodology registered impedance

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on a single dislocation. His extensive interdisciplinary knowledge and skills reflect in his academic degrees: Ph.D. in engineering (automatization of the experiment) from the Bulgarian Academy of Sciences (BAS); Doctor of Technical Sciences (technical cybernetics) from Zurich Polytechnical University, and Doctor of Chemical Sciences from BAS.

I had been wondering for many years about the source of Prof. Stoynov's limitless scientific curiosity and inexhaustible constructive energy to define new topics and undertake seemingly insoluble problems, transforming them into fertile and attractive research fields. Finally, I found the answer. While preparing my presentation for the official 80th anniversary ceremony, I asked Prof. Stoynov for some childhood photos... and there it was... I saw the same expression, the curiouslymischievous same smile - as open and playful at the age of 3-4 as it was at the age of 70-80 (Fig. 1). Throughout all this time, he has preserved and developed this childish curiosity and disregard for which. combined taboos limits and with extraordinary intelligence and the multidisciplinary knowledge accumulated during the years, makes him an extraordinary scientist, just as it is in the words of the renowned physical chemist Ivan Stransky: "A scientist must possess the capability to wonder. A scientist has to see voids where others see nothing."

Born in Kardjali on May 16, 1936, Zdravko Stoynov spent his childhood in Stara Zagora, in the family of his maternal grandfather Stefan juharov, the headmaster of the regional girls' high school, founded in 1863 and famous for its educational traditions since the time of the Bulgarian cultural revival. Stefan juharov's daughters were enthralled by literature - Zdravko's mother was a teacher, while her sister became a poetess in the literary circle of Georgi Bakalov, a famous Bulgarian literary critic and publisher from the beginning of the 20<sup>th</sup> century. His father, Boris Stoynov, was a lawyer, but both sons, Stefan and Zdravko himself cut ties with the social science family tradition and became engineers. Their professional orientation took such a sharp turn

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Zdravko's

battery) at the age of 8, he didn't have inkling that

batteries would become an integral part of his

professional destiny. This is how the "Matador"

technical construction game completely changed

and

determined

his

childhood

professional life - the life of an inventor.

thanks to... a matador!... a children's game, which became their game in life. After completing all levels of the "Matador" game, Stefan and Zdravko began to ask questions themselves, solve puzzles and complete tasks. When Zdravko Stoynov constructed his first battery (the Volta



Fig. 1. Zdravko Stoynov in: early 1940's (left); 2010's (right).

Hence, in 1960 Zdravko Stoynov graduated from the Technical University of Sofia by constructing the first in Bulgaria analog computer to calculate differential equations to the 12<sup>th</sup> order after the decimal point. In the next 2 years, he established the "Computing and Modeling Laboratory" at the Technical University and constructed a large analog computer to calculate non-linear differential equations up to the 120<sup>th</sup> order. At the same time, he developed non-standard equipment for researchers at the Bulgarian Academy of Sciences. As a result, in 1963 Prof. Todor Vitanov (a research fellow then), introduced him to the team of Academician Evgeni Budevski, who was feverishly working on creating a dislocation-free crystal. If successful, they would create the first in the world "perfect crystal" and confirm the Stransky-Kaischew theory of two-dimensional nucleation.

Thus, in 1963 Zdravko Stoynov became part not just of the Bulgarian Academy of Sciences, but also of a talented world-renowned research team on the verge of a significant discovery. In a matter of months, he considerably increased the sensitivity, precision and stability of the measuring equipment and, albeit coming from a completely different scientific field, started to actively participate in the scientific work of the team. Zdravko Stoynov himself enthusiastically described the atmosphere, emotions, and dedication of the entire team during those exiting times in his contribution for Academician Evgeni Budevski in this special issue of Bulgarian Chemical Communications.

In 1965, 33 years after the publication of the Stransky-Kaischew theory, came its experimental proof – the Budevski team successfully grew the first in the world dislocation-free single crystal. This accomplishment sparked extensive research of electrochemical behavior in a new, experimentally unexplored system with completely different behavior from systems with dislocations in the

crystal lattice. Zdravko Stoynov actively participated in the novel research by developing models for surface diffusion and monoatomic layer growth [1,2].

With such a strong scientific beginning, what to do next?! By participating in the development of ultra-sensitive equipment for a unique experiment, Zdravko Stovnov fell within the orbit of Academicians Rostislaw Kaischew and Evgeni Budevski - an orbit which determined to a great extent his professional path. His exceptional engineering and mathematical background gave him the unique independence to develop targeted task-specific equipment. From then on, he had freedom to choose what scientific peak to overcome next. He selected to go into electrochemical impedance spectroscopy (EIS) - a difficult and little exploited at the time, yet exciting field full of potential and enormous opportunities. In parallel, he continued to work in a pure engineering field automatization of the scientific experiment, developing a series of automated battery testing equipment for the newly established Central Laboratory of Electrochemical Power Sources with Director Evgeni Budevski, founded in 1967 (Figs. 2-4).



**Fig. 2.** The nucleus of the newly founded Central Laboratory of Electrochemical Power Sources (from left to right): Veselin Bostanov, Dechko Pavlov, Jordan Geronov, Evgeni Budevski (standing), Todor Vitanov, Georgi Staykov (standing), Zdravko Stoynov, Ilia Iliev.



Fig. 3. The Electrochemical Methods Department, founded by Zdravko Stoynov: 1976 (left); 2016 (right).

That equipment was implemented in the Bulgarian lead acid batteries plants (in Dobrich, Targovishte, Pazardjik). Prof. Stoynov's power potentiostats were introduced in the Laboratories of the German and Czech Academies of Sciences. During his specialization in Case Western Reserve University in Cleveland, he developed a newgeneration ultra-fast power potentiostat (BC 6000), which was put into production in Stonehard Ass. (USA) - the company owned by the inventor of the fuel cell for the American lunar rover.

Zdravko Stoynov never ceases to develop unique non-standard equipment (Figs. 5,6), but it serves as a means to a greater end as the focus of his work shifts to experimental methodologies.

Despite his interest and work in various scientific fields, his greatest and undying love remains electrochemical impedance. He is irresistibly drawn to this method by its exceptional informative capabilities and numerous exciting challenges. Electrochemical impedance has the unique advantage of separating the kinetics of the different steps describing the phenomenon or process under investigation. However, there are serious hurdles in the analysis of the experimental data, which need a statistical approach. he challenge is two-fold and consists in both the method and the system under investigation... and Zdravko Stoynov has been "digging" in both directions - for already more than 40 years.



Fig. 4. Zdravko Stoynov's computerized testing laboratory in CLEPS (1975)



**Fig. 5.** Zdravko Stoynov's "Hydrogen Laboratory" in IEES (2015).



**Fig. 6.** Zdravko Stoynov and Massimo Schiavetti in front of Stoynov's equipment for impedance testing of large batteries for accumulation of energy from solar cells (ENEL- Pisa, 2014).

Nowadays, measuring electrochemical impedance with frequency response analyzers is a mainstream method used by all. However, few know that they have to thank Zdravko Stoynov for implemented this equipment into this; he electrochemical measurements after a visit to the Solartron company in 1968. The first two frequency response analyzers were implemented by Prof. Epelboin in his laboratory in Paris (CNRS-UPMC, Université Pierre et Marie Curie) and by Prof. Stoynov himself in CLEPS (Bulgarian Academy of Sciences) – both in 1968.

Working in a "battery institute", Zdravko Stoynov decided to investigate the impedance of batteries – an object whose impedance was considered impossible to measure at the time. Under these circumstances, he started to systematically chisel away at the scientific taboos... and continues to do so to this day. For a start, he introduced measurements outside the point of chemical balance. Today, this is customary; however, it was out of the question of about 40 years ago. Prof. Stoynov developed specialized equipment and with his colleagues at CNRS in Paris measured, for the first time in the world, impedance of batteries – galvanostatically and quasistrationary [3] (Fig. 7). A year later, he measured the impedance of large-scale batteries. He promoted the introduction of this method in laboratories and practices of the European Space Agency, the Soviet space program, as well as, in the Lewis Center at NASA.

#### JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 539–544 SHORT COMMUNICATION Impedance measurement on Pb/H<sub>2</sub>SO<sub>4</sub> batteries M. KEDDAM, Z. STOYNOV,\* H. TAKENOUTI Groupe de Recherche no. 4 du C.N.R.S. Physique de: Liquides et Electrochimie', associt à l'Université P. et M. Curle, 4 place Jussieu, 75230 Paris Cedex 05, France Received 4 March 1977

1. Introduction	The purpose of this note is to demonstrate that
Relatively few works have been carried out on $Pb/H_2SO_4$ batteries from an electrochemical kinetics point of view. This is partly due to the	of electrochemical generators by means of a transfer function analyser over a very wide fre- quency range. The impedance measurements are

Fig. 7. The first publication for impedance on batteries.

What would be the next challenge? Delving deeper into the impedance of batteries, Prof. Stoynov focused on the non-steady state of batteries during the measurement process.

## Non-stationary (4-D) impedance analysis

Based on the classical method of the Transfer Function (TF). Electrochemical Impedance Spectroscopy gives a local, linearized and full (in a frequency aspect) description of the investigated electrochemical system, which is assumed to be a steady-state one. However, batteries behave as big statistical systems with distributed parameters on a macro and micro scale. During cycling, processes of mass and energy transfer take place. They change the object's structure and parameters. Thus, batteries show non-steady state behavior, which is a restriction for correct impedance studies. For further development of impedance of batteries, a liberation from the restriction of steady state conditions was needed and thus Zdravko Sotynov developed non-stationary (4-D) impedance analysis - a procedure which eliminates the delay errors [4-8]. This approach is based on the assumption that the state and the parameter space of the system is a continuum. It corrects the errors arising from the measurement delay during the frequency sweep. In contrast to classical electrochemical impedance spectroscopy, which works with a 3-dimensional (3D) set of data, Zdravko Stoynov formulated a 4dimensional initial set of experimental data, including the time of measurement. He approximated every iso-frequency dependence with a formal model and applied two orthogonal isofrequency cubic splines respectively for the real and the imaginary components. The interpolation (and extrapolation) for a given time  $t_j$  and a set of frequencies i gives the corresponding estimates of the real and imaginary parts. Thus, the data of each evolving diagram are reconstructed and the corresponding impedance diagrams already represent the impedances measured virtually at one and the same time for all frequencies which, as it can be seen in Fig. 8, in practice, corrects the deformations due to the non-steady state evolution.



**Fig. 8.** Simulated impedance diagrams of evolving simple Faradaic reaction deformed by measurement delay errors: a) iso-frequency dependence for the lowest frequency; b) fifth iso-frequency dependence (starting from the lowest frequency). *Reproduced with permission from Z. Stoynov and D. Vladikova (2006) Nonstationary differential impedance spectroscopy in energy sources. In: Stoynov Z and Vladikova D (eds.) Portable and Emergency Energy Sources, pp. 411–436. Sofia: Marin Drinov Academic Publishing House.* 

The developed 4-D approach improved significantly the impedance studies of batteries [8-12]. It has also been introduced in the battery testing software of Zahner Elektrik GmbH & Co. KG and successfully applied by Mitsubishi in Liion batteries research [13,14], as well as, for studies of other time-evolving systems. Two of the papers in this issue apply the 4D analysis and contribute to further development of its application window [15,16].

## Rotating Fourier Transform (RFT)

The non-steady state conditions of the electrochemical system during impedance measurements penetrate deeper, affecting the Fourier Transform (FT) which is the mathematical kernel of every impedance analyzer of our days. The FT is the best estimator of sinusoidal signals in steady-state conditions. However, out of those conditions, the FT produces specific errors dependent on the frequency. After a profound analysis of those errors, Stoynov succeeded to develop theoretically an advanced generalized form of this transform - the Rotating Fourier Transform. This was the subject of his doctoral dissertation in the Federal Institute of Technology - Zurich [17,18]. The RFT was proved both in simulations and in practice. The implementation of the RFT in impedance spectroscopy provides for precise measurements of time-evolving systems out of the steady-state conditions. It opens a new horizon for studies of batteries and fuel cells, corrosion and many other systems. Although created 30 years ago, in our days, the Rotating Fourier Transforms are entering in their application area, exploring the infra-low frequency range (down to the µHz region), where many important phenomena take place.

#### Differential Coulometry Spectroscopy

Battery testing is an important applicationoriented tool for evaluation of their operational capability and performance as sources of energy and power. The typical testing results give general information that represents the overall behavior and thus does not support the analytical understanding of the processes taking place. To fill this gap, Zdravko Stovnov developed the Differential Coulometry Spectroscopy (DCS) which extracts valuable information about the batteries' internal electrochemical design kinetics. and life degradation. This technique requires measurements of the voltage changes with the time followed by precise aperiodic function Spectral Transform analysis. [18,19]. In order to separate the thermodynamic kinetics from the masking dynamic effect of the intrinsically connected transport limitations, very slow rate galvanoctatic testing (charge/discharge) is required. In principle, the galvanostatic mode of testing is a sweep coulometry and provides for the evaluation of the quantity of electricity necessary for the propagation of the investigated process or its steps. DCS was found to be a useful tool for investigation of the electrochemical behavior and performance of rechargeable batteries based on intercalation materials (Fig. 9). Recently, it was included in the analysis package of BioLogic Science Instruments latest EC-Lab software version V11.01 [20].



Fig. 9. Four volts Li-ion sample with nominal capacity of 2200 mAh: (a) Slow sweep voltage–time charge curve (h = 100 hours); (b) Capacity spectrum of the slow sweep voltage–time charge and discharge curves (h = 100 hours). Reproduced with permission from Z. Stoynov and D. Vladikova (2006) Differential Coulometry spectroscopy In: Stoynov Z. and Vladikova D. (eds.) Portable and Emergency Energy Sources, pp. 411–436. Sofia: Marin Drinov Academic Publishing House.

## Differential Impedance Analysis (DIA)

Although electrochemical impedance as a TF gives a local, linear and full description of the system under study, this information has to be extracted from the experimental data, since impedance does not directly measure the processes caused by the perturbation signal, i.e. it is not a physical reality, but an information property of the object. The commonly applied approach for the interpretation of the experimental data is the construction and confirmation of a preliminarily derived hypothetical model. The model structure is chosen a priori, and thus the identification procedure is only parametric.

The main efforts towards the improvement of the impedance data analysis are focused on the advancements of the identification procedure. In this direction, Zdravko Stoynov's achievements concern the development of the original Model Reduction Method [20]. However, the data analysis advancements by improvements in the parametric identification did not satisfy him because of the principle discrepancy between the power of the impedance measurement technique, which ensures a large volume of precise data, and their analysis, based on the formulation of hypotheses, often built on subjective or oversimplified assumptions.

In Technical Cybernetics the Structural Identification approach is applied for data analysis. It does not require an initial working hypothesis and provides both structural and parametric identification. However, the application of this procedure to electrochemistry creates a multitude of problems, which for a long time had been accepted as insoluble. This challenge attracted Zdravko Stoynov and to overcome it, he developed the technique of Differential Impedance Analysis (DIA), introducing the Structural Identification approach in the frequency domain [21-28].

The DIA procedure starts with the initial set of experimental data (angular frequency, real and imaginary components of the impedance), and thus can be applied to previously measured data. The kernel is the local scanning analysis, performed with the so-called local operating model (LOM) with a simple structure consisting of a resistance  $R_1$  in series with parallel connection of capacitance C and resistance  $R_2$ . The effective timeconstant T = RC is also introduced as a LOM parameter. In contrast to the classical parametric identification, which is performed over the entire frequency range and estimates the parameters' vector as a preliminary chosen model structure, the identification of the LOM parameters' vector by local analysis is carried out within a narrow frequency range, regarded as an operating window. When the window width is a single frequency point, the solution is purely deterministic. The procedure of the structural and parametric identification can be described by the following steps:

- Scanning with the LOM throughout the whole frequency range with a scanning window of a single frequency point;

- Parametric identification of the LOM at every working frequency. Since the number of the independent data available inside the observation window is smaller than the number of the unknown parameters, the initial set of impedance data is extended with two additional terms - the derivatives of the real and imaginary components of the impedance with respect to the frequency. Thus, the set of equations for determination of the LOM parameters estimation becomes solvable;

- Frequency analysis of the LOM parameters' estimates. The results are presented in the so-called temporal plots, which give the frequency dependence of the LOM parameters' estimates (Fig.10). If the LOM parameters estimates are

frequency-independent in a given frequency region, the sub-model corresponding to this frequency segment follows the LOM structure, i.e. it is described with a parallel combination of capacitance and resistance, which determine a time-constant. Thus, the number of the plateaus gives the number of the time-constants in the model (Fig. 10b). The results may be transformed in spectra, where the plateaus are depicted as spectral lines (Fig. 10c, d) [25-28].



**Fig. 10.** DIA of three step reaction: (a) equivalent circuit and complex-plane impedance diagram; (b) temporal plots (c) spectral plots; d) time-constant spectra of motor oil Mobil Delvac MX 15W40: new (■); after 10000 km. (■). *Reproduced with permission from Z. Stoynov and D. Vladikova (2005) Differential Impedance Analysis. Sofia: Marin Drinov Academic Publishing House.* 

The presence of frequency dependence in the temporal plots marks either the regions of mixing between two phenomena or frequency dependent behavior. Those segments are additionally examined by Secondary DIA [25,27,28]. The procedure, known as differential temporal analysis, includes the differentiation of the LOM parameters' estimates with respect to the log frequency. It recognizes frequency-dependent elements (CPE, Warburg, Bounded Warburg etc.), as well as, their presence in more complicated models. DIA opens new horizons for EIS by increasing its information capability. It is successfully applied in electrochemical power source studies and other systems [28-37].

### Today's Challenges

In the last 15 years Zdravko Stoynov is "divided' between batteries and fuel cells. Water behavior in solid oxide fuel cells (SOFC) is as much important, as difficult. By performing precise impedance measurements with high accuracy at low frequencies (down to 1 mHz) he could monitor the formation, transport and evacuation of water in a new SOFC design [37]. In the moment he is developing new tools with increased sensitivity and enhanced information capability for "zoomed" monitoring and more accurate diagnostics of state of health of batteries and fuel cells (Fig. 11).



**Fig. 11.** DIVA of SOFC: (a) *I-V* curves; (b) spectral transform of the Differential Resistance dR (dU/dI).

The new analysis (DIVA) is based on the classical current-voltage (I-V) characteristics and surprises with its simplicity and originality. It works with the derivative of the voltage in respect to the current, which is more sensitive to small deviations and thus ensures increased sensitivity and noise immunity. The method can give information about the origin of the degrading phenomena via combination with impedance measurements in selected characteristic working points and numerical modeling. The analysis is about 10 times more sensitive than the classical evaluation of fuel cells degradation based on voltage decrease measurements at constant current.

## International Activities

Although engulfed in practical and applied research, Zdravko Stoynov is no less valued as a "social scientist" with an acute sense of establishment, with excellent teaching skills and an unwithering enthusiasm to educate and pass on his knowledge and skills. He is one of founders - a similarly minded enthusiastic group of colleagues fascinated by the potential of electrochemical impedance, who established an international impedance society. For over 30 years, it has been gathering within the framework of two international conference chains:

- The International Electrochemical Impedance Spectroscopy Symposia, dating from 1989 (Fig. 12);

- The International Electrochemical Impedance Analysis Symposia, dating from 1988 (organized in Bulgaria in 1991, 1994, 2014, Fig. 13).

On a regional level, he strongly supported and aided in the establishment of the Regional Symposium of Electrochemistry – South-East Europe (RSE-SEE) and acted as its co-organizer in 2015 (Fig. 14). Starting in 1996, Zdravko Stoynov established the national electrochemical event with international participation "Sofia Electrochemical Days" (Fig. 15).

# Dear Zdravko,



Bren anica

A best friendly message from the ancients of LISE Chantal & Hubert Cachet, Claude Gabrielli, Georges Maurin, Robert Wiart,...

We remember all the good time we had together. We are sharing this happy day with you.

Please keep on working hard...

so many discoveries are still ahead



Souvenirs of formal and less formal instants at two memorable EIS Symposia



Tasting the Italian "Grappa' , Val de Sole Marilleva, 5<sup>th</sup> EIS Symposium, 2001

Bombannes, 1<sup>st</sup> EIS Symposium,1989

Fig. 12. (a) International Symposium on Electrochemical Impedance Spectroscopy

#### D. Vladikova: Zdravko Stoynov - the scientist who turns curiosity into multidisciplinarity





**Fig. 12.** (b) Official Dinner, Algarve, Portugal,  $8^{th}$  EIS Symposium, 2010; (c) Lecture, A Toxa, Galicia, Spain,  $10^{th}$  EIS Symposium, 2016.

To this day, Prof. Stoynov continues to invigorate these scientific forums with his innovative and avant-garde ideas.

## Scientific management

In the first difficult years after the changes in Bulgaria, the Central Laboratory of Electrochemical Power Sources, as well as the Bulgarian Academy of Sciences as a whole were functioning under the impending doom of being closed down and a great number of researchers left Bulgaria to seek professional realization in Western Europe and the Americas. However, during those troubling times, Prof. Stoynov's sense of duty towards Bulgarian science and his remaining colleagues did not let him emigrate. Instead of packing his suitcases for California, where he was expected to joint Stanford University, he undertook the responsibility to preserve and develop the scientific legacy of his greatest teachers, Rostislaw Kaischew and Evgeni Budevski, accepting the position of Director of CLEPS in 1992. Four years later, he was elected as Chairman of the General Assembly (GA) of the Bulgarian Academy of Sciences - the executive body which needed to reform the Academy in order to preserve its existence.

Prof. Stoynov once again united seemingly disparate fields such as electrochemistry, management, economics, and policy-making.







**Fig. 13.** International Symposium on Electrochemical Impedance Analysis (EIA) (a) Castle Trest, Moravia, Czech Republic, 5th EIA Symposium, 2008; (b) Welcome party, Red Island, Croatia 9th EIA Symposium, 2011; (c) Opening session, Borovetz, Bulgaria, 10th EIA Symposium, 2014.



**Fig. 14.** 5<sup>th</sup> Regional Symposium on Electrochemistry- South East Europe (RSE-SEE5), Pravets, Bulgaria, 2015.



Fig. 15. Opening of Sofia Electrochemical Days, 2012.

He applied his rich experience from impedance studies of energy systems, knowing that they behave like large statistical systems with distributed parameters on a micro and macro scale, that due to mass and energy transfer, those systems change their structures and show non-steady state behavior. In spite of these severe restrictions, he saw great potential and developed new and more sophisticated tools. Well. the scientific infrastructure, being a large statistical system of similar behavior, could be described in a similar way. The tool he offered for this system on a micro and macro scale (IEES and BAS) was a new type of scientific management based on: (i) microeconomic reforms; (ii) stable project financing; (iii) global scientific market participation; (iv) high-quality and high-level scientific products with a new positive emphasis on applied research still adequately balanced with fundamental studies.

Now, 25 years later, this socio-economic experiment which Prof. Stoynov took an active leading role in, has been proven successful. Not only did the Central Laboratory of Electrochemical Power Sources grow into the Institute of Electrochemistry and Energy Systems - one of the most successful BAS institutes with strong participation in the European Research Area, but also the Bulgarian Academy of Sciences withstood the turmoil of the post-communist transition period and strengthened its position as a national research center with 150-year history and a bright future ahead.

Here are some facts to illustrate this point: in comparison with 1996 – the starting year of Stoynov's chairing of the GA in 2008 (his 3rd mandate), BAS' self-funding increased about 30 times. In a few short years, IEES also attained a balanced income with about 50% self-funding.

Zdravko Stoynov established the Innovation Centre at BAS, which has been a long-term partner in Enterprise Europe Network. He initialized the establishment of BAS Education Center, through which the Bulgarian Academy of Sciences obtained its accreditation for training and education. Noting the weakening of the BAS institutes in terms of the most valuable resource of any effective scientific infrastructure - the expert human resource, Prof. Stoynov implemented pro-active policies for career advancement and maintenance of the scientific staff above critical levels. While such policies sound trivial today, they were almost unheard of in Bulgaria during the 90's and the beginning of the 21<sup>st</sup> century.

It is a quite rewarding experience to be able to reap what you have sown. Today Zdravko Stoynov reaps the respect and appreciation of his friends and colleagues from IEES, BAS, and all over the world, who joined together physically and virtually to celebrate his 80's birthday, turning it into a joyous and heartwarming event (Fig. 16). The Bulgarian Academy of Sciences honored his exceptional service with the special medal of the President of BAS (Fig. 16).

The international electrochemical community and Bulgarian colleagues express their gratitude to Prof. Zdravko Stoynov for his avant-garde, and insightful contributions to the development of electrochemical science and its applications with this special issue of Bulgarian Chemical Communications.

Wishing Prof. Stoynov good health and high spirits, I would like to conclude with the greeting from Digby Macdonald, one of his closest friends from the circle of EIS pioneers:

"Zdravko Stoynov has been a giant in electrochemical impedance spectroscopy and we look forward to his future contributions".

D. Vladikova: Zdravko Stoynov - the scientist who turns curiosity into multidisciplinarity



**Fig. 16.** Celebration of Zdravko Stoynov's 80<sup>th</sup> Anniversary (16.05.2016): the official part and award (pictures 1,2); with the group (picture 3); dancing at the party (picture 4)

#### REFERENCES

- 1.E. Budevski, W. Bostanov, T. Vitanov, Z. Stoynov, A. Kotzewa, R. Kaischew, Keimbildungserscheinigung an versetzungsfreien (100) Flachen von Silbereinkristallen, *Electrochimica Acta*, **11**, 1697 (1966).
- E. Budevski, W. Bostanov, Z. Stoynov, A. Kotzewa, R. Kaischew, Zweidimensionale Keimbildung und Ausbreitung von monoatomaren Silbereinkristallen, *Phys. Stat. Sol.*, **13**, 577 (1966).
- 3.M. Keddam, Z. Stoynov, H. Takenouti, Impedance Measurement on PB-H<sub>2</sub>SO<sub>4</sub> Batteries, *Journal of Applied Electrochemistry*, **7(6)**, 539 (1977).
- 4.Z. Stoynov, B. Savova Stoynov, Impedance Study of Non-Stationary Systems - 4-Dimensional Analysis, *Journal of Electroanalytical Chemistry*, **183**(1-2), 133 (1985).
- 5. B. Savova Stoynov, Z. Stoynov, 4-Dimentional Estimation of the Instantenious Impedance, *Electrochimica Acta*, **37**(**12**), 2353 (1992).
- 6.Z. Stoynov, "Nonstationary Impedance Spectroscopy", *Electrochimica Acta*, **38(14)**, 1919 (1993).
- 7.Z. Stoynov, B. Savova Stoynov, Instrumental Error in Impedance Measurements of Non Steady-State Systems, *Journal of Electroanalytical Chemistry*, **112(1)**, 157 (1980).
- 8.Z. Stoynov, Advanced Impedance Techiques for Litium Batteries Study - Four Dimensional Analysis, Materials for Lithium-Ion Batteries, Ed. C. Julien and

Z. Stoynov, NATO Science Series, 3. High Technology, 85, p. 359, Kluwer Academic Publishers (2000).

- 9.Z. Stoynov, B. Savova-Stoynov, T. Kossev, Nonstationary Impedance Analysis of Lead-Acid-Batteries, *Journal of Power Sources*, **30(1-4)**, 275 (1990).
- 10. Z. Stoynov, T. Nishev, V. Vacheva, et al., Nonstationary analysis and modelling of battery load performance, *Journal of Power Sources*, **64(1-2)**, 189 (1997).
- 11. Z. Stoynov, D. Vladikova, Non-stationary differential impedance spectroscopy in energy systems in: Z. Stoynov, D. Vladikova (Eds.), "Portable and Emergency Energy Sources", Marin Drinov Academic Publishing House, Sofia, p. 411,2006.
- 12. M. Itagaki, A. Taya, K. Watanabe, *Electrochemistry*, **68**, 596 (2000).
- 13. M. Itagaki, S. Yotsuda, N. Kobari, K. Watanabe, S. Kinoshita, M. Ue, *Electrochim. Acta*, **51**, 1629 (2006).
- 14. M. Ujvári, D. Zalka, S. Vesztergom, S. Eliseeva, V. Kondratiev, G. Láng, Electrochemical impedance measurements in non-stationary systems- Application of the 4-dimensional analysis method for the impedance analysis of overoxidized poly(3,4-ethylenedioxythiophene)-modified electrodes (*in this issue*)
- 15. V. Horvat-Radoševi, K. Kvastek, K. Magdi Koši ek, Application of Stoynov's 4-D analysis for nonstationary impedance spectra corrections of thin

poly(o-ethoxyaniline) modified Pt electrode (in this issue)

- 16. Z. Stoynov, Fourier Analysis in the Presence of Nonstationary Periodic Noise, Dissertation No 1839, Swiss Federal Institute of Technology, Zurich, 1985.
- 17. Z. Stoynov, *Electrochimica Acta*, **37(12)**, 2357 (1992).
- 18. Z. Stoynov, D. Vladikova, Differential Coulometry spectroscopy in: Z. Stoynov, D. Vladikova (Eds.), Portable and Emergency Energy Sources, Marin Drinov Academic Publishing House, Sofia, 2006 p. 437.
- 19. http://www.bio-logic.net/wp-content/uploads/EC-BT-Lab-AN57.pdf
- 20. Z. Stoynov, B. SavovaSoynov, *Journal of Electroanalytical Chemistry*, **170(1-2)**, 63 (1984).
- 21. Z. Stoynov, Electrochimica Acta, 34, 1187 (1989).
- 22. Z. Stoynov, Polish J. Chem., 71, 1204 (1997).
- 23. Z. Stoynov, Advanced Impedance Techiques for Litium Batteries Study - Differential Impedance Analysis, Materials for Lithium-Ion Batteries, Ed. C. Julien and Z. Stoynov, NATO Science Series, 3. High Technology, 85, p. 371, Kluwer Academic Publishers (2000).
- 24. D. Vladikova, Z. Stoynov, J. Electroanal. Chem., **572**, 377 (2004).
- 25. D. Vladikova, P. Zoltowski, E. Makowska, Z. Stoynov, *Electrochimica Acta*, **47**, 2943 (2002).
- 26. Z. Stoynov, D. Vladikova, "Differential Impedance Analysis", Marin Drinov Publ. House, Sofia, 2005.
- 27. Z. Stoynov, D. Vladikova, Impedance Spectroscopy of Electrochemical Power Sources in: U. Garche (Ed.)

Encyclopedia of Electrochemical Power Sources, Elsevier, p. 632, 2009.

- 28. M. Viviani, M. Buscaglia, L. Mitoseru, A. Testino, P. Nani, D. Vladikova, *J. Europ. Ceram. Soc.*, **24**, 1221 (2004).
- D. Vladikova, A. Kilner, S. J. Skinner, G. Raikova, Z. Stoynov, *Electrochim. Acta*, **51**, 1611 (2006).
- D. Vladikova, G. Raikova, Z. Stoynov, H. Takenouti, J. Kilner, St. Skinner, *Solid State Ionics*, **176**, 2005 (2005).
- 31. A. Barbucci, M. Viviani, P. Carpanese, D. Vladikova, Z. Stoynov, *Electrochim. Acta*, **51**, 1641 (2006).
- 32. D. Vladikova, Z. Stoynov, A. Barbucci, M. Viviani, P. Carpanese, G. Raikova, The Technique of the Differential Impedance Analysis - Applications for SOFC studies" in: L. Mitoseriu (Ed.), New Developments in Advanced Functional Ceramics, Transworld Research Network, Kerala, India, Ch. 16, p. 457, 2007.
- 33. A. Kirchev, J. Power Sources, 170(2), 495 (2007).
- 34. A. Kirchev, J. of Power Sources, 191(1), 82 (2009).
- 35. A.Kirchev, J. of Power Sources, 179(2), 808 (2008).
- 36. D. Vladikova, Z. Stoynov, G. Raikova, A. Thorel, A. Chesnaud, J. Abreu, M. Viviani, A. Barbucci, S. Presto, P. Carpanese, *Electrochemica Acta*, **56**, 7955 (2011).
- D. Vladikova, Z. Stoynov, A. Chesnaud, A. Thorel, M. Vivianu, A. Barbucci, G. Raikova, P. Carpanese,
- M. Krapchanska, E. Mladenova, International Journal
- of Hydrogen Energy, 39(36), 21561 (2014).