TUNING OF ELECTRONIC PROPERTIES IN CONDUCTING POLYMERS

Guofeng LI[1], Mira JOSOWICZ[2] and Jiří JANATA[3],*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta,
GA 30332-0400, U.S.A.; e-mail: [1] guofeng@chemistry.gatech.edu,
[2] mira.josowicz@chemistry.gatech.edu, [3] jiri.janata@chemistry.gatech.edu

Structural and electronic transitions in poly(thiophenyleneiminophenylene), usually referred to as poly(phenylenesulfidephenyleneamine) (PPSA) upon electrochemical doping with $LiClO_4$ have been investigated. The unusual electrochemical behavior of PPSA indicates that the dopant anions are bound in two energetically different sites. In the so-called "binding site", the ClO_4^- anion is Coulombically attracted to the positively charged S or N sites on one chain and simultaneously hydrogen-bonded with the N–H group on a neighboring polymer chain. This strong interaction causes a re-organization of the polymer chains, resulting in the formation of a networked structure linked together by these ClO_4^- Coulombic/hydrogen bonding "bridges". However, in the "non-binding site", the ClO_4^- anion is very weakly bound, involves only the electrostatic interaction and can be reversibly exchanged when the doped polymer is reduced. In the repeated cycling, the continuous and alternating influx and expulsion of ClO_4^- ions serves as a self-organizing process for such networked structures, giving rise to a diminishing number of available "non-binding" sites. The occurrence of these ordered structures has a major impact on the electrochemical activity and the morphology of the doped polymer. Also due to stabilization of the dopant ions, the doped polymer can be kept in a stable and desirable oxidation state, thus both work function and conductivity of the polymer can be electrochemically controlled.
Keywords: Electrochemistry; Electrochemical doping; Perchlorate; Cyclic voltammetry; Conducting Polymers; Electronic Properties; Poly(phenylenesulfidephenyleneamine); PPSA.

There is a strong motivation for the development of novel electronic materials whose electronic properties can be controlled electrochemically in solution and remain defined in the dry state. Such materials are needed in design of molecular electronics in general and for fabrication of solid-state chemical sensors in particular. The level of the doping that determines the conductivity, optical properties and work function of the final material depends on its redox state. It can be easily controlled while the polymer is still in the solution with an external voltage applied. However, removal of the polymer from the electrolyte following the electrochemical doping step effectively returns it to the "open cell potential". Thus, this final step in the

preparation usually negates any previous adjustment. This is particularly true when strong acids, such as sulfuric or tetrafluoroboric acids are used. Their excess must be carefully removed from the polymer because any left-over acid causes progressive degradation and drift of all physical properties of such materials in the dry state. We have found that controlled electrochemical doping of polyaniline (PANI) from aqueous solutions of weak carboxylic acids yields a relatively stable material whose work function and resistivity can be electrochemically adjusted[1]. This fact can be explained by the buffering action of the dopant carboxylic acid. Thus, a small amount of acid washed out from the polymer following the preparation does not significantly affect the internal value of the pH in the bulk of the polymer and therefore its doping level.

Even better control can be obtained by "locking in" the dopant anion by formation of strong Coulombic/hydrogen bonds that lead to a permanent rearrangement of interior polymer chains. This effect has been studied in detail on poly(thiophenyleneiminophenylene) (PPSA). It is a polymer consisting of alternating aniline and phenylene sulfide units[2–4]. It has excellent chemical stability, as well as high solubility in cyclohexanone, THF, DMF, DMSO and NMP[5]. In its undoped state, the polymer is completely amorphous and electrically non-conducting. The doping of PPSA is usually done chemically, using oxidants such as bromine, iodine, $SbCl_5$ and $FeCl_3$ (ref.[5]). However, this method lacks control of the doping process and the reduced forms of these oxidants remain in the polymer, resulting in a poorly defined oxidation state and solid-state properties.

The overall objective of our study is to explore the possibility of controlling the level of doping and thus the value of work function in conducting PPSA by electrochemical means. Electrochemical doping has the inherent advantage of remarkable control over the doping process. Furthermore, when a non-oxidative dopant such as $LiClO_4$ is used, a much "cleaner" or "better defined" doped product can be obtained, as there is no interference from the reduced species that would have remained in the polymer matrix as the by-products from chemical doping with strong oxidants. The structural and electronic transitions taking place in PPSA upon electrochemical doping can be described by the common polaron–bipolaron model[6]. The results indicate that polarons are the predominant charge defects at low doping levels, yielding an electronically and mechanically stable material. Further electrochemical doping at high potentials induces a polaron to bipolaron transition. Furthermore, a peculiar electrochemical behavior prompted our spectroscopic investigation, which has revealed that the per-

chlorate ions were bound in the polymer matrix in two energetically distinct states that stabilized the material at desired doping levels.

EXPERIMENTAL

Sample preparation. PPSA polymer was dissolved in cyclohexanone and then spin-cast onto platinum substrates. PPSA films of various thicknesses were prepared by controlling the PPSA/cyclohexanone concentration and the spin rate. The film thickness was measured by a Dektak II profilometer using diamond stylus under 10 mg load.

Spectroscopic measurements. Infrared measurements were performed using a Biorad FTS-6000 Fourier transform infrared (FTIR) spectrometer attached to a UMA-500 infrared microscope and a slide-on germanium crystal ATR accessory in the frequency range of 400–4000 cm^{-1}.

Electrochemical measurements. The voltammetric apparatus was a CH Instruments model 660 electrochemical workstation. The cyclic voltammetry (CV) and square-wave voltammetry (SWV) were done at room temperature in a three-electrode cell using a platinum foil as counter-electrode and a silver wire as reference electrode. Platinum disk electrode (ϕ = 1.5 mm, Bioanalytical Systems) or platinum coated silicon substrate (active area 1.0 × 0.15 cm) with spin-cast PPSA film was used as the working electrode. The silver wire reference electrode was calibrated with the ferrocene/ferrocenium (Fc/Fc$^+$) reference redox system following the IUPAC recommendation[7]. The $E_{1/2}$ of 5 mM of Fc/Fc$^+$ in 0.25 M LiClO$_4$–acetonitrile was 0.54 V. The standard redox potential of the Fc/Fc$^+$ system in acetonitrile *vs* aqueous SCE is 0.307 V (ref.[8]). The CV measurements were done in a 0.2 M LiClO$_4$–acetonitrile solution in the potential range from –0.2 to 1.8 V with a scan rate of 10 mV s^{-1}. The SWV studies were performed with 4 mV increments and 25 mV of amplitude at the frequency of 15 Hz.

Materials characterization. The doped PPSA film was sandwiched between the platinum substrate and a polished silver electrode with constant pressure applied to ensure good electrical contact. The DC resistance was recorded with a Hewlett Packard (Model # 34401A) multimeter. The work function (WF) measurements were done on a Delta-Phi-Electronik Kelvin Probe Type S (Besocke, GmbH, Jülich, Germany). The WF of the doped PPSA film was determined against the vibrating gold grid reference plate (ϕ = 2.5 mm), which was facing the center of the investigated PPSA film. The PPSA films (*ca* 5 μm thick) were spin cast on stainless steel rods (ϕ = 1.2 cm) coated with 150 nm of sputtered platinum, using Ti–W as a glue metal. The transmission electron microscopy (TEM) was performed on a JEOL, JEM-100CX II electron microscope.

RESULTS AND DISCUSSION

Figure 1 is a typical cyclic voltammogram of a PPSA film in LiClO$_4$–acetonitrile. In general, the polymer is oxidized during the positive potential scan. The oxidation of PPSA is accompanied by the influx of ClO$_4^-$ ions into the film to maintain the overall charge neutrality. When sweeping the potential in the negative direction, the oxidized form of the polymer is reduced and the ClO$_4^-$ ions are expelled back into the solution. No changes in

the electrochemical behavior have been observed when perchlorates of tetrabutylammonium or sodium ions were used as dopant electrolyte, suggesting that the cations are not actively involved in the electrochemical doping of PPSA.

A striking feature of the CV is the large uptake of ClO_4^- ions on the first oxidation scan. In a normal reversible doping process, these ions would be expelled from the polymer, as is the case in electrochemical doping of polyaniline[9] (PANI). The fact that these ions do not leave the film even when a most negative potential is applied means that they are strongly bound, and that the material remains in a higher meta-stable oxidized state. The second remarkable feature is that the subsequent scans appear to be more reversible but the peak current is gradually decreasing. This suggests that the number of available exchange sites is progressively decreasing. Moreover, the oxidation peak occurs at a much higher potential at the first oxidation scan. This behavior indicates that initially, the influx of the ClO_4^- ion into the polymer matrix is hindered due to the tight packing of polymer chains caused by the interchain N–H hydrogen bonding. As for the cycles beyond the first scan, with remaining ClO_4^- ions and solvent molecules wedged between the polymer chains, the polymer matrix is relatively "open" and therefore the influx of the ClO_4^- ion peaks at a lower oxidation potential.

A similar but better resolved pattern was observed in the square wave voltammograms of thin PPSA films (Fig. 1 inset). As discussed earlier, the
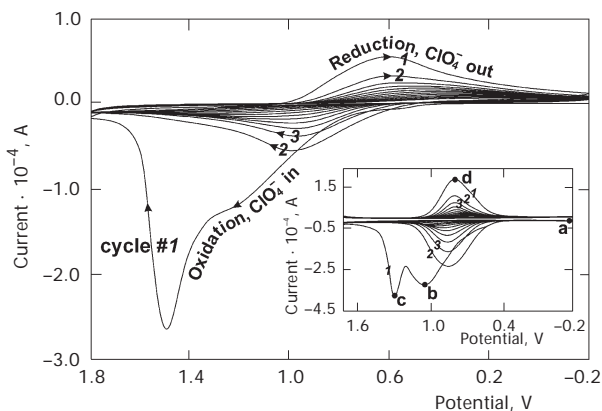

Fig. 1

Typical CV of PPSA film in 50 mM LiClO$_4$–MeCN on a Pt-disk electrode. Inset: SWV of a PPSA film in 0.2 M LiClO$_4$–MeCN

peak b at the first oxidation cycle corresponds to the polaron formation. At higher oxidation potentials, the polymer is further oxidized into a bipolaron state as indicated by the peak c. The gradual decrease of reversible peaks is again observed. On the other hand, the reversible ion exchange can be carried out without a loss of activity if the oxidation does not exceed the polaron stage, *i.e.*, the cycling is limited to the range from –0.2 to 1.1 V. In that case, both the CV and SWV peaks reach steady-state values.

The IR spectra corresponding to three redox states as indicated in Fig. 1 inset, undoped a, polaron b, and bipolaron c of PPSA are shown in Fig. 2A. They contain characteristic features that elucidate the doping process. In a comparison to the undoped PPSA, the spectrum taken at the peak b of the first oxidation wave shows several new features. The most noticeable ones are: the C=S stretching vibration at $1\ 074\ cm^{-1}$; a sharp absorption band at $1\ 550\ cm^{-1}$ due to the formation of phenyl radical; and a decrease in intensity of the skeletal vibrations ($1\ 500$ and $1\ 590\ cm^{-1}$) of the phenyl ring, indicating a change within the aromatic ring conjugation. Further, in the spectrum taken in the bipolaron state, an absorption peak at $1\ 650\ cm^{-1}$ ($\nu_{C=N}$) starts to emerge. In addition, the decrease in the peak intensity and the splitting of the skeleton vibrations suggest further configurational changes within the aromatic ring. These IR results validate that two structural transitions take place in PPSA upon electrochemical doping – the formation of polaron at low level of doping, followed by the transition from polaron to bipolaron as illustrated in Fig. 2B.
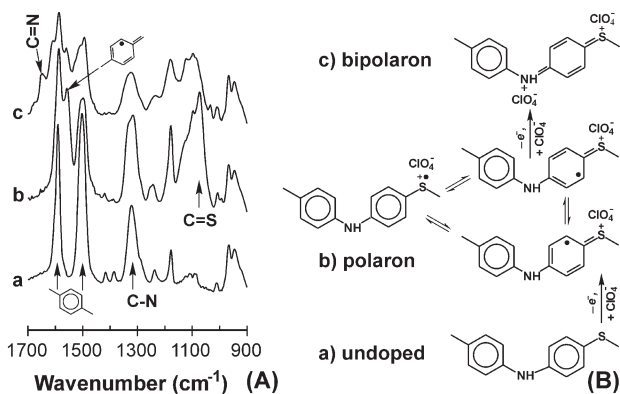

FIG. 2

FTIR ATR spectra of PPSA in three redox states as indicated in the inset of Fig. 1 (A). Comparison of the chemical structure of PPSA in the undoped, polaron and bipolaron state (B)

A careful examination of the subtle changes in the N–H stretching vibration upon doping reveals rich information. Three types of hydrogen bond are present, as indicated in Fig. 3A. When the doping progresses, the interchain N–H hydrogen bonds (3 393 cm^{-1}, peak a) gradually break up. The entrainment of the solvent (acetonitrile) molecules and ClO_4^- ions manifest themselves by the appearance of new hydrogen bondings between the N–H and acetonitrile (3 345 cm^{-1}, peak b) or between the N–H and the ClO_4^- ion (3 258 cm^{-1}, peak c). Further increase in the doping level will eventually shift both the N–H stretching absorptions at 3 393 and 3 345 to 3 258 cm^{-1} as ClO_4^- ion accumulates in the polymer. Thus, the perchlorate ion interacts in PPSA both Coulombically and by hydrogen bonding. Moreover, it forms an interchain link between two adjacent chains in the doped polymer as illustrated in Fig. 3B. We will call this type of site a "binding site". As the electrochemistry proves, this interaction is very strong. It induces a matrix reorganization that is responsible for the decrease in magnitude of the voltammetric peaks (Fig. 1).

Further oxidation to the bipolaron state leads to the formation of a heavily doped material where most S and N atoms are positively charged. In that case, the polymer has greatly increased chain mobility due to a large amount of intercalated ClO_4^- ions and a considerably smaller degree of interchain N–H hydrogen bonding. In other words, oxidation of PPSA to the polaron stage and slightly beyond, favors the formation of a networked
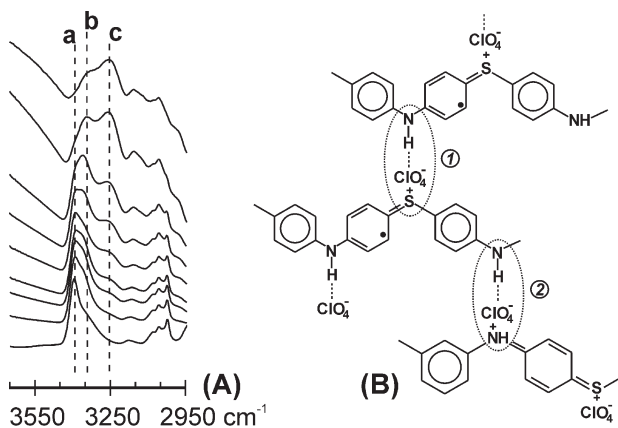

FIG. 3

Changes in the N–H stretching vibration upon doping (A). Schematic representation of two types of interchain anion ClO_4^- hydrogen/Coulombic bonded "bridges" in the doped PPSA (B)

structure linked together by the ClO_4^- hydrogen/Coulombic "bridges". Such organized structure retains the ClO_4^- ions, giving rise to the stabilization of the oxidized form of PPSA. In the repeated cycling, the continuous and alternating influx and expulsion of ClO_4^- ions serves as a self-organizing process for the formation of a networked complex. It results in a gradual decrease in the magnitude of both the oxidation and reduction CV peaks following the first cycle.

The essential prerequisite for this multiple binding of the perchlorate ion is a favorable spatial configuration of two polymer chains. Obviously, there are many chains where such bridging is not possible. Yet, the ClO_4^- can and must interact Coulombically with the positively charged S and N atoms of individual chains in order to maintain charge neutrality in the doped polymer. In such case, when the ClO_4^- ion is not hydrogen bonded, we will call these "non-binding sites". Because the ClO_4^- ions are only Coulombically bound at these sites, they can be readily expelled when the doped polymer is reduced, and are responsible for the peak d in Fig. 1. Their number decreases as the polymer undergoes dynamic self-reorganization discussed above. The anomalous size of the first oxidation scan is due to the uptake of the ClO_4^- ions and the bonding at the "binding sites". These sites represent a fraction of polymer chains that exists in favorable spatial configurations as the film is cast.

The occurrence of an ordered structure in the electrochemically doped PPSA was confirmed by high-resolution transmission electron microscope (HRTEM) data. The TEM image of the doped PPSA in its polaron state after heat treatment reveals dispersed dark spots (domains doped with ClO_4^- ions) in the film with the size of around 1 μm (Fig. 4A) The electron diffraction pattern (Fig. 4B) of a large domain located in the center of the TEM image verifies the formation of the polycrystallites in the doped PPSA. Similar observation of ordered structure in the emeraldine form of polyaniline has been reported[10–12]. But the nature of the ordering is believed to be quite different due to the uniquely formed Coulombic/hydrogen-bonded networked complex in the doped PPSA. Previous study on PPSA in its undoped state has shown that it is completely amorphous and crystallization cannot be achieved even by annealing the polymer at temperatures above the glass transition[5]. Clearly, the influx of the perchlorate ions and the occurrence of the Coulombic/hydrogen-bonded networked complex have great impact on the morphological changes observed in the doped polymer.

The morphological changes in the doped PPSA introduced by the electrochemically induced chain organization described in this work also have a profound impact on the electronic properties of the doped PPSA film.

Along with the hydrophobic nature of the PPSA film, the stabilization of the dopant ions at the "binding sites" leads to the stability of the doped PPSA superior to that of polyaniline or polypyrrole in ambient atmosphere. Both the resistivity and the work function of the dry, electrochemically doped PPSA have been measured. Since the doping of PPSA was carried out electrochemically, the level of doping could be conveniently adjusted by regulating the amount of the charge injected. Details on the methods of evaluating the doping levels in PPSA were discussed elsewhere[13]. Hence only the results are shown in Figs 5 and 6. The resistance of a doped film decreases exponentially, while its work function increases logarithmically with the amount of the injected charge in analogy with the changes commonly seen in the Fermi level of the conventional semiconductor upon doping[14].
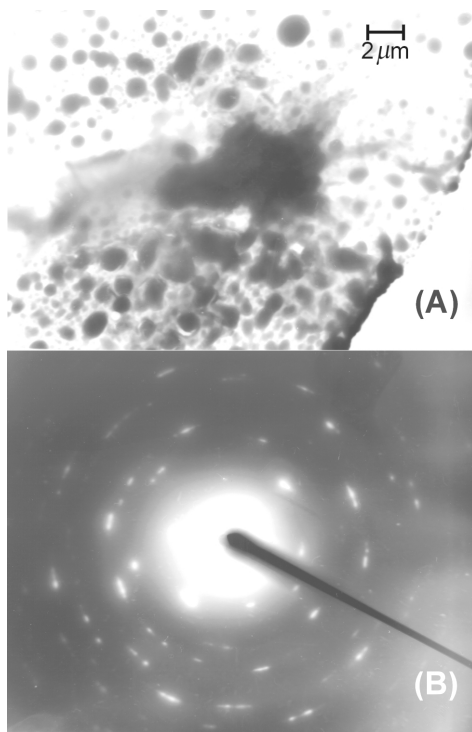

FIG. 4
TEM image of the doped PPSA in its polaron state (A) and selected area diffraction (SAD) pattern of the crystallite in the center of the TEM image (B)
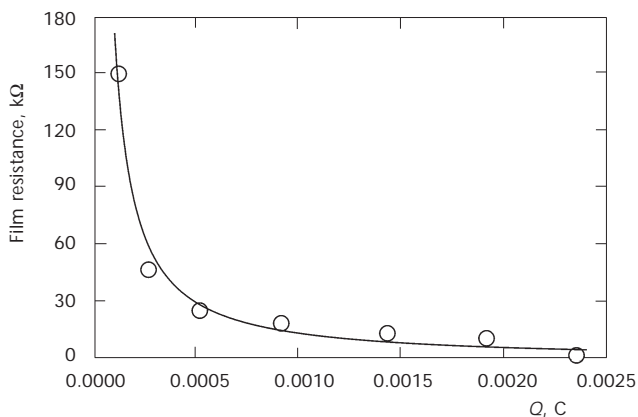
FIG. 5
Changes in the resistance of a PPSA film (< 1 μm) as a function of the charge Q injected during electrochemical doping

FIG. 6
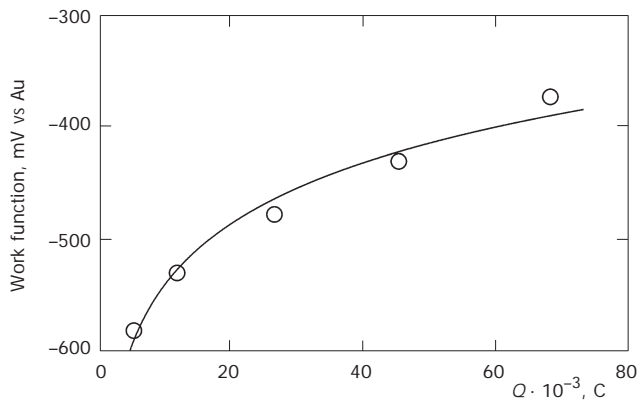Changes in the work function of a PPSA film (*ca* 5 μm) as a function of the charge Q injected during electrochemical doping

CONCLUSION

The electrochemical doping of PPSA with ClO_4^- can be described by two distinctly different types of binding sites. The first type, the so called "binding sites", involves the formation of the ClO_4^- bridge between a positively charged S or N atom in one chain and the available secondary amine in the neighboring chain. This form of binding results in an irreversibly incorporated ClO_4^- that cannot be electrochemically exchanged. This, in turn, means that ClO_4^- anions bound in these sites represent a permanent level of doping. The Gibbs energy of formation of the "binding site" is so large that repetitive potential cycling induces conformational changes favoring this type of bonds and leads to major structural reorganization of the polymer network. The other type of ClO_4^- binding involves only Coulombic interaction with positively charged S or N atoms but no hydrogen bonding ("non-binding sites"). The ClO_4^- ions thus bound can be reversibly removed upon potential cycling.

Any solid state application of conducting polymers requires that such materials have a stable and well defined work function value. However, transferring from solution to the dry state is inevitably a trivial, yet poorly defined step since the level of the doping depends on the amount of the counter-ion left in the polymer. Since the dopant ions are retained in the polymer matrix, electrochemical doping of PPSA offers the possibility of fine-tuning this parameter. It was demonstrated that in PPSA, electrochemical doping was proved to be an effective method for fine-tuning the electronic properties of the doped polymer. We have shown that in doped PPSA, both the conductivity and work function could be electrochemically adjusted to desirable levels. Furthermore, considering their structural similarity, the doping mechanism found in PPSA can exist also in polyaniline and even other conducting polymers, under carefully selected conditions that allow the formation of this type of interchain bonding. Indeed, our preliminary experiments have shown that self-organized doping and conformational stabilization of polyaniline takes place and leads to an electronically important form of this ubiquitous material. The results of those findings will be reported in the upcoming publication[15].

REFERENCES

1. Hatchett D. W., Josowicz M., Janata J.: *J. Phys. Chem. B* **1999**, *103*, 10992.
2. Wang L., Soczka-Guth T., Havinga E., Müllen K.: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1495.
3. Klarner G., Leuninger J., Former C., Soczka-Guth T., Müllen K.: *Macromol. Symp.* **1997**, *118*, 103.
4. Wang L., Jing X., Wang F., Zhang J., Wang R., Soczka-Guth T., Müllen K.: *Synth. Met.* **1999**, *101*, 320.
5. Leuningher J., Wang C., Soczka-Guth T., Enkelmann V., Pakula T., Müllen K.: *Macromolecules* **1998**, *31*, 1720.
6. Li G., Josowicz M., Janata J., Müllen K.: *J. Phys. Chem. B* **2001**, *105*, 2191.
7. Kuta G.: *Electrochim. Acta* **1984**, *29*, 869.
8. Bard A. J., Faulkner L. R.: *Electrochemical Methods*, p. 701. John Wiley & Sons Inc., New York 1980.
9. Maranhao S. L., Torresi R. M.: *J. Electrochem. Soc.* **1999**, *146*, 4179.
10. Mazerolles L., Rolch S., Colomban P.: *Macromolecules* **1999**, *32*, 8504.
11. Wan M., Zhu C., Yang J., Bai C.: *Synth. Met.* **1995**, *69*, 157.
12. Nicolau Y. F., Djurado D.: *Synth. Met.* **1993**, *55*, 394.
13. Li G., Josowicz M., Janata J.: *Synth. Met.*, in press.
14. Sze S. M.: *Physics of Semiconductor Devices*, 2nd ed., Chap. 2. Wiley, New York 1981.
15. Li G., Josowicz M., Janata J.: Unpublished results.

Dr. Janata received his M.Sc. and Ph.D. degrees in analytical chemistry from The Charles University, Prague in 1961 and 1965, respectively. After two years as postdoctoral fellow at the University of Michigan he worked at the Corporate Laboratory of ICI Ltd, in Runcorn, England. In 1976 he joined the University of Utah where he became Professor in Bioengineering Department in 1981 and Professor of Materials Science in 1987. In 1992 he left the University of Utah and became Associate Director of Environmental Molecular Sciences Laboratory of the Pacific Northwest National Laboratory in Richland, Washington. He came to Georgia Tech in March 1997. Dr. Janata is Associate Editor of Field Analytical Chemistry and Technology, member of the Advisory Board of Analytical Chemistry, member of editorial boards of Biosensors, Sensor Technology and Talanta. He received Senior Alexander von Humboldt Prize (1987), Outstanding Research Award from the U. of Utah (1990), Finalist Medal of "Science pour l'Art" from Moet Hennessy&Louis Vuitton (1992), Outstanding Achievement Award from the Electrochemical Society (1994). He chaired Gordon Research Conferences on Electrochemistry (1995), Nuclear Waste and Energy (1996) and is Chair-elect for GRC on Chemical Sensors&Interfacial Design (1998). In 1995–1996 he served on National Research Council, Panel on Airline Passenger Security. He held visiting professorships at the Wolfson College (Oxford), EPFL (Lausanne), U. of Bundeswehr (Munich) and Tokyo Institute of Technology (Tokyo).