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Giselle Sandi and Petr Vanysek

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Northern Illinois University
Department of Chemistry
DeKalb, IL 60115-2862

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by

Giselle Sandí and Petr Vanýsek
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Department of Chemistry
DeKalb, IL 60115

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**Impedance and voltammetric studies of electrogenerated
polyaniline conducting films**

Giselle Sandí and Petr Vanýsek

**Northern Illinois University, Department of Chemistry
DeKalb, IL 60115 (U.S.A.)**

Abstract

Polyaniline films were electrochemically synthesized from three acidic media; sulfuric, hydrochloric and perchloric acids. Cyclic voltammetry was used in the electro-synthesis and the effects of voltammetric parameters on the properties of the films were investigated. The main tool of film characterization was impedance spectroscopy. Semiautomated plotting of three-dimensional Argand diagrams with potential parameter was used for synoptic view of the system and nonlinear least square data fitting was used for rigorous treatment. Charge storage capacity, resistance and changes in constant phase element parameters are analyzed in relation to the use of three acidic media.

Introduction

The physics and chemistry of conducting polymers have developed into a rich interdisciplinary research with ever widening perspectives over the past 15 years. The current interest started in 1977 by the discovery of Nigrey, MacDiarmid and Heeger [1] of doping polyacetylene (PA) with iodine, which increased its conductivity by 10 orders of magnitude. The successful doping of PA, which, in electrochemical terminology, is the equivalent of oxidation or reduction, encouraged the same scientists [2] to use PA as an electrode for a rechargeable battery. Conducting polymers with properties similar to those of PA were discovered, such as polypyrrole, polythiophene and polyaniline (PANI) [3] which will be an object of this paper.

All important conducting polymers, with the exception of polyacetylene, can be produced electrochemically by anodic oxidation of monomer precursors. In contrast to chemical bulk oxidation methods, the conducting films that are formed electrochemically are deposited directly on the electrode, which can be advantageous if further electrochemical studies of this material are conducted.

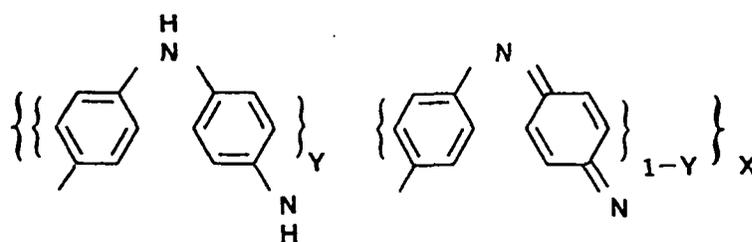
During a conventional electrochemically initiated addition polymerization, a soluble initiator is oxidized or reduced on an electrode surface, producing an active species, which may be an anion, a cation or a free radical. Subsequent polymerization takes place in a solution, and it is generally assumed that the polymer remains dissolved in the reaction medium since the precipitation of a layer of an electrically insulating polymer on the electrode surface would stop any further reaction. The advantage of generating the initiating species is in the degree of control that can be maintained over the initiation rate and the concentration of active centers [4].

To synthesize a polymer electrochemically on an electrode requires that a conductive and insoluble product be formed. This will cause the polymer to precipitate on the electrode surface as a cohesive film that does not passivate the electrode, allowing further electropolymerization, and may be possibly removable from the electrode for further study.

Polyaniline

Polyaniline was known long before the current interest in its ill defined form of so called aniline blacks, which are undesirable deposits formed on anodes during electrolysis of aniline [5]. Four polyaniline octamers of different oxidation states were characterized in 1912 [6]. A publication from 1954 describes oxidation of aniline both electrochemically and chemically by FeCl_3 [7].

The term polyaniline, as it is commonly used, refers to a class of polymers consisting of 1000 or more ring-nitrogen repetitive units that can be derived from a general formula



(I)

which consists of alternating reduced (indexed Y) and oxidized ($1-Y$) units. In principle the Y can be varied continuously from one, which yields a completely reduced polymer (leucoemeraldine base), to zero, which gives a completely oxidized polymer (pernigraniline base). For $Y \approx 0.5$ the material is called an

emeraldine base. While the bases are insulators, their conductive form can be achieved by oxidation of leucoemeraldine, protonation of emeraldine or protonation and reduction of pernigraniline bases [8].

Polyaniline can be conveniently synthesized as a cohesive thin film by electrochemical oxidation of aniline on metal electrodes in aqueous acidic media. Its structure corresponds to the emeraldine form. It is now well established [9] that the highest conductivity has the protonated emeraldine form, whose pH is usually less than zero.

The objective of this work is to find what influence on growth of polyaniline films and their protonation has the nature of the acid medium. The polymers were grown in several acids of different concentration. Cyclic voltammetry and impedance spectroscopy were used to characterize the resulting films deposited on a platinum electrode.

Experimental

Aniline (Aldrich, analytical grade) was twice distilled before use at normal pressure. Aqueous solutions of HClO_4 (Curtin Matheson Reagent ACS), HCl (Fisher Reagent ACS) and H_2SO_4 (Fisher Reagent ACS) were used at desired concentrations to acidify the solutions and to supply the necessary anions. Similarly K_2SO_4 , KCl and KClO_4 (Mallinckrodt analytical reagents) were used as a source of anions. Aqueous solutions were prepared from water doubly distilled from glass.

Both the electrochemical deposition and the subsequent studies were carried out in a single three-electrode compartment 20 ml cell. The cell was placed on a

cell stand C1B-120 (BAS, Bioanalytical Systems, Inc., Indiana) that allowed electrode connections, stirring of the solution and deaeration with nitrogen. The working electrode was a BAS platinum disk electrode with diameter 1.6 mm (area 2 mm^2). A BAS Ag/AgCl electrode filled with saturated KCl was the reference and a piece of Pt wire was the counter electrode. The working electrode was cleaned before deposition by sonication in 50% H_2O_2 for 10–20 minutes, and then thoroughly rinsed with distilled water and finally polished with alumina (particle size of $0.05 \mu\text{m}$).

The deposition and voltammetric studies were performed with an EG&G 273 potentiostat. The integrator part of the potentiostat was used to record the total charge passed through the system in the course of the electrodeposition. Impedance measurements were done on a Solartron 1250 Frequency Response Analyzer, connected to a 1286 Solartron Electrochemical Interface (a 4-electrode potentiostat). A $1 \text{ k}\Omega$ resistor was placed between the second reference electrode and the working electrode inputs to change the instrument into a 3-electrode potentiostat. The frequency range was 1–65000 Hz, integration time 2 s and perturbing voltage amplitude 10 mV. The fitting of the experimental results to equivalent circuits was made by a complex, non-linear, least square fit program by B. Boukamp, University of Twente.

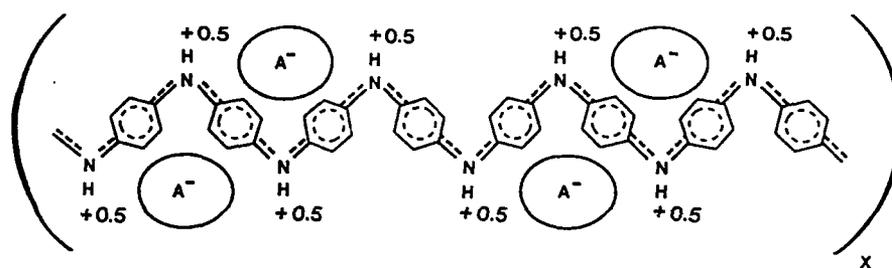
The polymer films were deposited from deaerated acidified aqueous media containing 0.1 mol/l aniline. The deposition proceeded during cyclic voltammetry between 0.0 and 0.9 V vs. saturated KCl Ag/AgCl electrode at 50 mV/s. The sweep was stopped after 17 cycles at 0.9 V vs. Ag/AgCl and the electrodes were disconnected from the circuit. The coated working electrode was removed rapidly from the monomer solution and the film, mechanically strong enough to endure this process, was rinsed thoroughly with doubly distilled water. The coated

electrode was characterized both by voltammetry and by analysis of its AC impedance response.

The rinsed polymer coated electrodes were immersed in a desired acidic solution in absence of monomer, and kept continuously stirred for about 24 hours. A nitrogen blanket eliminated access of oxygen to the system before its impedance spectrum or a voltammogram were recorded. To learn such characteristic parameters as charge transfer resistance, capacitance, etc., of the PANI films, the impedance response of the film in three different acids, H_2SO_4 , HClO_4 and HCl was measured. The data were obtained using 1 mol/l acid concentration. Additional data set was collected for 0.1 mol/l H_2SO_4 .

Results and Discussion

The conductivity of polyaniline depends on two variables, its degree of oxidation and its degree of protonation. Addition of protons results in partial depopulation of the π system. It is proposed [10,11] that the emeraldine salt form of polyaniline shows high conductivity because of an extensive π conjugation in the polymer chain. If this was the case, then all nitrogen atoms, all C-N bonds and all C_6H_4 rings would be identical. Each nitrogen atom would bear formally a + 0.5 charge and all nitrogen atoms would be intermediate between benzenoid and quinoid:



(II)

The highly conjugated π system, in addition to contributing to the high conductivity, also imparts more chemical stability.

The appearance of voltammograms obtained during PANI growth depends on the nature of the acid in the electrolyte. In 1 mol/l H_2SO_4 the voltammogram has two gradually growing anodic peaks, with potentials of approximately 0.23, and 0.52 V vs. Ag/AgCl (Fig. 1). After 17 cycles the current density for those peaks reaches 1.39 and 0.30 mA/cm^2 respectively. In HClO_4 , however, a voltammogram of the polymer showed three anodic peaks (Fig. 2), at 0.20, 0.54 and 0.79 V vs. Ag/AgCl, respectively. The current density during the 17th sweep corresponds to 0.42, 0.08 and 0.39 mA/cm^2 . Films obtained in HCl as the doping acid (Fig. 3) resulted also in three peaks which are situated at 0.23, 0.52 and 0.81 V vs. Ag/AgCl. The highest overall current for all the studied acids was obtained with polyaniline in HCl, with current density after 17 cycles of 3.3, 0.17 and 2.48 mA/cm^2 respectively.

The peaks on the voltammograms correspond to the change of the oxidation state of the film that can be related to the ratio between amine and imine content in the film. This ratio, accessible by X-ray photoelectron spectroscopy, was studied by Snauwaert et al. [10] as a function of electrochemical potential (Table I). At -0.20 V vs. saturated calomel electrode only amine is detected, indicating that the polymer chains are in the leucoemeraldine state. As the

potential is increased, the imine concentration rises gradually to around 25% (protoemeraldine), then to 50% (emeraldine) and finally up to 75% (nigraniline).

A comparison between the values of differential capacitance of PANI, obtained by means of impedance spectroscopy and cyclic voltammetry was done for the acids mentioned above. Values for capacitive current were calculated from cyclic voltammetric curves [12]. Using the following expression:

$$C_d = (I_c/A)(dt/dE) \quad (1)$$

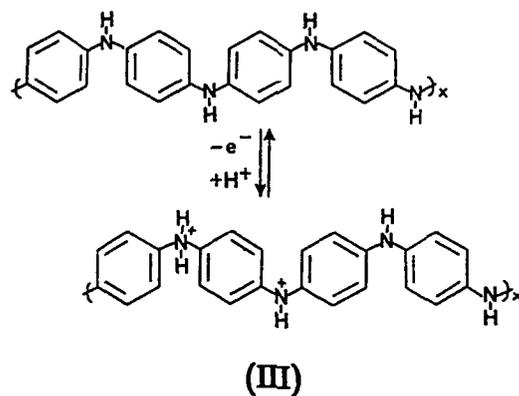
the differential capacitance was calculated. Here I_c represents the anodic charging current, A is the geometrical area of the electrode and dE/dt represents the potential scan rate. The scanned potential range in which electrode processes are absent was between 0.38 V and 0.40 V vs. Ag/AgCl, with a scan rate of 10 mV/s. A second set of values for C_d were obtained from the imaginary component of the impedance data [13], using relationship:

$$Z_{img} = -1/\omega C_d \quad (2)$$

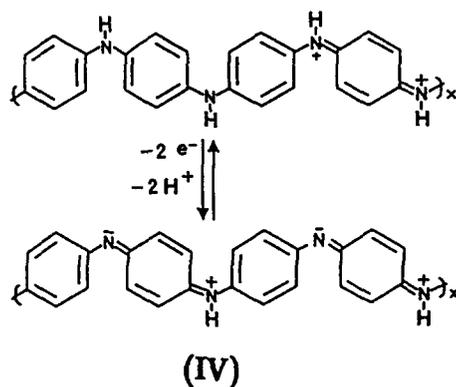
Table II summarizes these results. It can be inferred that the differential capacitance of PANI with monomer absent is dependent of the nature of the anions in solution, implying that there is an exchange of the doping anions (perchlorate, chloride and sulfate) during the potential scan. It is important to mention that the values of C_d obtained from impedance measurements were always smaller than the previous ones calculated from cyclic voltammetry sweeps. This difference between both set of results was also found for polypyrrole [14], where a similar comparative study was carried out.

According to Lapkowski [15] oxidation of PANI proceeds in two steps. In the initial stage of the first process, polyaniline is oxidized to the first polaron. At this stage only one per 10–12 nitrogen atoms is oxidized, and the rest remains in a reduced state. The oxidation significantly changes the pK of polyaniline which

becomes more basic. Thus, the protonation level of $-NH-$ groups increases. The local pH of the solution in direct contact with the polyaniline electrode must increase since protons are transferred from the solution to the polymer:



The second electrochemical step is manifested by a decrease of the local pH of the electrolyte solution. Polyaniline deprotonation starts at potentials $E = 0.35$ to 0.40 V vs. SCE. A marked increase of the electrolyte solution acidity occurs immediately prior to the second oxidation potential at $E = 0.5$ V. The second electrode process is therefore accompanied by the PANI deprotonation:



Charge Measurements

The total charge that passed through the polymer during a single cycle

sweep from 0.0 V to 0.9 V and back to 0.0 V (at 50 mV/s) was measured as a function of the bathing acidic solutions concentration. This change, assuming 100% efficiency, corresponds to the amount of PANI deposited. The result for H₂SO₄ is given in Figure 4. As the concentration of the acid increases, both the charge of anodic and cathodic parts of the sweep increase. These results are similar to those found by Geniès, Penneau and Vieil [12], who proposed that there is a simultaneous increase in the capacitive charge and a reduction in the faradaic charge as the pH increase. The monotonous trend is broken at the lowest bulk acid concentration, 10⁻⁵ mol/l which is probably too low to buffer the ion concentration in the film.

Impedance Spectroscopy

Impedance spectroscopy is useful for characterization of many electrical properties of materials and their interfaces with electronically conducting electrodes.

The parameters that can be derived from the data fall generally into three categories:

a) those pertinent only to the material itself such as conductivity, permittivity, mobility of charges, equilibrium concentrations of the charged species, and bulk generation-recombination rates.

b) those pertinent to the electrode material interface, such as adsorption-reaction rate constants, capacitance of the interface region, and diffusion coefficients [16].

c) extraneous parameters such as bulk properties of the solvents, drift of

parameters during measurement, or experimental artifacts, elimination of which is not always trivial [17].

Impedance data of the polyaniline films without the monomer present immersed in the three different acids, were obtained at several applied potentials. Two sets of data for 1 mol/l and 0.1 mol/l were recorded for H_2SO_4 . For the other two acids, 1 mol/l was used. A parametric diagram was constructed for each acid and concentration, showing the complex plane (Argand) diagram as a function of the polarization potential (Figures 5–8). These diagrams summarize information about real impedance, imaginary impedance and the polarization potential applied for each measurement. Each curve consists of 59 points that correspond to the frequencies of the analysis, starting from 1 Hz and ending at 65 kHz, with 12 logarithmically spread data points per frequency decade.

Figure 5 shows that at 1 mol/l H_2SO_4 the low-frequency impedance of the PANI coated electrode decreases between potentials 0.0 to 200 mV. Once past this potential, the response remains practically constant. Similar behavior can be observed for 0.1 mol/l H_2SO_4 (Fig. 6). However, the response is clearly different when HCl (Fig. 7) or HClO_4 (Fig. 8) are used, which reveals the different effect of the doping anions on the impedance of the polymer film. Based on the foregoing results, an analysis of the impedance spectra using nonlinear least square fit (NLLSF) was done. It was found that for H_2SO_4 at both concentrations the film can be modeled as a resistor R_1 and a constant phase element Q_1 in series (Fig. 9a) at both the low and high frequencies.

R_1 corresponds to the bulk resistance or overall resistance which arises from the resistance of the supporting electrolyte and the electrodes placed in the system. Q_1 is the so called constant phase element (CPE).

It is helpful to introduce a CPE in the analysis of impedance spectra,

instead of pure capacitance, because an RC circuit is not always sufficient for appropriate description of AC response of an electrode [18]. CPE often finds often a use if the analyzed material cannot be described as homogeneous. Due to the nature of the PANI films this would appear to be true.

The impedance representation of Q is given by:

$$Z_Q(\omega) = K^{-1} (j\omega)^{-n}, \quad (3)$$

where ω is angular frequency, j the imaginary unit, and n varies from 0 to 1. The CPE has a dimension of $S^{-1} s^{-n}$. For $n = 0$, Q is reduced to a resistance $R = K^{-1}$; for $n = 1$ Q becomes a capacitance $C = K$, and for $n = 0.5$ the impedance corresponds to charge transfer impedance known as Warburg impedance.

Figure 10 shows variation of Q and n with the applied potential. For the films bathed in 0.1 mol/l H_2SO_4 , the obtained response has two maxima, the first around 200 mV and the second at 750 mV. Average n is 0.86. For the 1 mol/l H_2SO_4 the curve has three maxima (Figure 11). These maxima correlate with the anodic peaks of cyclic voltammograms of PANI in a monomer-free solution (Figure 12). Average n is 0.92, closer to the ideal capacitive behavior than the lower concentration. As the concentration of the supporting electrolyte decreases, the value K of the CPE increases (value of the capacitance increases as the resistance of the solution increases), which is the expected behavior for a conducting material.

The most adequate model for PANI film impedance in 1 mol/l HCl as the supporting electrolyte is shown in Fig. 9b. R_1 has the same meaning as in H_2SO_4 data and R_2 is the charge transfer resistance. Two independent processes can be associated with this system depending upon the working frequency, such as mass control at low frequencies (straight line) and kinetic control at higher frequencies (semicircle) (Figure 7) [19]. Figure 13 shows the variation of the bulk resistance,

the charge transfer resistance and the two parameters n as a function of the applied potential.

Another equivalent circuit was assigned to results with 1 mol/l HClO_4 supporting electrolyte (Fig. 9c). There are three elements in parallel, Q_1 , Q_2 and R_2 , while the bulk resistance R_1 is in series with the rest of the elements. Notice that unlike the corresponding circuit for HCl , Q_1 is in parallel with the bulk resistance R_1 . A graph that summarizes the dependence of these parameters on the applied potential is shown in Figure 14.

Impedance measurements were also performed on bare platinum to be able to assign impedance contribution of the PANI film. Two main aspects of impedance response are noted. First, as the acid concentration decreases, the value for the exponent n also decreases which is not the case for the coated electrode. Second, plots constructed for Q as a function of the applied potential reach a minimum at approximately 600 mV vs. Ag/AgCl (Fig. 15). Position of this minimum is dependent of the acid concentration of the solution and in the experiments it did not correspond to the potential of zero charge (pzc), since the value for platinum electrode in acid solution should be -0.077 V vs. Ag/AgCl [20]. The capacitance value obtained at the minimum Q at 600 mV (about $40 \mu\text{F}/\text{cm}^2$) is consistent with capacitance expected for bare platinum in H_2SO_4 . This capacitance is much smaller than the capacitance obtained once the film is formed and therefore its contribution can be ignored. Further analysis of the impedance response of the uncoated platinum electrode reveals that an R_2 (charge-transfer resistance) can be observed at intermediate potentials. Again, this contribution can be neglected once the PANI film is formed.

Conclusions

The constant phase element used in these evaluations appears to be a suitable element for describing the polyaniline film properties. The K value of CPE for bare platinum is significantly lower than that for the film at any applied potential and therefore the film response can be separated from the background.

Impedance measurements of PANI films in H_2SO_4 reveal that the CPE used to successfully model the system behavior is concentration dependent. Its K magnitude increases with decreasing acid concentration. This corresponds to a decrease in the measured capacitance with concentration. This capacitance in magnitude of microfarads per square centimeter is a charge-storage capacity of the film [21]. In order for the supercapacitor to exist, an available pool of charge has to be available in the surrounding solution. Therefore, the capacitance is expected to decrease with decreasing concentration of the bathing solution.

Another important aspect in the analysis of this conducting polymer is that the charge exchange during anion doping of the film is proportional to the anion (acid) concentration. This analysis was done using sulfuric acid at several different concentrations as the source of anions.

The fact that the differential capacitances obtained with impedance experiments are smaller than those found electrochemically reveals that the plateau current in the cyclic voltammetry plots is not only capacitive in nature. Currents charging the polyaniline films can be divided into a faradaic component and a capacitive component.

The data leading to the three-dimensional parametric Argand diagrams can be obtained easily from Solartron using automated data acquisition program written by us. The graphics is done using inexpensive software Graphtools by 3-D

Vision, Manhattan Beach, CA. The value of these diagrams is in quick qualitative conveyance of results. Nonlinear least square analysis can then be made on those data sets that show promising features.

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Table I: Relationship between the different structures presented by the polyaniline as a function of the electrochemical potential [10].

Potential/mV	Amine(%)	Imine(%)	Name of the Oxidation State
-200	97	3	Leucoemeraldine
150	76	24	Protoemeraldine
300	54	46	Emeraldine
600	50	50	Emeraldine
800	20	80	Nigraniline

Table II: Differential capacitance for PANI films obtained in different acidic media. Data are based on impedance spectroscopy measurements (a) and cyclic voltammetry capacitive current measurements (b). The films were prepared during 17 voltammetric cycles in aniline monomer.

Acidic media	$I_c/\mu A$	$10^3 C_d$	$10^3 C_d$
		[Fcm ⁻²] (a)	[Fcm ⁻²] (b)
HClO ₄	0.61	3.05	0.57
H ₂ SO ₄	1.78	8.89	5.30
HCl	4.50	22.5	16.6

^a Data obtained from voltammetric sweeps.

^b Data obtained from impedance spectroscopy measurements

Legend for figures

- Fig. 1 Cyclic voltammogram during growth of PANI in 1 mol/l H_2SO_4 . Concentration of aniline 0.1 mol/l. Scan from 0 to 0.9 V vs. Ag/AgCl, rate 50 mV/s, 17 cycles. Electrode area 2 mm².
- Fig. 2 Cyclic voltammogram of PANI in 1 mol/l HClO_4 . Aniline concentration 0.1 mol/l. Scan from 0 to 0.9 V vs. Ag/AgCl, rate 50 mV/s, 17 cycles. Electrode area 2 mm².
- Fig. 3 Cyclic voltammogram of PANI in 1 mol/l HCl Concentration of aniline 0.1 mol/l. Scan from 0 to 0.9 V vs. Ag/AgCl, rate 50 mV/s, 17 cycles. Electrode area 2 mm².
- Fig. 4 Total electroactive charge passed through the coated platinum electrode as a function of the concentration of H_2SO_4 in the absence of monomer. The film was grown for 17 cycles in 1 mol/l H_2SO_4 .
- Fig. 5 Parametric 3-D complex plane impedance diagram for polyaniline film synthesized in 1 mol/l H_2SO_4 at varying applied bias potential measured in 1 mol/l H_2SO_4 . Frequency range 1 Hz to 65 kHz.
- Fig. 6 Parametric 3-D complex plane impedance diagram for polyaniline film synthesized in 1 mol/l H_2SO_4 at varying applied bias potential measured in 0.1 mol/l H_2SO_4 . Frequency range 1 Hz to 65 kHz.
- Fig. 7 Parametric 3-D complex plane impedance diagram for polyaniline film synthesized in 1 mol/l HCl at varying applied bias potential measured in 1 mol/l HCl. Frequency range 1 Hz to 65 kHz.
- Fig. 8 Parametric 3-D complex plane impedance diagram for polyaniline film synthesized in 1 mol/l HClO_4 at varying applied bias potential

measured in 1 mol/l HClO_4 . Frequency range 1 Hz to 65 kHz.

- Fig. 9 Equivalent circuits used in modeling of impedance of PANI films prepared in H_2SO_4 (a), HCl (b) and HClO_4 (c). R – resistance, Q – constant phase element (CPE).
- Fig. 10 Evaluated parameters for a series equivalent circuit. Results based on impedance data for the system PANI electrode – 0.1 mol/l H_2SO_4 .
- Fig. 11 Evaluated parameters for a series equivalent circuit. Results based on impedance data for the system PANI electrode – 1 mol/l H_2SO_4 .
- Fig. 12 Cyclic voltammogram of PANI in a free-monomer acidic solution containing 1 mol/l H_2SO_4 .
- Fig. 13 Evaluated parameters for a series/parallel equivalent circuit. Results based on impedance data for the system PANI electrode–1 mol/l HCl .
- Fig. 14 Evaluated parameters for a series/parallel equivalent circuit. Results based on impedance data for the system PANI electrode–1 mol/l HClO_4 .
- Fig. 15 Evaluated parameters for a series equivalent circuit. The results are based on the impedance spectra for bare Pt immersed in 1 mol/l H_2SO_4 at varying applied bias potential.

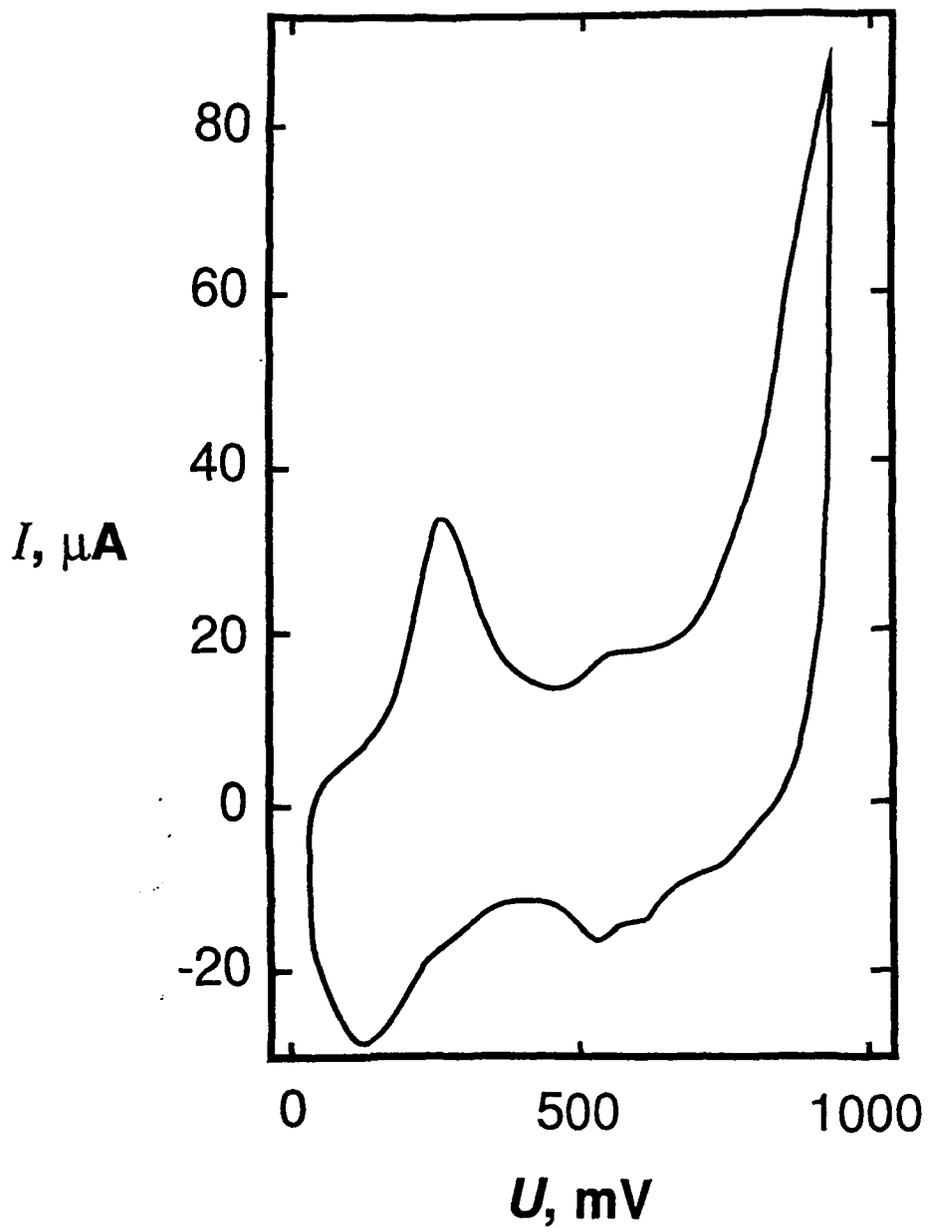


Fig. 1

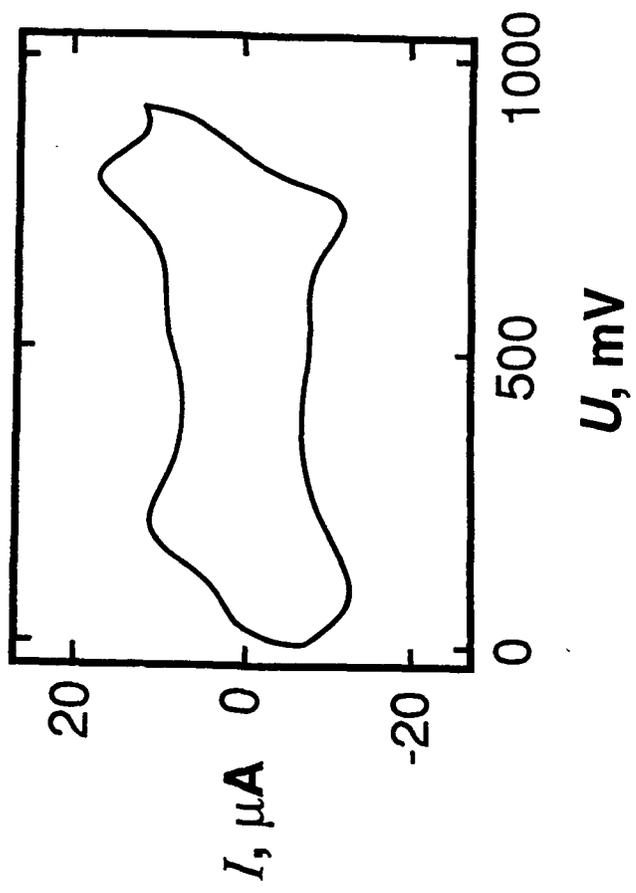


Fig. 2

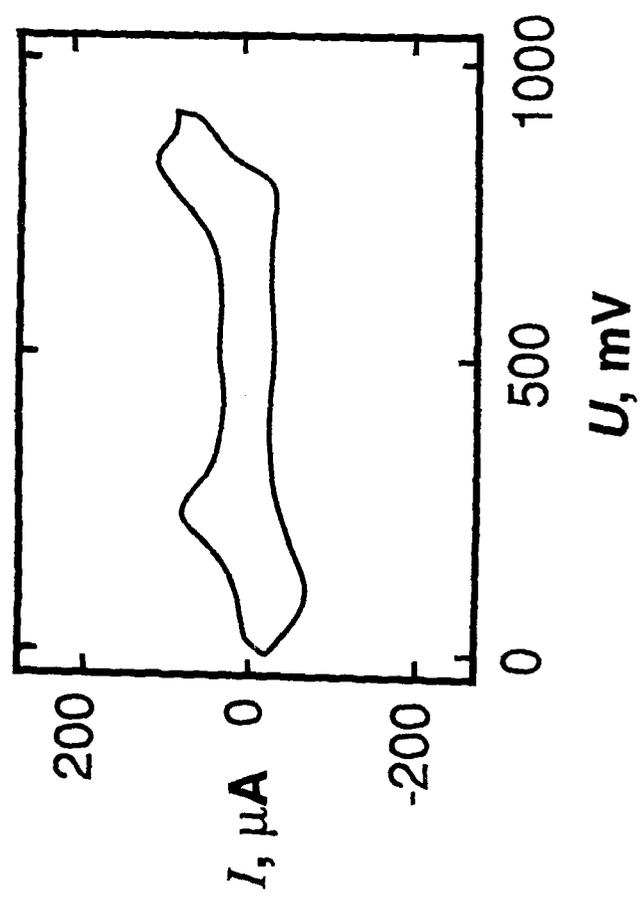


Fig. 3

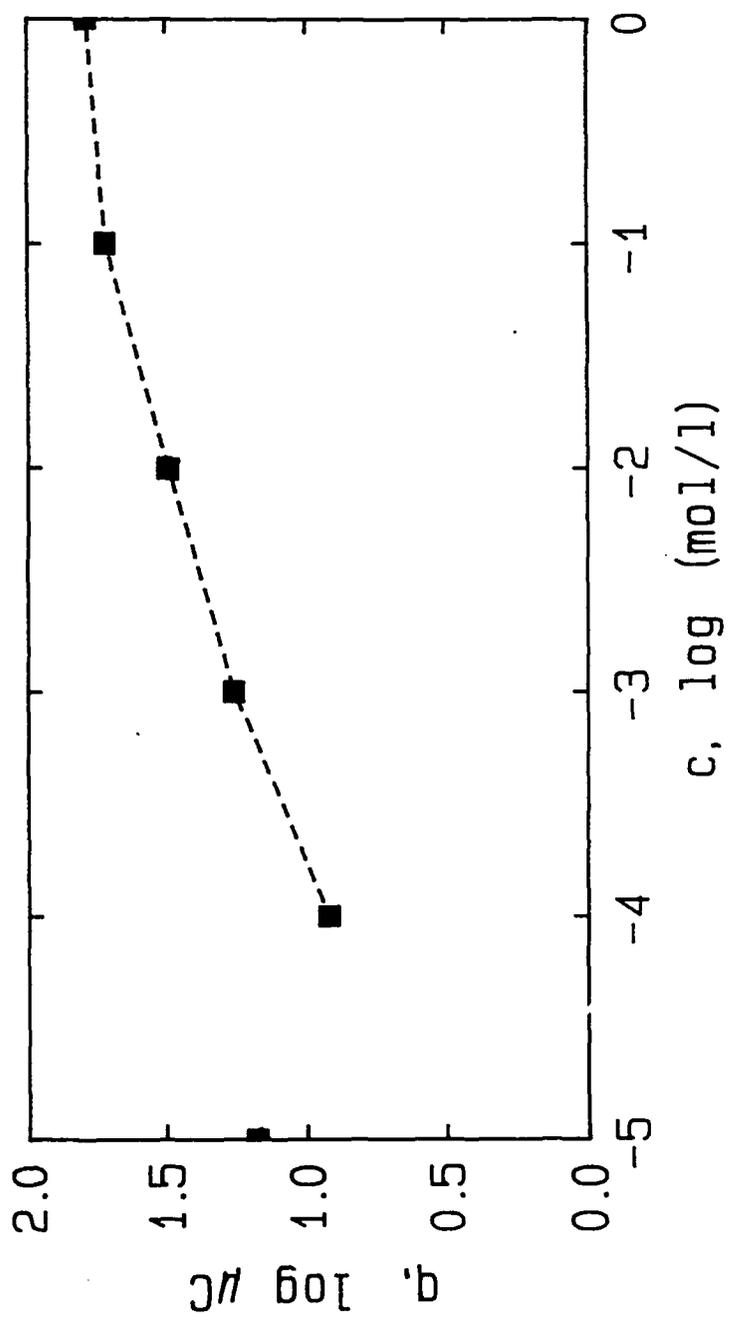


Fig. 4

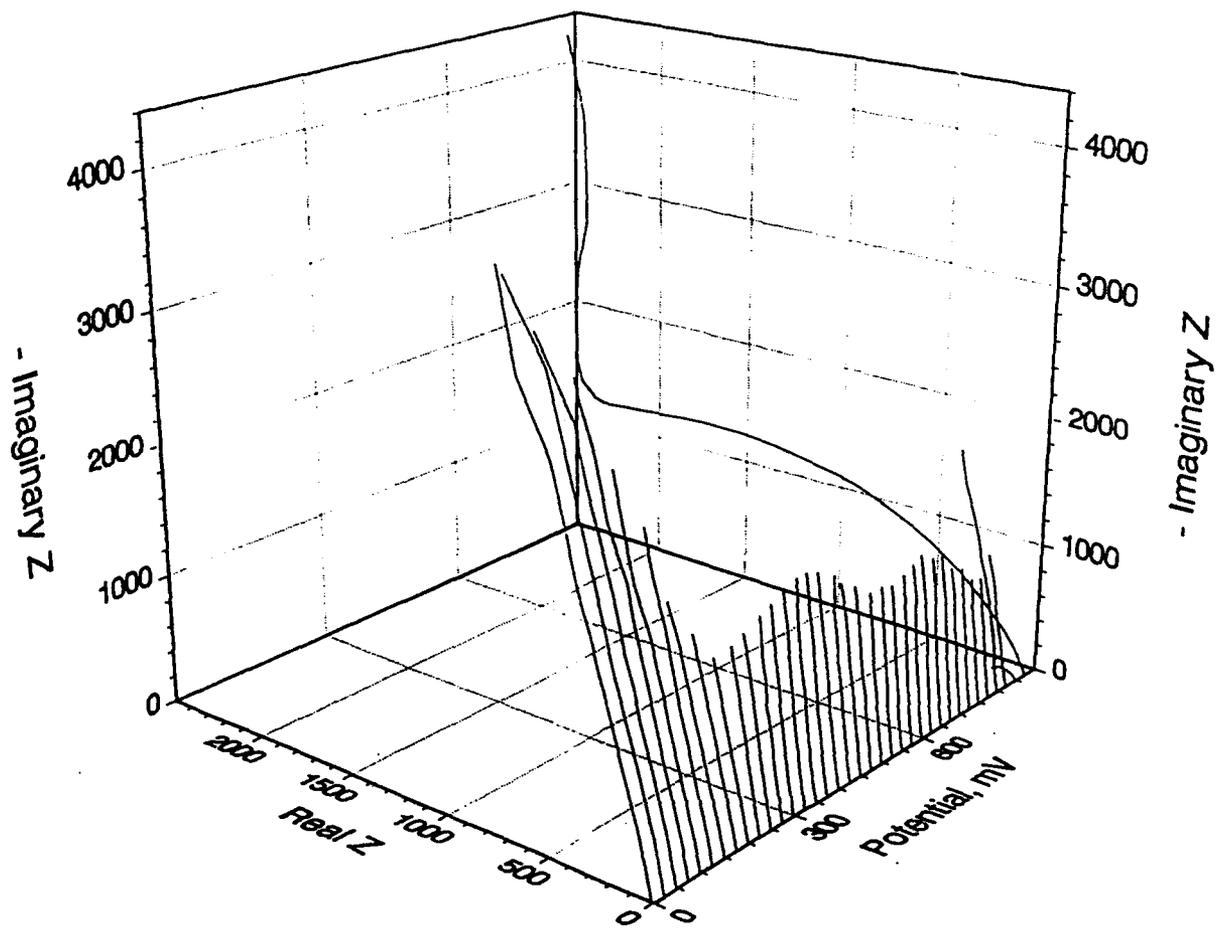


Fig. 5

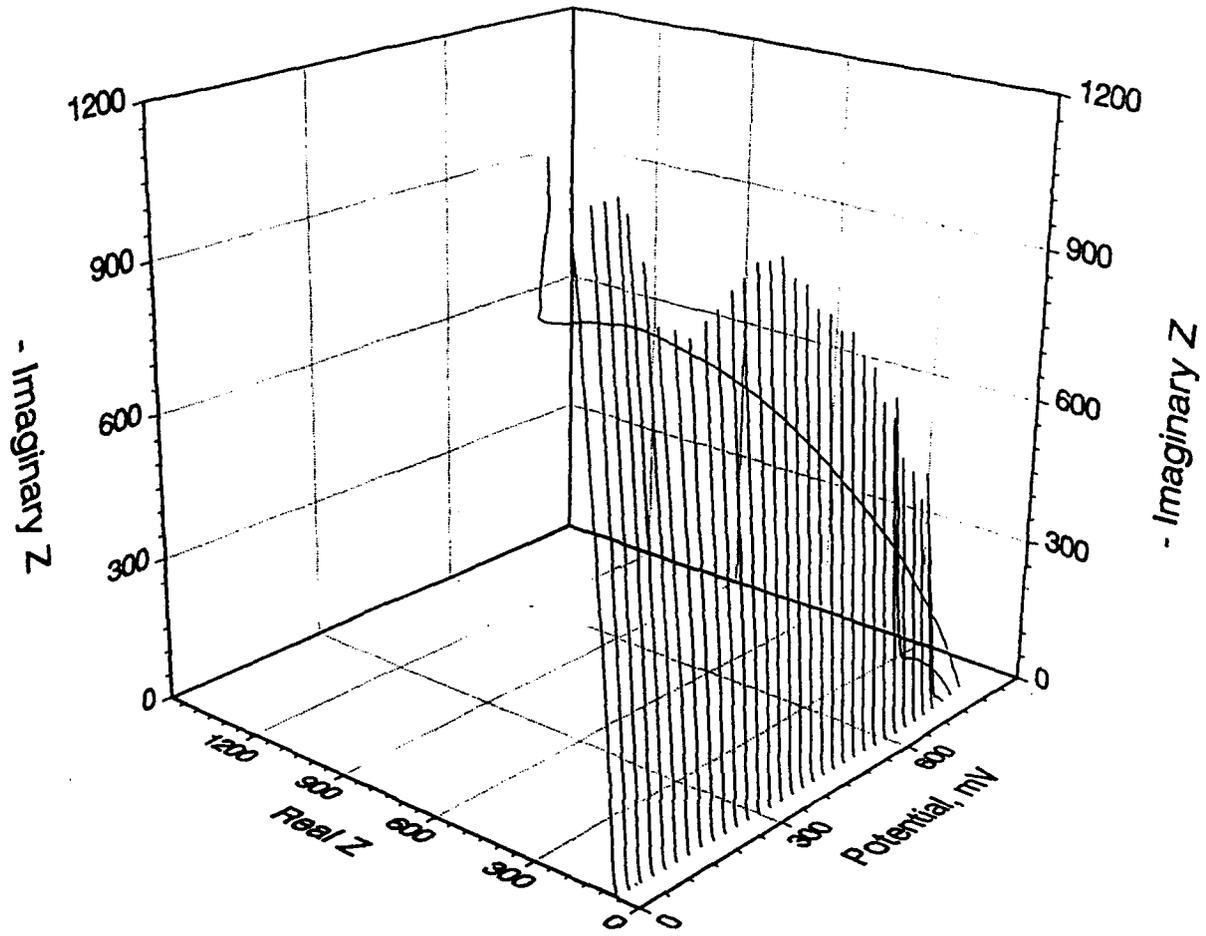


Fig. 6

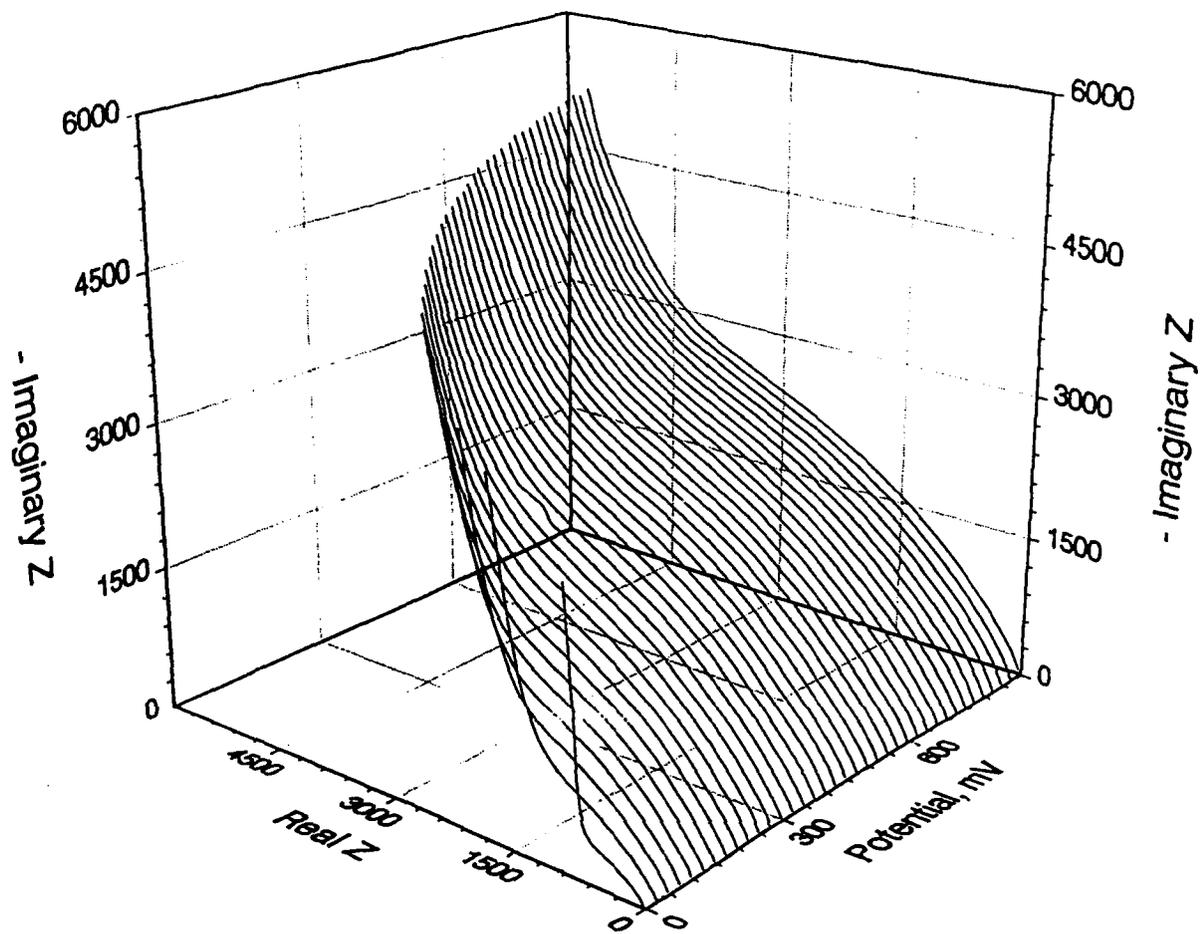


Fig. 7

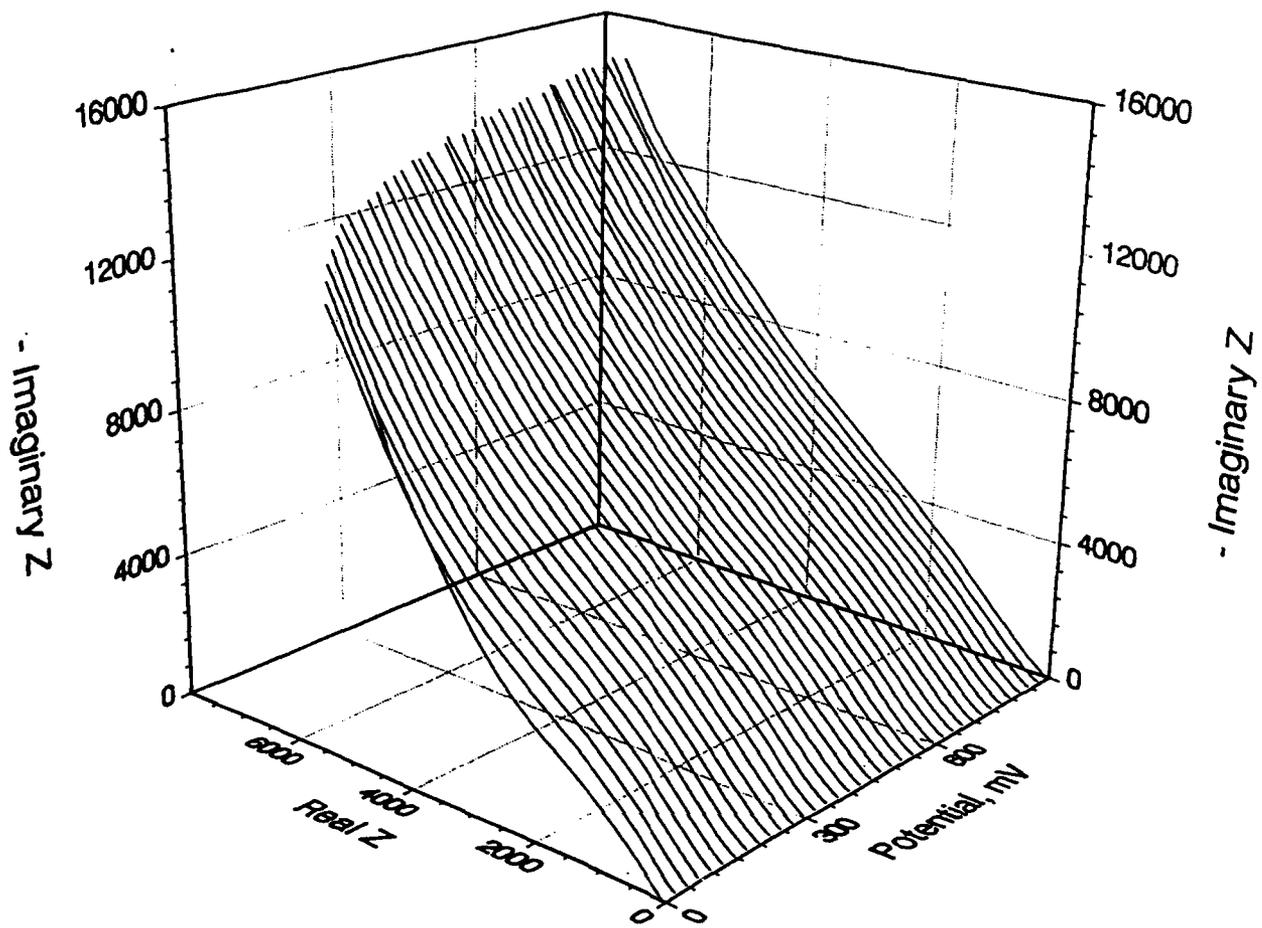


Fig. 8

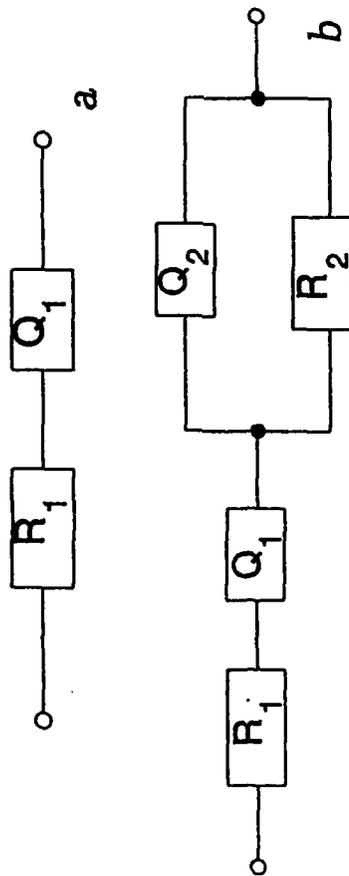
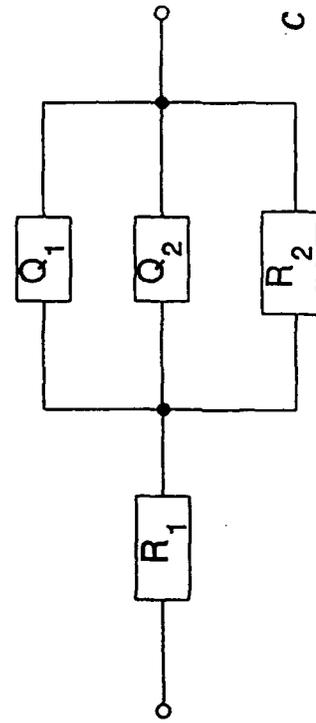


FIG. 9

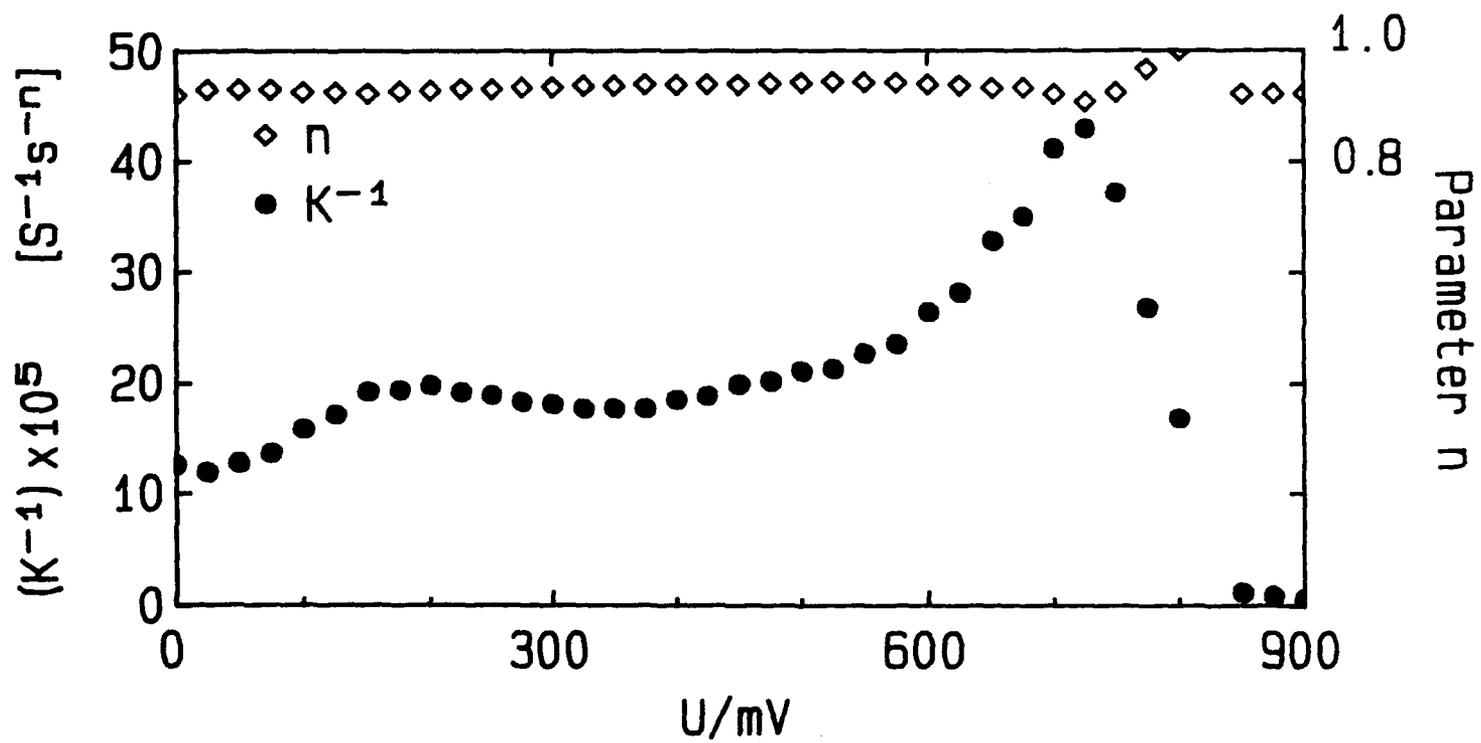


Fig. 10

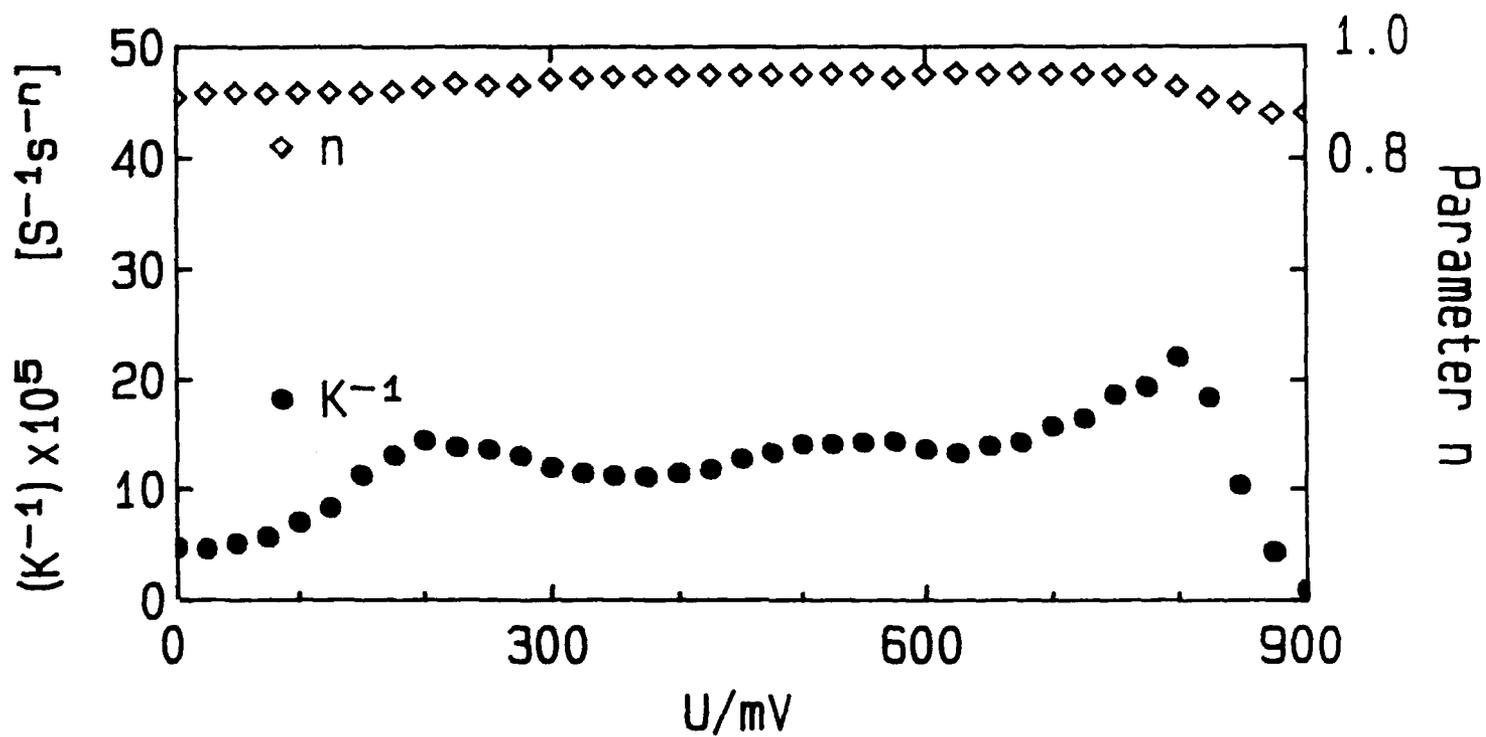


Fig. 11

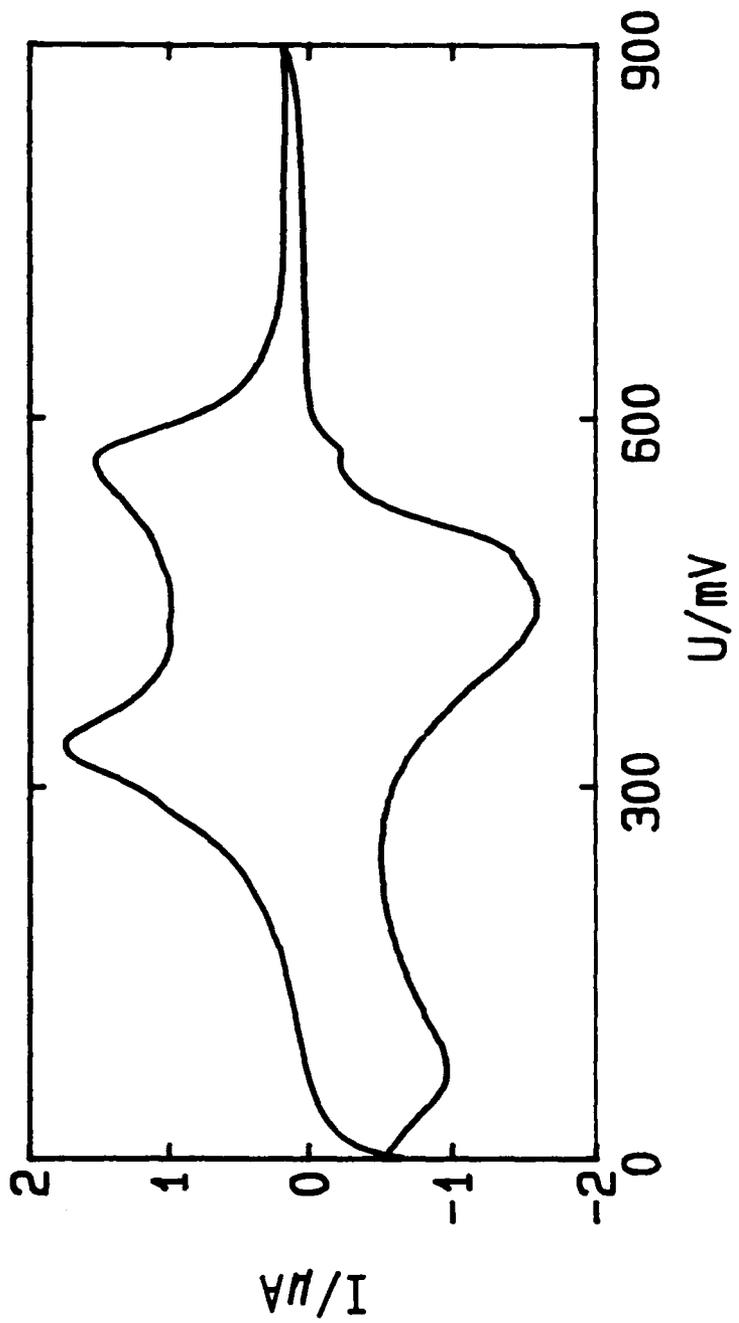


Fig. 12

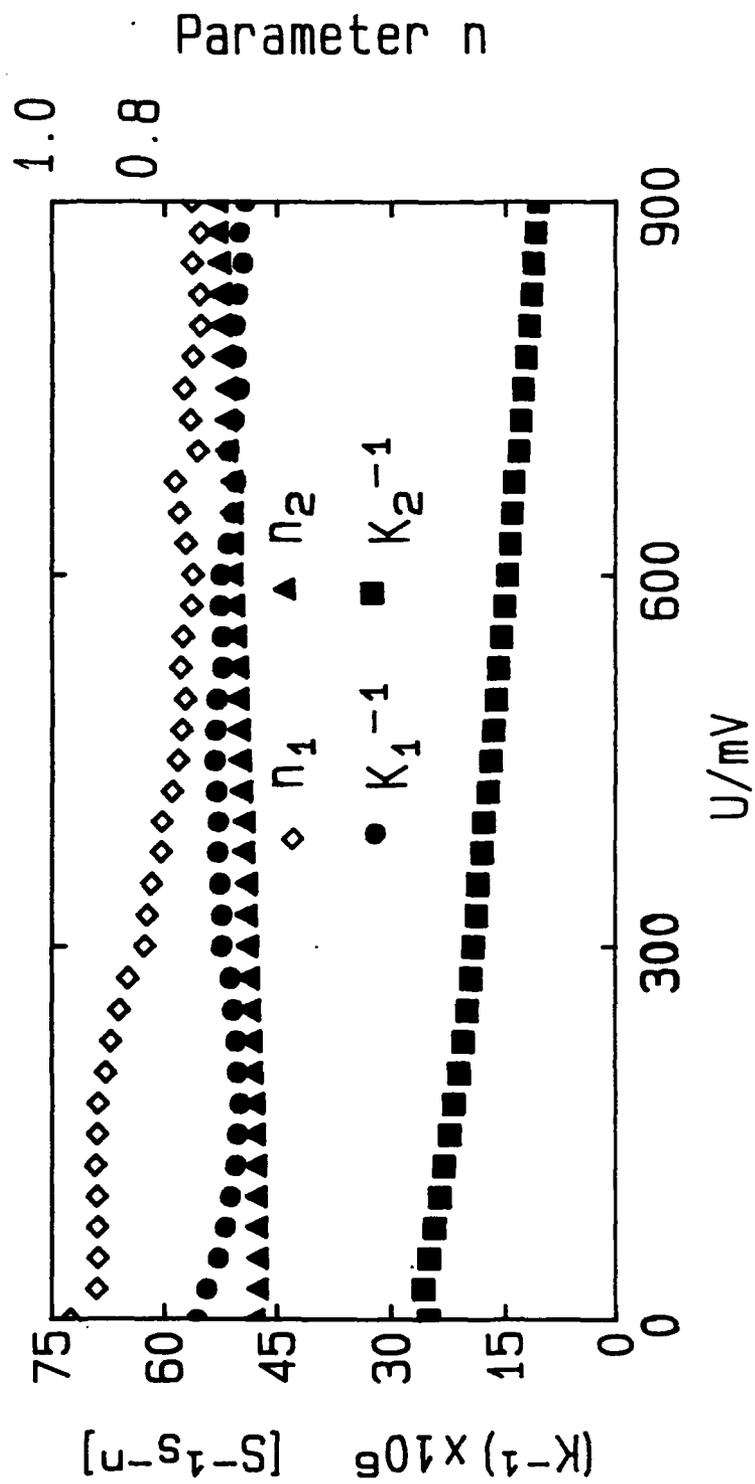


Fig. 13

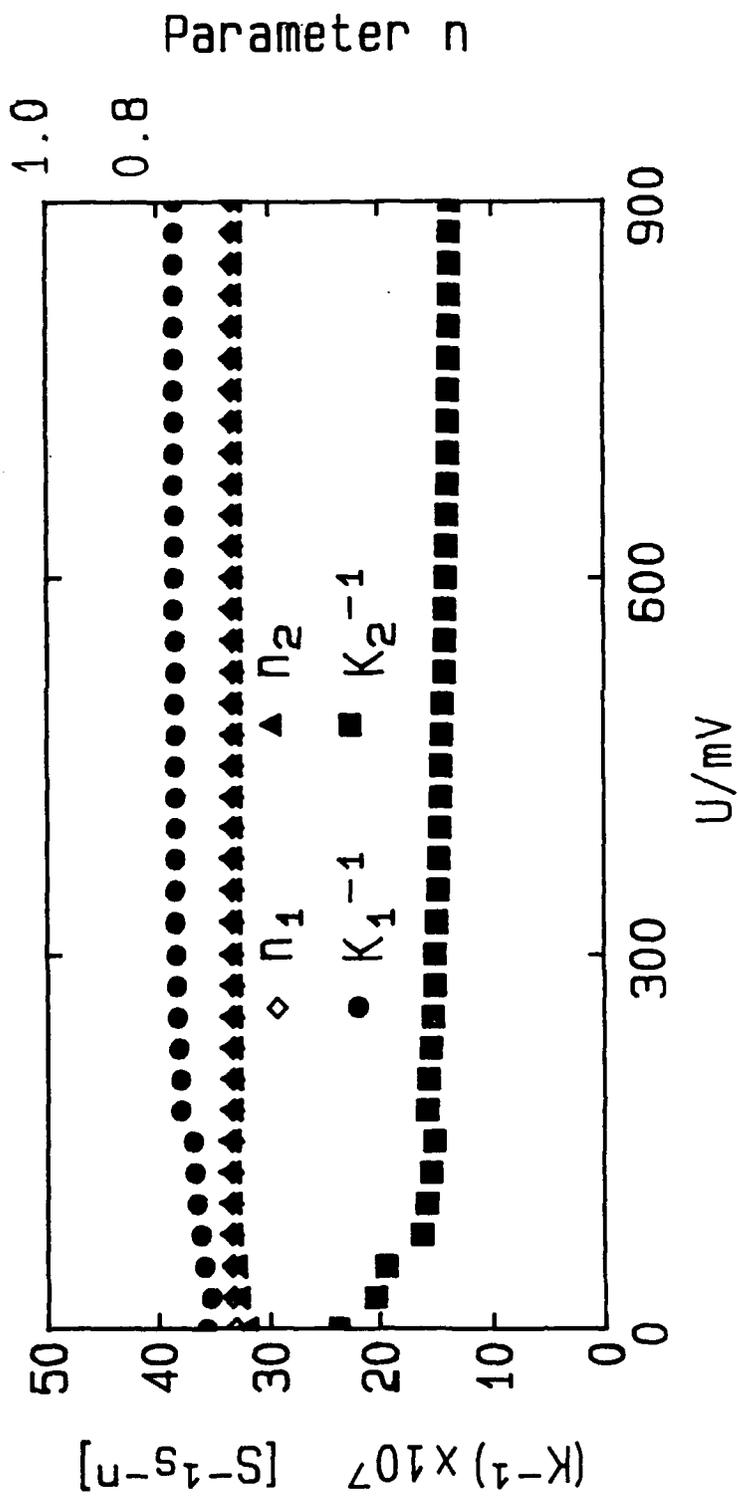


Fig 14

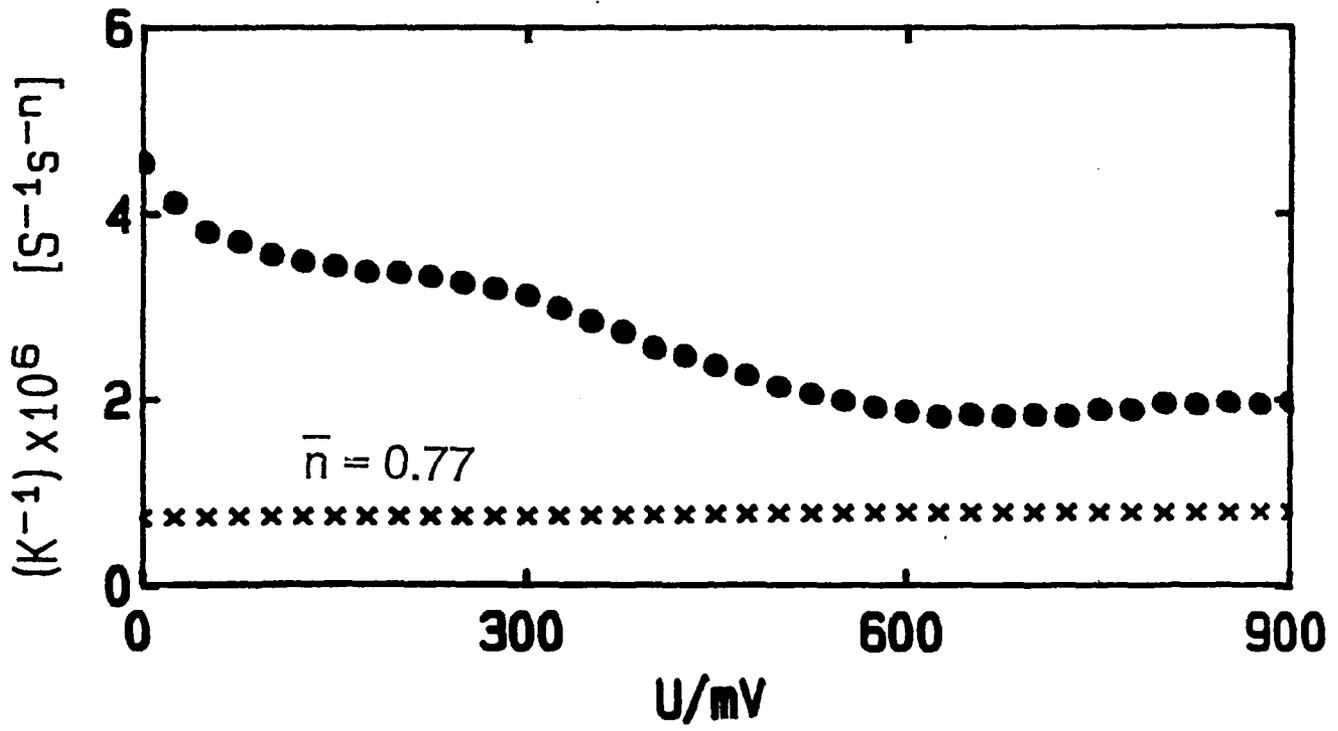


Fig. 15

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