

Changes in Some Properties of Polyaniline Films with the Anion in the Electrolyte

Sonia R. Biaggio* and Cassio L.F. Oliveira

Departamento de Química, Universidade Federal de São Carlos, C.P. 676
13560-970 São Carlos - SP, Brazil

María Jesús Aguirre and José H. Zagal

Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile,
Casilla 307, Santiago 2, Chile

Received: April 30, 1994

As propriedades de filmes de polianilina (PANI), formados eletroquimicamente por voltametria cíclica sobre eletrodos de Pt em soluções de HClO₄ e H₂SO₄, foram estudadas através de perfis potenciodinâmicos, espectroscopia de impedância eletroquímica e microscopia eletrônica de varredura. Observou-se que algumas dessas propriedades dependem da solução na qual os filmes são imersos para se fazer as medidas e não apenas de sua história de formação.

The properties of polyaniline (PANI) films electrochemically prepared by continuous potential cycling a Pt electrode in HClO₄ and H₂SO₄ solutions containing the monomer were studied using cyclic voltammetry, electrochemical impedance spectroscopy and scanning electron microscopy. It was found that some PANI properties are dependent on the electrolyte in which they are immersed, and not only on their history of growth.

Keywords: polyaniline films, electrochemical impedance spectroscopy, effect of electrolyte

Introduction

Polyaniline (PANI) has received considerable attention in the literature in the last decade because of its numerous applications in batteries, electrochromic devices, ion exchange, microelectronic devices and sensors^{1,2}. PANI can be prepared by the chemical or electrochemical oxidation of aniline³. Electrochemical methods involve: (i) synthesis at constant current; (ii) synthesis at constant potential; (iii) continuous potential cycling; and (iv) potential pulses. Both the physical properties and kinetics of electropolymerization depend on parameters such as temperature⁴, nature of the electrolyte used in the synthesis⁵⁻⁸, potential sweep rate^{9,10}, and the shape of the E/t profile used as the perturbation for polymer growth^{11,12}. The effect of anions on the properties of PANI films has been extensively investigated^{5,6,13-17}.

It is possible to characterize conducting polymer films using Electrochemical Impedance Spectroscopy (EIS)¹⁸⁻²⁴, but due to their complexity, there are no general models that describe their frequency response. Musiani¹⁹ has re-

viewed the systems most commonly analyzed by EIS, including both redox and intrinsic conducting polymers. For PANI films in particular there is good agreement between different groups²⁰⁻²²; it has been suggested that the film behaves like a combination of a resistor and a capacitor in series in the oxidized conducting state. In the reduced state, two time constants are observed. As possible interpretations for the lower frequency relaxing processes, Rubinstein *et al.*²⁰ have suggested the presence of a diffusional controlled process, or a pseudo capacitance due to a large-thickness film and a double-layer capacitance of a porous material.

This study compares the morphology, potentiodynamic response and electrical properties of PANI films prepared in H₂SO₄ and in HClO₄, and discusses the influence of the electrolyte present during electrochemical measurements on a pre-electroformed film.

Experimental

PANI films were prepared by electropolymerization under continuous potential cycling between - 0.20 and

+ 0.69 V vs. SCE at 0.1 V s^{-1} in 0.1 M aniline + 0.5 M H_2SO_4 or 0.5 M HClO_4 solutions. All reagents were analytic grade from Merck. For films prepared in HClO_4 , a first scan up to + 0.8 V at 0.002 V s^{-1} was performed followed by scans at 0.1 V s^{-1} in the range - 0.20 V to + 0.69 V. Both synthesis and electrochemical measurements were carried out under nitrogen atmosphere and 20°C . Bi-distilled water was employed in the preparation of all solutions. PANI films were prepared on a 1 cm^2 geometrical area Pt sheet (99.99% pure, from Johnson Matthey). The counter electrode, a 99.99% pure Pt coil, was separated from the main compartment of a three-compartment Pyrex glass cell by fritted glass during polymer growth. A platinum gauze arranged cylindrically around the Pt/PANI working electrode was used for the electrochemical impedance measurements. The reference was a saturated calomel electrode (SCE), separated from the working electrode compartment by a Luggin probe. All potentials in this work are referred to the SCE.

PANI films were analyzed by EIS measurements in fresh acid solutions without any aniline. The frequency range extended from 5 mHz to 10 kHz using an AC potential perturbation of 10 mV. For each film, the frequency response was measured under steady-state potentiostatic conditions at - 0.25, - 0.10, 0.03, 0.20 and 0.40 V. For films grown in HClO_4 , impedance data were obtained at a high fixed frequency (1000 Hz) during anodic sweeps at a low rate (1 mV s^{-1}).

The electrosynthesis and CV measurements were conducted on an EG&G PARC 273 electrochemical set-up, and the potentiodynamic profiles were recorded on an EG&G PARC RE0089 X-Y recorder. The EIS measurements were performed by interfacing a PARC 273 potentiostat to a Solartron-Schlumberger 1255 frequency response analyzer (FRA). Data acquisition was computer assisted via PARC M388 software. The microphotographs were obtained on a ZEISS 960 Scanning Electron Microscope.

Results and Discussion

Voltammetric studies

It is well known that a PANI film in an acid electrolyte shows two typical redox processes in the potential range from - 0.2 V to 0.8 V vs. SCE. Continuous potential cycling up to 0.7 V in acid electrolytes without aniline in solution leads to gradual degradation of the film^{15,16,21}. Due to this limitation, this study centered on the first redox process. As illustrated in Fig. 1, the potentiodynamic response of a film prepared in HClO_4 is different when cycled in HClO_4 compared to the response in H_2SO_4 . Figure 2 shows that the peak potential shifts differently when cycled in HClO_4 or in H_2SO_4 and the response is more reversible when cycled in H_2SO_4 . The difference in behavior is more pronounced for HClO_4 at high scan rates as shown in this

figure. Further, the peak currents are also different in both electrolytes, as depicted in Fig. 1. The lower values of peak currents for HClO_4 do not necessarily imply less reactivity of the polymer in this medium as the potential scan rate increases, since the electrical charge under peak I is approximately the same in both electrolytes. The broadening of the peak in the presence of perchlorate could be attributed to the larger size of this anion^{25,26}. Diffusion of perchlorate ions in or out of the film during the redox process to compensate the electrical charge occurs more slowly than that of sulfate during potential cycling, and this effect becomes more pronounced at higher sweep rates. This effect is more evident for thicker films as previously demonstrated¹⁷. However, these differences could not be

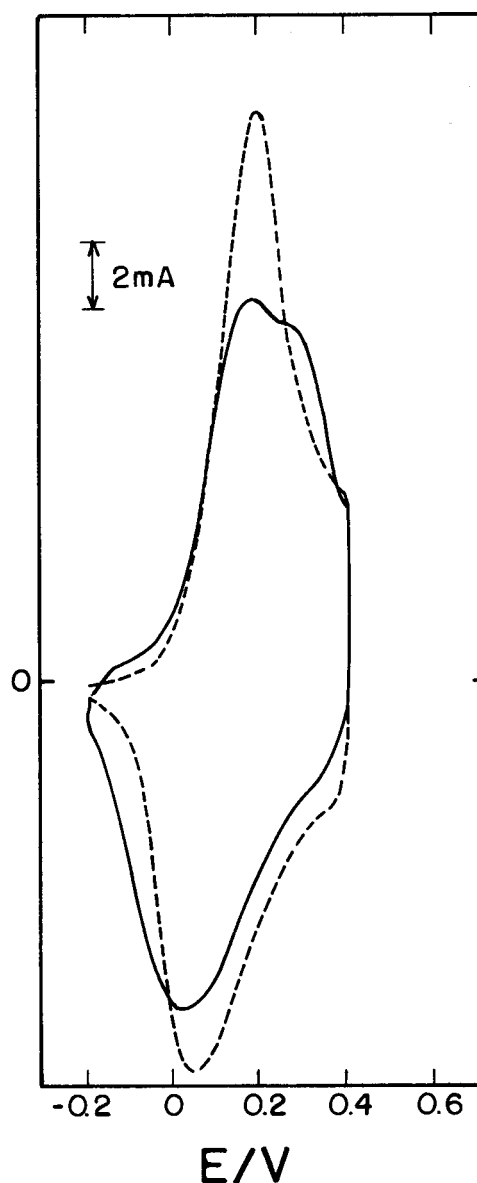


Figure 1. Cyclic voltammograms obtained on a PANI film prepared in 0.5 M HClO_4 after 500 cycles. The CV curves were obtained in (—) 0.5 M HClO_4 and (---) 0.5 M H_2SO_4 . Scan rate: 0.1 V s^{-1} .

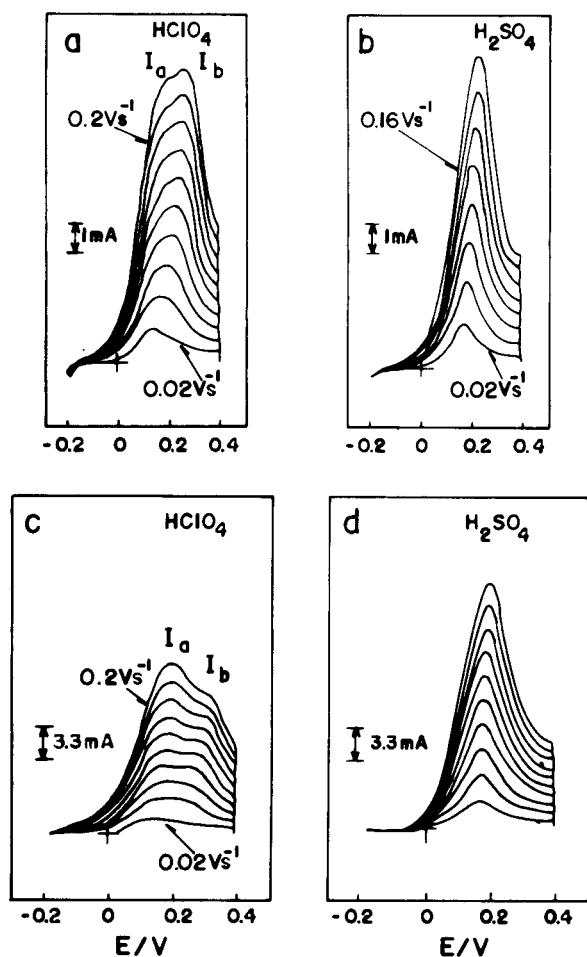


Figure 2. CV curves (only positive scan shown) of PANI films obtained in 0.5 M HClO₄ after 300 cycles (curves a and b) and after 500 cycles (curves c and d), recorded in 0.5 M HClO₄ (a and c) and in 0.5 M H₂SO₄ (b and d), at different scan rates, with increments of 0.02 V s⁻¹.

solely attributed to a size effect since other authors²⁴ have found that potentiodynamic responses of PANI in the presence of Cl⁻ and BF₄⁻ anions are similar and these species have different sizes. Another factor that needs to be considered is that perchlorate anion stabilizes the protonated anilinium moiety in PANI, *via* ion-pair formation, making oxidation more difficult than when sulfate and/or bisulfate is present^{25,26}. Peak Ib in the curves of Fig. 2 would then correspond to oxidation of ion-pair centers of the protonated amine containing perchlorate, and peak Ia to oxidation of the non-protonated amine (leucoemeraldine). The process corresponding to peak Ib predominates for thinner films since most of the film is exposed to the perchlorate-containing electrolyte, and the opposite is true for thicker films (see Fig. 2). For even thinner films only peak Ib appears in HClO₄, as shown in a previous paper¹⁷. All this is consistent with the potential scan rate dependence of peak Ib, which at low rates is practically indistinguishable

from peak Ia, but since it involves a slow process, shifts to positive potentials at higher scan rates.

Impedance studies

Complex-plane (Nyquist) plots were obtained from impedance measurements performed at various potentials, for PANI films prepared in both electrolytes. In order to test the effect of the electrolyte where films are immersed, measurements were first carried out in HClO₄. Films were then thoroughly washed with bi-distilled water and transferred to a H₂SO₄ solution, and a new set of impedance data was obtained. Following these procedures, a third set of data was obtained in HClO₄ again. Figure 3 shows some of those complex-plane plots for reduced PANI film at -0.25 V, where two characteristic dispersions at high and low frequencies can be seen. High-frequency ohmic resistance and low-frequency capacitance values were calculated using the partial NLLS fit method²⁷. Figure 4 compares the low-frequency differential capacity as a function of potential for thick PANI films prepared and measured in H₂SO₄ (600 cycles), and HClO₄ (1070 cycles) having similar charges (15 mC cm⁻², considering the platinum geometric area). The capacity is about 20% higher for the oxidized film prepared in H₂SO₄, and the maximum capacity shifts to more positive potentials. The capacity increases after polymer oxidation is reflected in the relatively high capacitive currents observed in the voltammogram after the first redox process (see Figs. 1 and 2). Figure 4b shows results obtained on a PANI film prepared in HClO₄. Data in Fig. 4b demonstrate that the capacity of PANI films at different potentials depends on the electrolyte medium where it is measured, and not just on the electrolyte in which the films

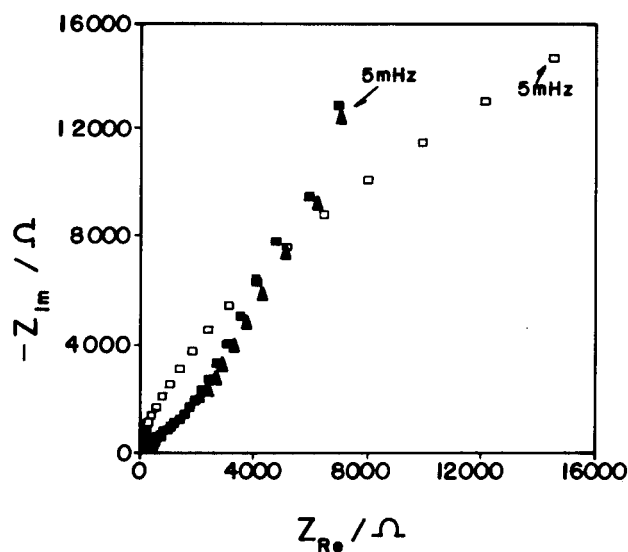


Figure 3. Complex-plane plots for PANI films: (■) grown and measured in 0.5 M HClO₄, then measured in 0.5 M H₂SO₄ (□) and finally measured in 0.5 M HClO₄ again (▲).

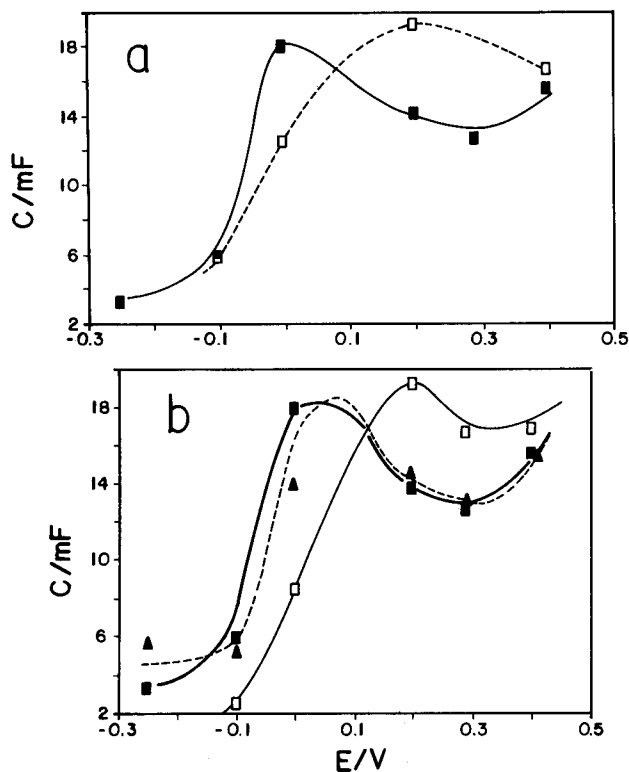


Figure 4. Differential capacity vs. potential curves for PANI films: a) grown (1070 cycles) and measured in 0.5 M HClO₄ (■) and grown (600 cycles) and measured in 0.5 M H₂SO₄ (□); b) grown and measured in 0.5 M HClO₄ (■), then measured in 0.5 M H₂SO₄ (□), and finally measured in 0.5 M HClO₄ again (▲).

are synthesized. This result is interesting since the morphologies of the films obtained in HClO₄ and H₂SO₄ are quite different, as shown in the microphotographs in Fig. 5. However, the dynamic morphology of PANI films in the presence of an electrolyte and applied potential could differ from that observed in vacuum. Results from Fig. 4 are consistent with the potentiodynamic response of these films, reinforcing the idea that the electrochemical properties of PANI films are also determined by the electrolyte where measurements are done, and not only by their history.

The values of high-frequency capacitance data also differ considerably with polymer film thickness and working electrolyte, as shown in Figs. 6a and b. As previously reported^{20,21}, a substantial increase in capacity is observed as the film is oxidized. However, the shape of the curves obtained when the polyaniline film is in HClO₄ solution (Fig. 6a) suggests that two potential-dependent processes are involved, as mentioned above. Again, the capacities in the presence of sulfate/bisulfate anions are about double those observed in HClO₄ (Fig. 6b). This means that, once the film is formed, its active redox sites can still be more numerous by changing the electrolyte. As shown in Fig. 7, an equivalent situation occurs for the ohmic resistance of the films. Pre-formed PANI films in HClO₄ solution present smaller resistance when measured in H₂SO₄ solution. Since the resistance depends on the poten-

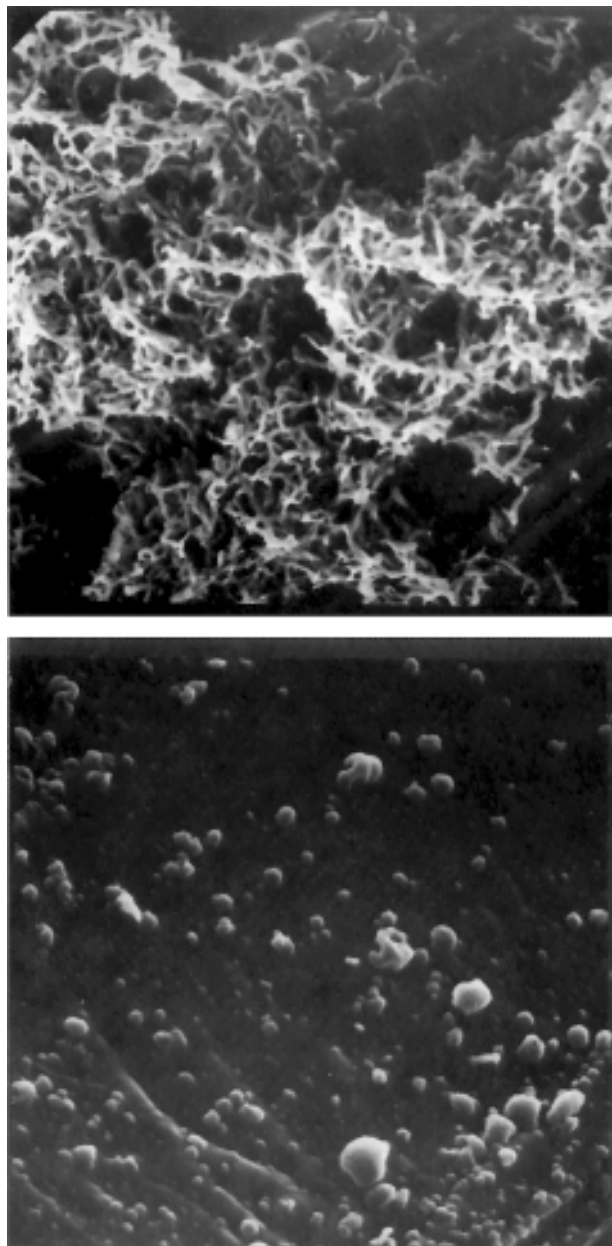


Figure 5. SEM micrographs obtained on PANI films prepared in (a) 0.5 M HClO₄ and (b) 0.5 M H₂SO₄ after 500 cycles. Magnification: 4000 x.

tial, and sharply decreases in the potential region where the polymer film becomes conductive, the resistance of the electrolyte solution is taken as the constant value at higher potentials, as already pointed out in a previous paper⁸. For films of about the same thickness (Fig. 7b), the higher resistance values found for films immersed in HClO₄ solution compared to the ones in H₂SO₄ solutions support the idea of ClO₄⁻ ions stabilizing charge-transmission centers through ionic pair formation. Furthermore, a report²⁸ on the conductivity of PANI films as a function of the basicity of counter ions has shown no direct correlation between conductivity and film morphology. This means that morphological variations

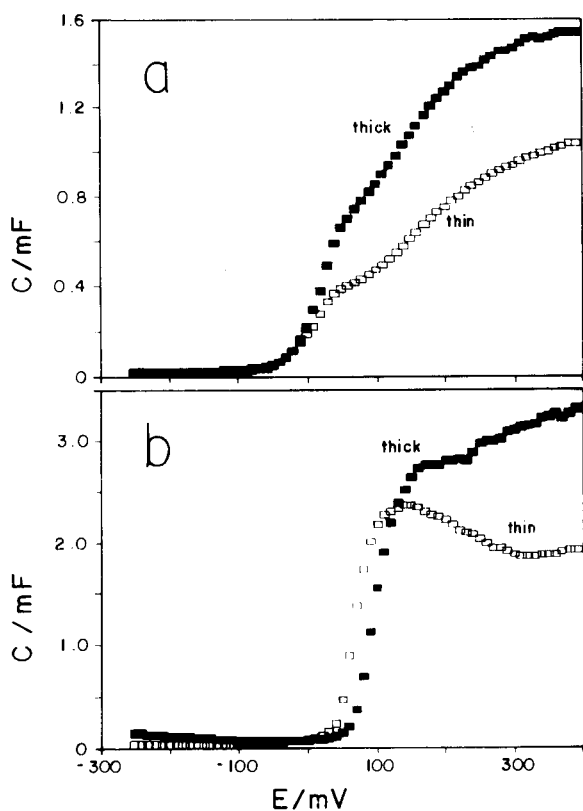


Figure 6. Differential capacity (obtained at 1000 Hz) vs. potential curves for: a) thick and thin films prepared in 0.5 M HClO₄ and measured in the same electrolyte; b) thick and thin films prepared in 0.5 M HClO₄ and measured in H₂SO₄.

due to the electrolyte nature are not necessarily responsible for the changes in the electrical properties pointed out in this paper.

Conclusions

The results presented in this paper clearly show that the response of PANI films is dependent on the nature of the electrolyte in which they are immersed, and not necessarily on the electrolyte in which the films are prepared. The response of PANI films in the presence of ClO₄⁻ ions clearly indicates that some redox processes become slower due to ion pair formation. This has been demonstrated by kinetic studies of PANI growth in HClO₄ solutions²⁹. The two distinct processes observed during the first oxidation of polyaniline films in HClO₄ solutions deserve further study, in order to better understand the electrochemical response of these films.

Acknowledgments

This work was supported by the Fundación Andes / Antorchas / Vitae (1992-1994 Trinacional Project), the CNPq (Brazil) / Conicyt (Chile), by Fondecyt Grants 459/91 and 1088/93 and by DICYT-USACH.

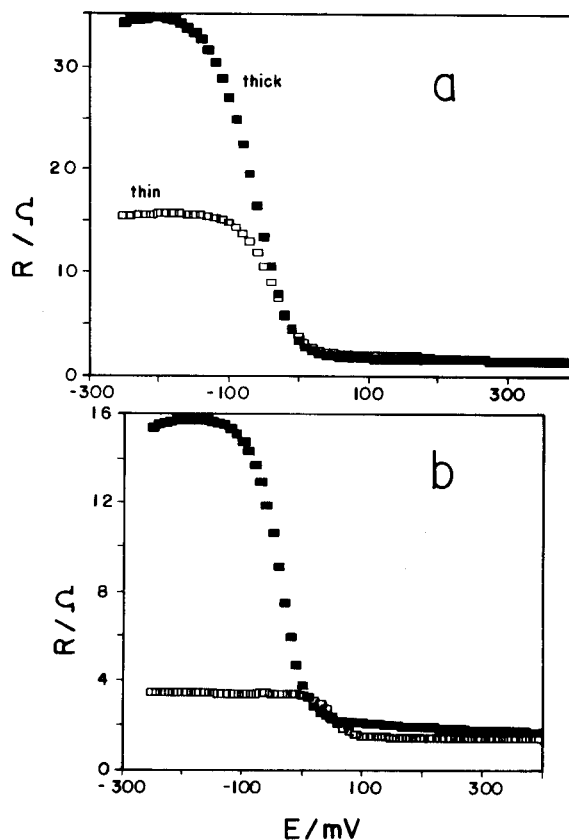


Figure 7. Ohmic resistance as a function of potential for: a) thick and thin films prepared in 0.5 M HClO₄ and measured in the same electrolyte; b) thin films prepared in 0.5 M HClO₄ and measured in HClO₄ (■) and H₂SO₄ (□).

References

1. J. Heinze and M. Dietrich, *Mater. Sci. Forum* **42**, 63 (1989), and refs. cited therein.
2. R. A. Zopi and M.-A. De Paoli, *Química Nova* **16**, 560 (1993).
3. A. A. Syed and M. K. Dinesan, *Talanta* **38**, 815 (1991).
4. M. Gholi and A. Q. Contractor, *J. Electroanal. Chem.* **252**, 291 (1988).
5. P. Nunziante and G. Pistoia, *Electrochim. Acta* **34**, 223 (1989).
6. M. Lapkowski and E. M. Genies, *J. Electroanal. Chem.* **279**, 157 (1990).
7. M. J. Aguirre, B. A. Retamal, M. S. Ureta-Zañartu, J. H. Zagal, R. Córdova, R. Schrebler and S. R. Biaggio, *J. Electroanal. Chem.* **328**, 349 (1992).
8. S. R. Biaggio, C. L. F. Oliveira, M. J. Aguirre and J. H. Zagal, *J. Appl. Electrochem.* **24**, 1059 (1994).
9. Y. T. Kim, H. Yang and A. J. Bard, *J. Electrochem. Soc.* **138**, 271 (1991).
10. H. Yang and A. J. Bard, *J. Electroanal. Chem.* **339**, 423 (1992).
11. V. Tsakova and A. Milchev, *Electrochim. Acta* **36**, 1579 (1991).

12. V. Tsakova, A. Milchev and J.W. Schultze, *J. Electroanal. Chem.* **346**, 85 (1993).
13. C.M.A. Brett, A.M.C.F. Oliveira Brett, J.L.C. Pereira and C. Rebelo, *J. Appl. Electrochem.* **23**, 332 (1993).
14. L. Duic and Z. Mandic, *J. Electroanal. Chem.* **335**, 207 (1992).
15. R. Saraswathi, S. Kuwabata and H. Yoneyama, *J. Electroanal. Chem.* **335**, 223 (1992).
16. J. Bácskai, V. Kertész and G. Inzelt, *Electrochim. Acta* **38**, 393 (1993).
17. M.J. Aguirre, B.A. Retamal, M.E. Vaschetto, R. del Río and J.H. Zagal, *Bol. Soc. Chil. Quím.* **38**, 207 (1993).
18. G. Láng, J. Bácskai and G. Inzelt, *Electrochim. Acta* **38**, 773 (1993).
19. M.M. Musiani, *Electrochim. Acta* **35**, 1665 (1990).
20. I. Rubinstein, E. Sabatani and J. Rishpon, *J. Electrochem. Soc.* **134**, 3078 (1987).
21. S.H. Glarum and J.H. Marshall, *J. Electrochem. Soc.* **134**, 142 (1987).
22. W.J. Albery and A.R. Mount, *J. Electroanal. Chem.* **305**, 3 (1991).
23. G. Inzelt, G. Láng, V. Kertész and J. Bácskai, *Electrochim. Acta* **38**, 2503 (1993).
24. M. Grzeszczuk and G. Zabinska-Olszak, *J. Electroanal. Chem.* **359**, 161 (1993).
25. D.C. Harris, *Quantitative Analysis* (W.H. Freeman & Co. Eds., New York, 1982).
26. H. Lethely, *J. Chem. Soc.* **15**, 161 (1962).
27. B.A. Boukamp, *Solid State Ionics* **20**, 31 (1986).
28. R. Saraswathi, S. Kuwata and H. Yoneyama, *J. Electroanal. Chem.* **335**, 223 (1992).
29. R. Córdova, M.A. del Valle, A. Arratia, H. Gómez and R. Schrebler, *J. Electroanal. Chem.*, in press.