

Electrochemical Characterization of Sol-Gel Formed Ir Metal Nanoparticles

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Electrochemical studies of a sol-gel (SG) derived Ir-containing film have shown conclusively that films formed by air drying or heating at temperatures below ca. 500°C are metallic in nature, exhibiting the typical signature of Ir metal. Both compact oxide formation and reduction, and the hydrogen adsorption and desorption underpotential deposited peaks are seen in cyclic voltammetry experiments in sulfuric acid solutions. The metallic nature of these films has also been confirmed by electron diffraction analysis. Transmission electron microscopy examination has revealed that the Ir particles are uniform in size, ranging from 1 to 2 nm in diam. These Ir nanoparticles can be converted to hydrous Ir oxide by the normal potential cycling and pulsing route, apparently converting all of the Ir sites to the oxidized form. The resulting Ir oxide films are electrochromic, exhibit high charge densities, and are extremely adherent. Ir oxide films can also be formed directly using the SG route by heating the coated electrodes at temperatures above approximately 500°C.

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While the sol-gel (SG) technique has been known for ca. 100 years,¹ it has seen a resurgence in popularity due to the simplicity and flexibility of synthesis of useful materials of controlled composition and having a range of forms and shapes, e.g., fibers, powders, monoliths, and thin films.² Some of the emphasis in recent years has been on the SG synthesis of silica and alumina-based materials, used for many applications including as a matrix for specifically implanted reagents such as biosensing species.^{3,4} Other unique uses of SG-formed materials include the deposition of semiconducting materials such as TiO₂, MnO₂, ZnO, and SiO₂⁵ within the pores of template materials, such as electrochemically formed porous Al oxide films. SG-formed V₂O₅ has also been employed as a high surface area material for use in Li batteries.⁵

We have gained our experience in the SG deposition of thin films through parallel work with Ni, Co, and mixed Ni-Co oxide films.^{6,7} These films have been characterized electrochemically and using various surface analysis techniques. It has been discovered that the mixed Co:Ni oxide films, particularly those of 1:1 composition, have superior charge densities (achieved by optimizing the experimental variables) and redox kinetic properties as compared to similar Ni-Co oxides formed electrochemically or by other conventional deposition methods.⁷

Primarily because of the electrochemical advantages of SG-formed Ni-Co oxide films, our attention has recently turned toward attempting the SG deposition of Ir oxide (IrOx) films, used in applications as diverse as interneural stimulating electrodes,⁸ electrochromic devices,⁹ and as supercapacitive electrodes.¹⁰ In the past, IrOx films have often been formed electrochemically by repetitive cycling or pulsing of the potential (between critical upper, E^+ , and lower, E^- , limits) of an Ir metal substrate in a range of aqueous solutions.⁹⁻¹⁴ In each cycle of potential, a maximum of one monolayer of a hydrous IrOx film can be formed,¹¹ up to a maximum film thickness of a few microns.^{9,10,12} However, this method of film formation, while resulting in advantageous kinetic and capacitive properties, is slow, involves some loss of Ir metal via a simultaneous dissolution process, and unavoidably leaves a thin layer of unreacted Ir beneath the oxide film. Also, the hardness of the underlying Ir metal makes specimen cutting difficult during ultramicrotomy and in other preparation methods used for surface analysis.

In the present work, a first-time study of the electrochemical properties of Ir-containing films, derived using the SG technique, was carried out. The SG method has been employed previously to prepare IrOx^{15,16} and mixed oxides such as IrO₂-Ta₂O₅,¹⁶ IrO₂-SnO₂,¹⁷ and RuO₂-IrO₂¹⁸ in powdered form. IrO₂ coatings were also

obtained by painting^{19,20} and dip-coating²¹ techniques, using a variety of substrates. However, only compositional and/or structural studies of these materials were carried out previously. In the current study, electrochemical results have shown that, contrary to most other reported materials formed using the SG technique,² the initial film product can be made to be metallic in nature and that high temperatures are required to form IrOx directly. The material formed at low temperatures consists of nanosized Ir metal particles, which are extremely adherent to all substrates studied to date. This approach overcomes the known difficulty of producing metallic Ir films, and also yields useful nanosized Ir structures. These films can subsequently be electrochemically converted to the redox-active, electrochromic IrOx film material, yielding high charge densities and excellent Ir(III)/(IV) kinetics.

Experimental

SG synthesis of Ir-based films.—The Ir-containing SG solution was prepared as described elsewhere,¹⁵ using IrCl₃ (or IrCl₃•3H₂O) as the precursor, in a molar ratio of ca. 1:3 with Na ethoxide. These reagents were dissolved in ethanol, refluxed under Ar for several hours, and then filtered. Au foils and wires (Aldrich, 5 N purity), either sealed in soft glass tubing or fixed in a special Teflon holder, were dip-coated by withdrawing them from the SG solution at various fixed rates between ca. 1 and 120 cm/min. It is known that, the more rapid the withdrawal rate, the thicker is the surface film.^{6,7} The Au substrate surface area varied from ca. 0.1 to 1 cm², with some evidence for a lower coverage of the SG coating at the higher area electrodes. The coatings were then either dried at room temperature in air, or were heated at temperatures between 100 and 650°C for times between 15 min and 1 h.

Electrochemical equipment, electrodes, and cells.—A PARC EG&G 173 potentiostat and 175 programmer were used in this work, with the data being recorded on either a Goertz Servogor 790 or an HP 7045B X/Y recorder. The SG-coated working electrode (WE) was placed in the same compartment as the high surface area Pt gauze counter electrode. The reversible hydrogen electrode (RHE), placed in a second compartment joined to the first via a Luggin capillary, served as the reference electrode. All experiments were conducted in 0.5 M sulfuric acid, deaerated by the continuous passage of nitrogen either through or above the solution in the WE compartment. All experiments were conducted at room temperature, 21 ± 2°C.

Transmission electron microscopy (TEM) and electron diffraction (ED) analyses.—A range of Ir-based SG-formed films were coated on carbon-supported or plain copper grids (J. B. EM Services, Inc.) and were then either air dried for 48 h or were heated at various temperatures for 15 min. Subsequently, TEM analysis, and associated ED studies, were performed using a Hitachi H7000 instrument (Health Sciences Center, University of Calgary).

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Results and Discussion

Electrochemical response of SG-formed films.—Figure 1a shows the cyclic voltammetric (CV) response of a fresh SG-prepared Ir-containing film, deposited on a Au foil substrate by withdrawal from the SG solution at 36 cm/min. The coated electrode was then heated at 190°C for 15 min prior to immersion in the 0.5 M sulfuric acid solution. In this range of potential, the current due to the double layer charging of the Au substrate is very small, only ca. 2 $\mu\text{A}/\text{cm}^2$, and therefore does not contribute to the response in Fig. 1a.

For comparison, Fig. 1b shows the CV response of a freshly polished Ir wire electrode in the same solution. The hydrogen adsorption and desorption underpotential deposited (upd) peaks (oxidation-reduction of strongly adsorbed hydrogen is seen at ca. 0.25 V, weakly adsorbed hydrogen at ca. 0.1 V) that are characteristic of Ir metal in acidic solutions,^{11,12} are clearly seen in this CV. Also, the hysteresis between compact oxide film formation (commencing at ca. 0.5 V) and reduction (cathodic peak potential moves negatively as more oxide is formed with increasing E^+ values) seen in Fig. 1b is the typical signature of metallic Ir in acidic solutions.

A comparison of Fig. 1a and b shows that the general CV features of Ir metal are seen for the SG-derived film on Au. In particular, the current/potential response during compact oxide formation and removal in Fig. 1a is characteristic of metallic Ir. For the SG film (Fig. 1a), it is interesting to note that the hydrogen upd peaks depicting the reaction of weakly adsorbed hydrogen are clearly delineated and are somewhat rounded in shape, while the peaks expected at ca. 0.25 V are not present. This probably indicates that the crystallinity of the SG-formed film differs from that of the polycrystalline Ir wires and foils that are normally examined. It can also be seen in Fig. 1a that, as E^+ is gradually increased, the hydrogen upd peaks increase somewhat in size at the SG-formed Ir surface. This probably reflects the electrochemical removal of adsorbed organics and/or chloride that are retained on the Ir surface from the SG solution. In the case of the Ir wire electrode (Fig. 1b), the magnitude and shape of the H peaks does not change under these potential cycling conditions.

It is known that, similar to the case of Pt electrodes, the charge passed in the hydrogen adsorption and desorption peaks at Ir (0.21 mC/cm^2 for a full monolayer of H atoms, although only 65% of the surface Ir atoms has been suggested to be occupied^{21,22}) can be used to estimate the true Ir surface area in contact with solution. In the case of the SG-formed film of Fig. 1a, this calculation yields a true surface area of almost 21 cm^2 , while the apparent Au substrate area is only 0.64 cm^2 (roughness factor of 32). In comparison, integration of the charge in the H upd peaks for the Ir wire electrode (Fig. 1b) yields a true Ir surface area of 0.36 cm^2 , close to the geometric area of 0.3 cm^2 . These results show that the SG method of film formation yields a very high surface area metallic Ir film.

The outcome of continuous cycling of the potential between 0.0 and 1.45 V is shown for the SG-derived Ir surface in Fig. 2a and for the Ir wire electrode in Fig. 2b. In both cases, the development of the mirror-image CV peaks (A_1/C_1), characteristic of the Ir(III)/IV redox reaction in a hydrous Ir oxide film, is seen. However, for the SG material, peaks A_1/C_1 reach a steady-state size and do not increase in size with cycling time, while at Ir metal, these peaks continue to increase as more IrOx is formed. The other typical characteristics of IrOx films formed electrochemically at Ir (Fig. 2b), the A_0 and A_2/C_2 peaks, are also seen in the CV of the sol-gel derived film (Fig. 2a).

The number of monolayers of hydrous Ir oxide film can be estimated by integration of the charge passed in the CV up to 1.3 V,¹² and the realization that a single monolayer of this oxide film is equivalent to 0.11 mC/cm^2 .¹¹ Based on the true Ir surface area obtained above from the hydrogen peaks, this yields a value of ca. 0.22 mC/cm^2 for the SG-derived film shown in Fig. 2a. This suggests that the hydrous oxide film is only ca. 2 monolayers in thickness in this particular case. However, due to the large real area of the electrode, the apparent charge density (based on the area of the underlying Au electrode) is still quite high, i.e., 7 mC/cm^2 .

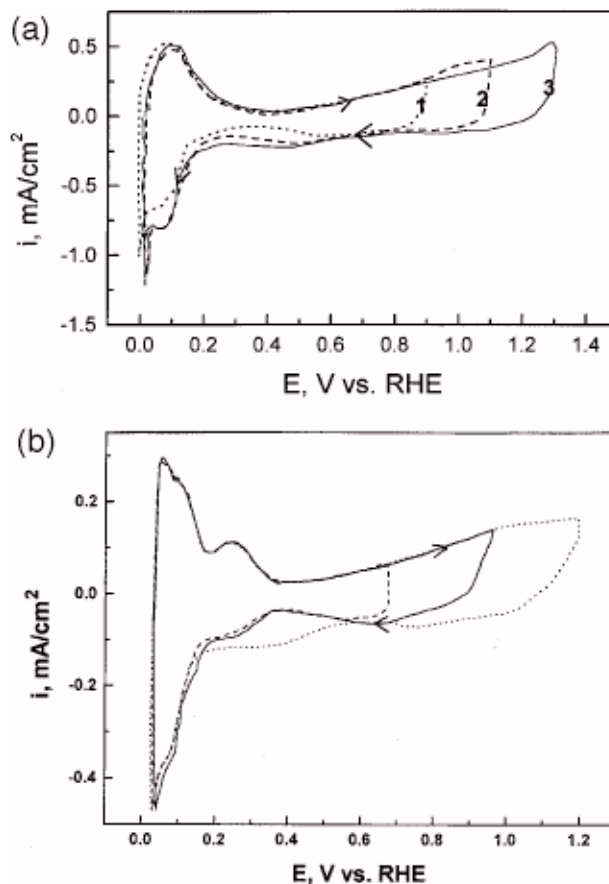


Figure 1. Initial CV response (a) (20 mV/s) in 0.5 M sulfuric acid, with increasing E^+ values, of SG-formed Ir film, formed on Au foil (0.64 cm^2) at a withdrawal rate of 36 cm/min and heated at 190°C for 15 min, (b) (100 mV/s) in 0.5 M sulfuric acid of fresh, polycrystalline Ir wire electrode (0.1 cm^2).

It is important to note in Fig. 2b that, at the Ir wire substrate, the hydrogen upd peaks remain of constant magnitude, even as more hydrous Ir oxide film is deposited. This has been interpreted previously as reflecting complete solution accessibility to the underlying Ir metal, indicating also that electrochemically formed Ir oxide films are extremely porous in nature.^{11,12,23} Also, the fact that essentially a complete monolayer of hydrogen can adsorb on Ir beneath the oxide may suggest that the Ir oxide film is actually partially released from the Ir surface in this potential range.²³ Surprisingly, this does not seem to affect its stability and adhesion to the Ir substrate.

In contrast to what is seen in Fig. 2b for the Ir wire, at the SG-formed Ir film, Fig. 2a shows that the H upd peaks continuously decrease in size as the conversion from compact to hydrous Ir oxide occurs. Eventually, the H upd peaks disappear completely. By comparison with the behavior of polycrystalline Ir electrodes, this must indicate that all of the Ir has been converted to Ir oxide, such that only the Au substrate is present beneath the Ir oxide film. Another explanation might have been that hydrous IrOx film formation at the SG-formed Ir surface results in the complete blocking of some unreacted Ir metal, such that solution can no longer access it and the H upd reaction can no longer occur. However, this is considered unlikely. The fact that the CV characteristics, as well as the compact to hydrous oxide conversion process, are so similar at the two surfaces indicates that a similarity also exists in the film nanostructure.

Structure and composition of SG-derived Ir-based films.—Figure 3 shows a TEM image of a SG-deposited film, formed by the withdrawal of a Cu grid from the Ir SG solution at a rate of 12 cm/min, and then dried in air. The smallest individual particle sizes range between 1 and 2 nm in diam. A prediction of the maximum charge density obtainable from a hydrous IrOx film formed from these Ir

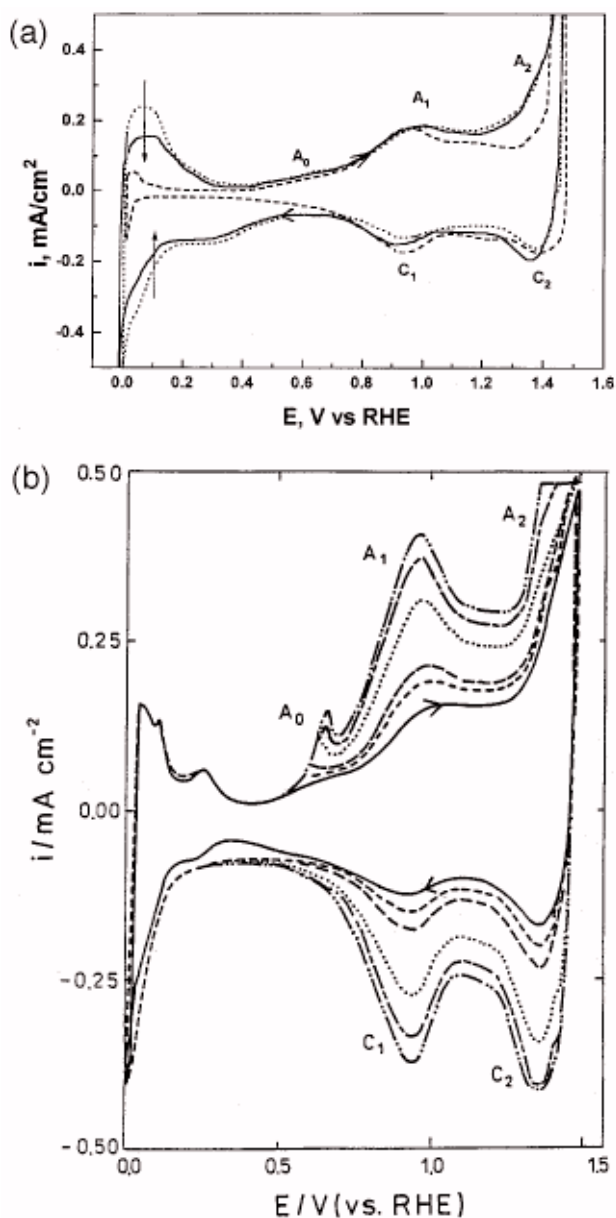


Figure 2. CV response (a) (20 mV/s) in 0.5 M sulfuric acid of SG-formed Ir film (see Fig. 1a) with continuous potential cycling (dotted, then solid, then dashed) between 0 and 1.45 V. Film formed on Au foil (0.64 cm²) at a withdrawal rate of 36 cm/min and heated at 190°C, (b) (100 mV/s) in 0.5 M sulfuric acid of polycrystalline Ir wire (0.1 cm²) electrode with continuous potential cycling between 1 and 1.45 V. Oxide growth is seen, depicted in cycle numbers 1, 4, 7, 15, 21, and 24.



Figure 3. TEM view (530,000 times magnification) of Ir nanoparticles on plain Cu grid, formed by the SG technique, using a withdrawal rate of 1.2 cm/min and air-dried for 25 min. 100 kV accelerating voltage was employed.

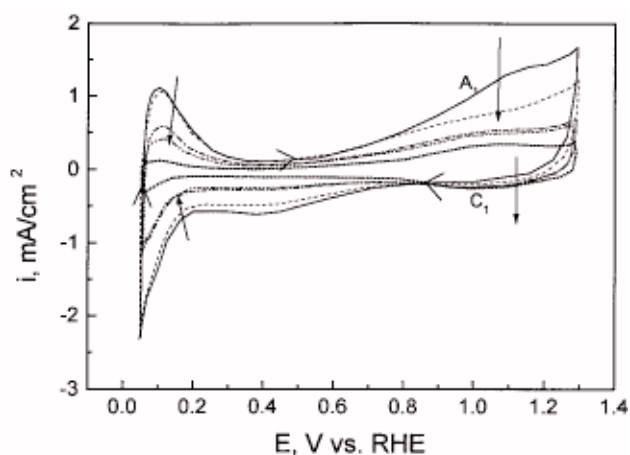


Figure 4. CV response (100 mV/s) in 0.5 M sulfuric acid of SG-formed Ir oxide with continuous potential cycling between 1 and 1.3 V. Film formed on Au foil (5.7 cm²) using a withdrawal rate of 24 cm/min, and then air dried for 48 h.

nanoparticles is made here. It is assumed first that the Ir particles are spherical in nature, with a 2 nm diam. It is also assumed that each surface Ir atom is involved in the H adsorption reaction and that, ultimately, every Ir atom in the particle is involved in the one-electron Ir(III)/(IV) redox reaction. Also, it is assumed that no Ir is lost by dissolution. Based on this, the predicted maximum charge to area ratio for the hydrous IrOx film is ca. 0.39 mC/cm². For the 1 nm diam Ir particles, the predicted IrOx charge density, based on otherwise the same assumptions, is 0.2 mC/cm². These approximate calculations yield similar values to that obtained experimentally above in Fig. 2a, i.e., 0.22 mC/cm². Note that the observed charge density ranged from 0.2 to 0.6 mC/cm² in the present work, depending on the conditions used to prepare the SG film. This probably reflects a range in the size of the Ir nanoparticles.

Electron diffraction data obtained for a film, formed using the same conditions as in Fig. 3, confirmed that the SG derived film is Ir metal, and not IrOx. Lattice spacings were 0.859, 1.141, 1.358, 1.823, and 2.615 Å, similar to those for Ir metal in the diffraction data base.²⁴ This conclusion is also in agreement with that obtained in an earlier nonelectrochemical study of SG-formed Ir-containing films.²⁰

Effect of temperature of drying of SG-derived Ir-containing films.—The effect of the drying temperature of the SG-formed Ir-based film was also examined. Figure 4 shows that, for a film dried in air for 48 h, the same transformation from Ir metal to hydrous Ir oxide occurs with continuous potential cycling, as seen in Fig. 2a. In this experiment, E^+ was extended only to 1.3 V, and therefore, the conversion process is somewhat slower. It is notable, however, that the H upd peaks are less well structured vs. the case of the 190°C film, more similar to those seen at the Ir wire electrode (Fig. 1b and 2b). It was generally seen that as the drying temperature during SG-film formation was increased, the H upd peak at ca. 0.1 V became more well defined and the upd peak at ca. 0.25 V disappeared, at least up to a drying temperature of 350°C. This suggests that the orientation of the Ir grains changes with temperature, as was expected.

For films formed at a temperature of 650°C, a very different CV response is obtained in sulfuric acid solutions. None of the characteristics of Ir metal appear, as seen by the absence of the H upd peaks and of the hysteresis characteristic of the formation and reduction of the first monolayer of compact Ir oxide. Instead, a reversible CV, revealing only a relatively small set of mirror-image A_1/C_1 peaks, is obtained (Fig. 5). This demonstrates that, under these conditions, an Ir oxide film is formed directly, similar to what was seen from X-ray diffraction studies of SG-formed Ir-containing powders heated to a similar temperature.²⁰ An analysis of the charge density of the oxide in Fig. 5, based on the underlying Au surface area yields a value of only ca. 2 mC/cm² (compared to 7 mC/cm² in Fig. 2a). In general,

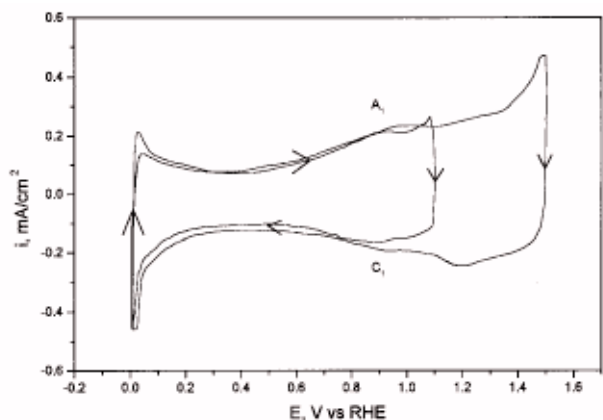


Figure 5. CV response (100 mV/s) in 0.5 M sulfuric acid of SG-formed Ir oxide film, deposited at 24 cm/min on Au (0.54 cm²) and dried at 650°C for 15 min.

the achievable oxide charge densities are lower for the high temperature films vs. those formed at lower temperatures.

Conclusion

The SG technique, using Ir chloride as the precursor, has been used to form a range of Ir-based films on Au electrode surfaces. The film thickness was controlled by the rate of withdrawal of the electrode from the sol solution, and samples were then either air-dried or heated at temperatures between 100 and 650°C. Samples prepared at temperatures below ca. 500°C were found to be metallic Ir, based primarily on the cyclic voltammetry response in sulfuric acid solutions, but also confirmed from electron diffraction analyses. The CVs initially showed the formation and reduction of a compact Ir oxide film, characteristic of Ir metal. TEM studies revealed that the freshly formed Ir metal particles were in the range of 1 to 2 nm in diam. The SG synthesis of these films, forming high surface area Ir metal, overcomes the known difficulty of producing metallic Ir films, and also yields useful nanosized Ir structures.

With time of potential cycling between 0 V and upper potentials between 1.3 and 1.5 V, the reversible CV, typical of hydrous Ir oxide, is obtained. Importantly, the hydrogen adsorption/desorption peaks disappear with time of cycling, indicating the complete consumption

of Ir in its conversion to the hydrous oxide film material. Even after conversion to Ir oxide, the films are very adherent to the electrode surface. The Ir oxide film is electrochromic and exhibits high charge densities. Films formed by heating to 650°C are no longer metallic in nature. Rather, they exhibit the CV characteristics reminiscent of thermally formed Ir oxide films. Also, they yield lower charge densities vs. the oxide films formed at lower temperatures and converted to Ir oxide by potential cycling.

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References

1. A. Ebelmen, *Ann. Chim. Phys.*, **16**, 129 (1846).
2. C. J. Brinker and G. W. Scherer, *Sol-Gel Science*, Academic Press, Toronto (1990).
3. C. Hsuen and M. M. Collinson, *J. Electroanal. Chem.*, **420**, 243 (1997).
4. B. C. Dave, B. Dunn, J. S. Valentine, and J. I. Zink, *Anal. Chem.*, **66**, 1121A (1994).
5. B. B. Lakshmi, C. J. Patrissi, and C. R. Martin, *Chem. Mater.*, **9**, 2544 (1997).
6. I. Serebrennikova and V. I. Birss, *J. Electrochem. Soc.*, **144**, 566 (1997).
7. I. Serebrennikova, Ph.D. Thesis, University of Calgary (1999).
8. C. L. Ballestrasse, R. T. Ruggeri, and T. Beck, *Ann. Biomed. Eng.*, **13**, 405 (1985).
9. B. E. Conway and J. Mozota, *Electrochim. Acta*, **28**, 9 (1983).
10. B. E. Conway, *J. Electrochem. Soc.*, **138**, 1539 (1991).
11. P. G. Pickup and V. I. Birss, *J. Electroanal. Chem.*, **220**, 83 (1987).
12. P. G. Pickup and V. I. Birss, *J. Electrochem. Soc.*, **135**, 126 (1988).
13. H. Elzanowska and V. I. Birss, *J. Appl. Electrochem.*, **23**, 646 (1993).
14. L. D. Burke, J. K. Mulcahy, and D. P. Whelan, *J. Electroanal. Chem.*, **163**, 117 (1984).
15. F. H. Moser and N. R. Lynam, U.S. Pat. 4,855,161 (1989).
16. Y. Murakami, S. Tsuchiya, K. Yahikozawa, and Y. Takasu, *Electrochim. Acta*, **39**, 651 (1994).
17. Y. Murakami, H. Ohkawauchi, M. Ito, K. Yahikozawa, and Y. Takasu, *Electrochim. Acta*, **39**, 2551 (1994).
18. Y. Murakami, K. Miwa, M. Ueno, M. Ito, K. Yahikozawa, and Y. Takasu, *J. Electrochem. Soc.*, **141**, L118 (1994).
19. G. Lodi, A. DeBattisti, A. Benedetti, G. Fagherazzi, and J. Kristof, *J. Electroanal. Chem.*, **256**, 441 (1988).
20. A. Osaka, T. Takatsuna, and Y. Miura, *J. Non-Cryst. Solids*, **178**, 313 (1994).
21. D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, **55**, 375 (1974).
22. J. Mozota and B. E. Conway, *J. Electrochem. Soc.*, **128**, 2142 (1981).
23. V. I. Birss, C. Bock, and H. Elzanowska, *Can. J. Chem.*, **75**, 1687 (1997).
24. JCPDS International Centre for Diffraction Data, no. 06-0598 (1996).