

Short communication

Electrocatalytic reduction of platinum phosphate blue on carbon surfaces: A novel method for preparing fuel cell electrodes

Anima B. Bose^a, Mohosin Sarkar¹, Rathindra N. Bose^{b,*}

^a Department of Mechanical Engineering, Northern Illinois University, DeKalb IL 60115, USA

^b Department of Chemistry & Biochemistry, Northern Illinois University, DeKalb IL 60115, USA

Received 12 April 2005; accepted 3 June 2005

Available online 2 November 2005

Abstract

An electrodeposition process for platinum metal onto carbon surfaces through an electrocatalyzed reduction of a mixed valence oligomeric platinum phosphate blue is described. Cyclic voltammograms of the platinum phosphate blue revealed adsorption of the platinum substrate at the electrode surface followed by reduction first to Pt(II) and then to metallic platinum. These reductions appear to be electrocatalyzed processes as evidence from the almost featureless voltammograms at the first cycle followed by initial continuous growth of both reduction waves and then a leveling off after a few cycles. At the end of 5–10 cycles depending on the concentrations of the precursor, a thin platinum metal film was observed on the carbon. When pure platinum metal was used as the working electrode, both the reduction waves showed steady current over multiple scans indicating an absence of catalysis. The platinum-coated carbon electrodes function like pure platinum metal electrodes as demonstrated by comparing the cyclic voltammograms of the potassium hexacyanoferrate(III/II) redox system recorded with platinum working electrodes and platinum-coated carbon electrodes. The platinum-coated carbon electrode with a coating of 0.03 mg cm^{-2} (geometric area) did not lose its properties even when the electrodes were kept at 2.5 M perchloric acid solution over several days. At the low coating level, a monolayer platinum loading was observed by scanning electron microscopy. These ultra-low platinum loaded electrodes exhibit large active surface areas and have potential for applications in PEM and PAF fuel cells.

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Keywords: Platinum thin film electrodes; Platinum-coated carbon electrodes; Electrochemistry of platinum phosphate blue; Monolayer platinum coating on carbon surfaces; Electrodes for fuel cells

1. Introduction

In recent years, significant efforts have been directed to developing highly efficient fuel cell electrodes [1] and electrode assemblies [2,3] that are durable and capable of delivering much higher kW g^{-1} Pt with reduced cost. Although tremendous progress has been made in reducing platinum loading, higher power delivery and durability require further improvement for the sluggish reduction kinetics of oxygen. Likewise, the development of a relatively less expensive metal loading method remains highly attractive for cost reduction. Since effective catalysis, especially for the reduction of oxygen, depends largely on the

particle size and structure of the catalyst surface, factors that affect both the structure and function of catalysts need to be fully understood in order to optimize the redox processes. We describe here a strategy for electrodeposition of platinum with variable particle size and surface coverage by taking advantage of the electrochemistry of a mixed-valence platinum phosphate blue complex.

Platinum blues are mixed valence platinum complexes [4–8] with an average oxidation state of +2.25. Based on the redox and spectroscopic data, platinum phosphate blue was formulated to be a tetramer (Fig. 1) in which two bis-phosphato-bridged diammine-platinum dimers are attached by a platinum–platinum bond analogous to platinum alpha pyridone blue whose X-ray crystallographic structure has been established [5]. In an attempt to understand the redox properties of platinum phosphate blue, we discovered a unique method of electrodepositing ultra-low amounts of platinum at carbon surfaces and succeeded in making thin-film platinum electrodes [9,10]. In this article, we describe

* Corresponding author. Tel.: +1 815 753 1883; fax: +1 815 753 1631.

E-mail address: rbose@niu.edu (R.N. Bose).

¹ Present address: Department of Chemistry, The Ohio State University, Columbus, OH 43210, USA.

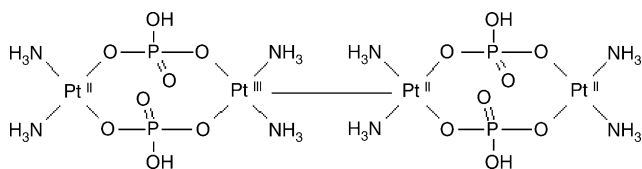


Fig. 1. Structure of platinum phosphate blue.

a strategy of loading ultra-low platinum from an oligomeric platinum phosphate blue [4–7] that not only offers an efficient electrocatalytic surface deposition of platinum on carbon surfaces but also opens the possibility of controlling the surface chemistry by manipulating the size and structures of spacer ligands that bridge platinum atoms. Furthermore, the article reveals the rich electrochemistry of a mixed valence platinum phosphate blue, which to the best of our knowledge has not previously appeared in the literature.

2. Experimental

cis-Diaminedichloroplatinum(II) was prepared by the method of Dhara [11]. Platinum phosphate blue was prepared from *cis*-DDP by dissolving known quantity of the platinum complex (1.0×10^{-4} mole) and sodium dihydrogen phosphate (3.0×10^{-4} mole) in 20 mL water. The pH of the solution was adjusted to pH 5.0 by NaOH. The solution was left overnight. The blue color slowly developed over time. The completion of blue formation was determined by monitoring the visible spectrum when no further changes in the electronic absorption band at 650 nm were observed. Alternatively, *cis*-diaquadiamineplatinum(II) solution (1.0×10^{-4} mole), prepared in situ from the dichloro species by adding two equivalents of silver nitrate, and NaH_2PO_4 were mixed in a similar manner to form the platinum blue complex. A much accelerated formation of the phosphate blue was observed from the diaqua-complex. However, the blue formed in this manner was also accompanied by the formation of a black precipitate. No such precipitation was observed in the preparation from the dichloroplatinum species.

The concentrations of the platinum blue solutions were adjusted to 2.0–5.0 mM for cyclic voltammetry experiments. Carbon rods were purchased from Spi Supplies (West Chester, PA 19381, USA; catalog no. 1685) and carbon cloth (Torrax, TGPH120) was obtained from ETEk, Inc.

Ultraviolet–visible spectra were recorded on a Perkin-Elmer spectrophotometer. Cyclic voltammetric measurements were made on a computer interfaced PAR potentiostat/galvanostat (PAR 273) which was controlled and operated by Corrware software. Details of voltammetric set up have been described elsewhere [12]. A conventional three-electrode electrochemical cell with a carbon rod or carbon cloth as a working electrode, Ag/AgCl as a reference electrode, and a platinum wire as an auxiliary electrode was used. These electrodes were immersed in platinum phosphate blue solutions of 2.0–5.0 mM in 0.5 M NaClO_4 .

Platinum coverage on geometric areas was determined by estimating platinum content by ICP-MS technique. In these experiments coated platinum was completely reoxidized in con-

centrated aqua regia and then subjected to ICP-MS measurement. Surface morphology was determined by scanning electron microscopy (Hitachi S-4700).

3. Results

Fig. 2 shows the cyclic voltammograms recorded by scanning potentials from 0.2 to -1.0 V versus saturated calomel electrode. As can be seen from the figure, the voltammogram recorded from the first cycle appeared to be almost featureless, displaying only a shoulder at about -0.95 V. This first voltammogram indicates that the phosphate blue is very weakly electroactive at the carbon surface. The next sets of voltammograms clearly exhibited two distinct reduction waves. The potential for the first reduction wave at -0.53 V remained constant while the second wave moved from initial -0.94 to -0.72 V. Also distinct is the magnitude of the current for both waves. Magnitudes of current for the redox waves initially increase and finally level off. These voltammograms were then compared with those obtained with a platinum metal working electrode. Fig. 3 shows a typical cyclic voltammogram of the phosphate blue with a platinum metal working electrode. In this voltammogram, two reduction waves and two oxidation waves in the region -0.42 and -0.73 V were observed. Separations between the reduction and oxidation waves indicate quasi-reversible redox processes. Next, platinum-coated carbon electrodes were cleaned in 2.0 M perchloric acidic solution and then reused to record voltammograms of the blue. These voltammograms recorded with platinum-coated carbon electrodes as the working electrode exhibited identical features to those obtained with platinum metal working electrodes. Furthermore, repetitive scans using the platinum-coated carbon electrodes exhibited conventional

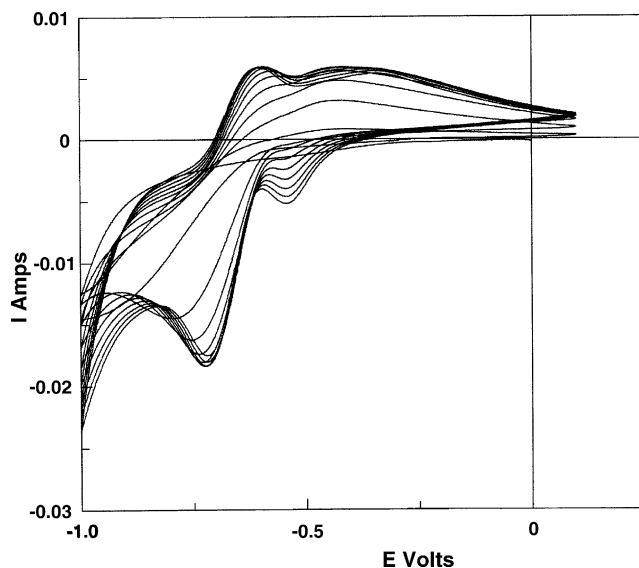


Fig. 2. Cyclic voltammograms of platinum phosphate blue (2.0 mM) at pH 6.0 in 0.50 M NaClO_4 . The voltammograms were recorded at a sweep rate of 100 mV s^{-1} with a carbon rod as the working and Ag/AgCl as the reference electrodes. The first cycle shows negligible electroactivity while the subsequent cycles clearly exhibit reduction and oxidation waves with increasing current densities.

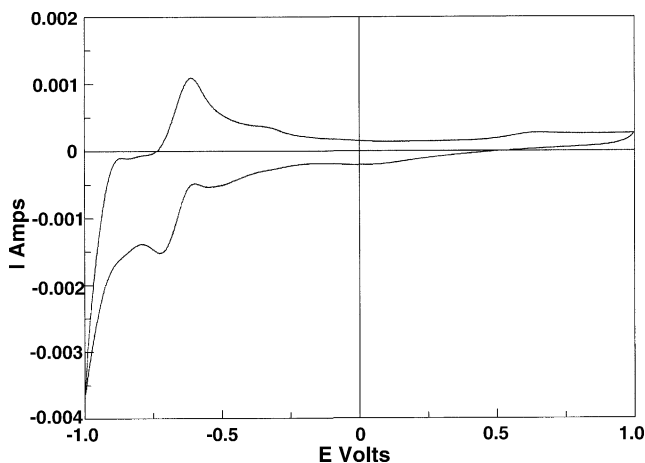


Fig. 3. Cyclic voltammograms of platinum phosphate blue (2.0 mM) at pH 6.0 in 0.50 M NaClO₄ solution with a platinum wire working electrode at 100 mV s⁻¹ sweep rate. Reduction and oxidation waves were clearly observed from the very first cycle with no significant changes in the current densities in subsequent cycles.

voltammetry (Fig. 4) in that a small decrease in current was observed over repetitive scans due to the depletion of the electroactive species at the electrode surface. These data clearly indicate that platinum-coated carbon electrodes function like a pure platinum metal electrode. To further demonstrate the utility of the coated electrode as the pure platinum electrode, cyclic voltammograms of Fe(CN)₆^{3-/2-} redox couple were recorded. The voltammogram of the Fe^{3+/2+} couple III/II was identical to that obtained with a platinum metal electrode both in peak positions and peak currents when identical surface areas were used (Fig. 5). The equal surface area of the platinum-coated carbon electrode was adjusted in the following way. First, the voltammogram of the blue was recorded using a platinum metal working electrode. Then, platinum-coated carbon electrode was dipped in the same solution and the depth of the electrode insertion was adjusted until it reached to the same current level as

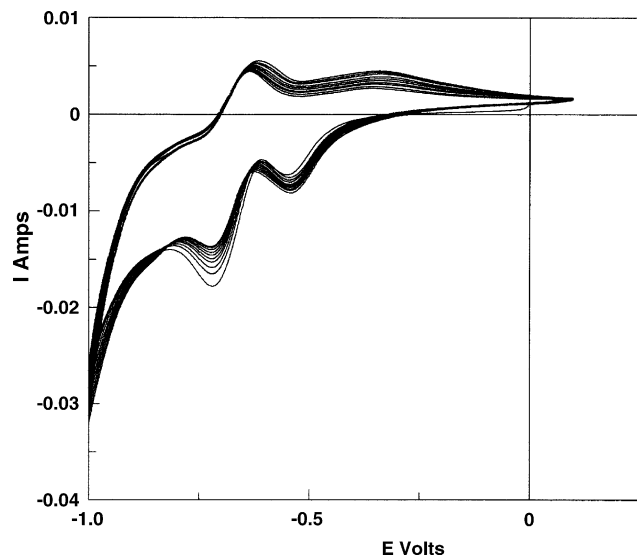


Fig. 4. Cyclic voltammogram of phosphate blue (2.0 mM) at pH 6.0 in 0.50 M NaClO₄ by using a platinum-coated carbon electrode.

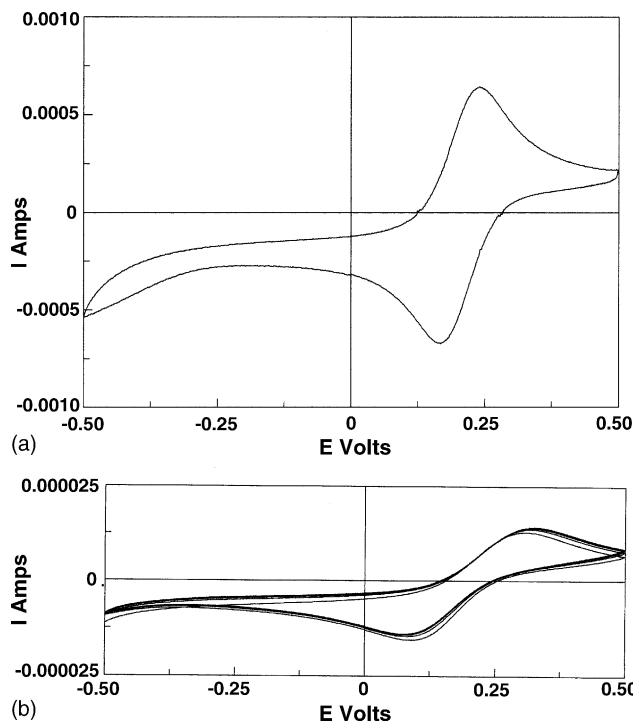


Fig. 5. Comparison cyclic voltammograms of Fe(CN)₆^{2-/3-} redox couple using a platinum wire and a platinum-coated carbon electrode in 0.50 M NaClO₄ at pH 2.0.

measured at a potential away from the oxidation and reduction waves.

To demonstrate the ability to irreversibly coat platinum on other carbon surfaces, carbon papers were used as working electrodes. Fig. 6 shows typical voltammograms of the blue recorded with those carbon papers. Here again, the first cycle was distinctly different from the subsequent cycles as observed for the graphite surface. However, these voltammograms show a greater

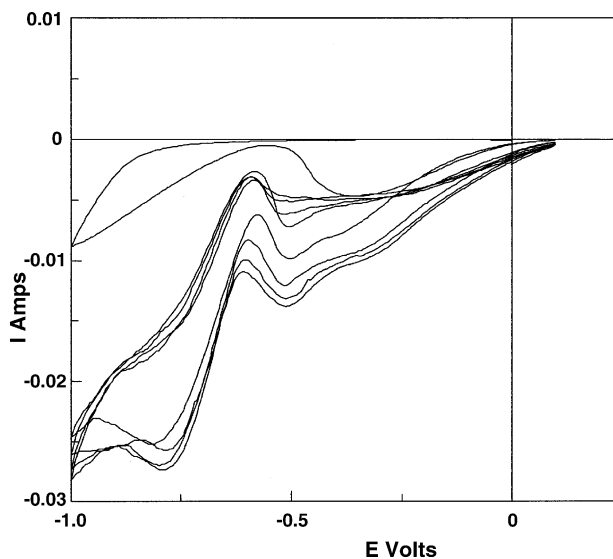


Fig. 6. Cyclic voltammograms of platinum phosphate blue on a carbon paper (Troy) exhibiting the similar characteristics as those observed in Fig. 2. Conditions are the same as stated in Fig. 2.

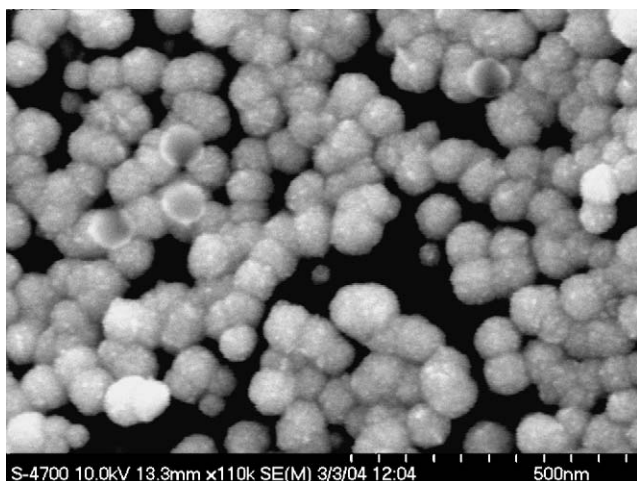


Fig. 7. SEM image of a platinum-coated carbon surface (0.05 mg cm^{-2} on carbon rod) using platinum phosphate blue.

degree of irreversibility in that the cathodic to anodic current ratios were larger for the carbon paper, indicating even more efficient electrodepositions on the carbon paper.

The degree of coating was measured by quantitative analysis of platinum content as a function of the number of cycles. As expected, platinum loading depended on the concentration of the blue solutions and the number of cycles employed in recording voltammograms. These determinations reveal that when 2.0 mM solution was used, the loading varies between 0.03 and 0.22 mg cm^{-2} with 5 and 20 cycles. Furthermore, the highest loading represents the saturation point as no further increase in loading was observed. The electron microscopy of the 0.05 mg cm^{-2} loaded sample reveal formation of platinum monolayer (Fig. 7).

4. Discussion

The platinum phosphate blue exhibited two successive quasi-reversible redox waves on a pure platinum working electrode corresponding to the electrode reactions:



The reduction potentials at pH 6.0 can be estimated as -0.47 and -0.68 V versus Ag/AgCl electrode. On the other hand, the appearance of an almost featureless voltammogram with a shoulder at -0.95 V , recorded in the first cycle using carbon as the working electrode, indicates that platinum phosphate blue is weakly electroactive on this carbon surface. The replacement of the shoulder by well defined reduction waves and dramatic increases of current in the next few successive cycles are indicative of the formation of a modified electrode on which the phosphate blue is easily reducible. Such an increase in current in subsequent cycles is a characteristic of an electropolymerization process [13,14]. This modified electrode functions in completely the same way as a platinum metal electrode as indicated by several independent chemical and electrochemical experiments described below. First, subsequent cycles revealed two

well defined quasi-reversible redox couples as were observed on a pure platinum working electrode. After a few cycles, a shiny platinum layer was quite transparent on the carbon surface. Secondly, an analysis of platinum content on the carbon electrode by ICP revealed a cycle dependent platinum coating. By using 2.0 mM phosphate blue solution and a carbon rod of 3.18 mm diameter, this coating varied from 0.03 to 0.25 mg cm^{-2} . Thirdly, the voltammograms of $\text{Fe}(\text{CN})_6^{2-/3-}$ redox couples exhibit identical features, both in peak positions and magnitude of current, when the equal electrode surface areas of a platinum metal electrode and platinum-coated carbon electrode were utilized.

The mechanism of electrodeposition on the carbon surface deserves some comment. First, the remarkable increase in current at and near the reduction potentials of the blue in the second cycle implies that a catalytic nucleation process must be involved. This is due the fact that uncatalyzed deposition of platinum would be accompanied by an equal or less gradual increase in current density compared to the first cycle. Since the platinum phosphate blue is an oligomeric species, it is likely that further polymerization of the oligomers by adsorption on the carbon surface might have led to this very efficient electrodeposition process. Furthermore, the activation energy barrier for such polymerization was perhaps overcome by the adsorption process and the potential applied during the voltammetry experiments.

Further evidence for the catalytic electrodeposition process can also be found by comparing the amount of platinum deposition onto the carbon surface by reduction of PtCl_4^{2-} with that obtained from the platinum blue. By using identical concentrations of the platinum complexes, a much reduced coating of platinum on carbon surfaces was observed from the chloro-complex even when a more negative cut-off potential (-1.2 V versus Ag/AgCl) was employed. Also, the electrodeposition from the tetrachloro-complex appears to be gradual and linearly proportional to the number of scans.

The second interesting feature of the limiting current after a few cycles of voltammetry points to a unique characteristic of the electrode, e.g., monolayer formation. Once the carbon surface is covered with a monolayer, further deposition did not increase the effective surface area of the electrode and therefore no significant increase in current density was observed. Furthermore, after 15–20 cycles no significant changes in the platinum deposition were observed. This is due to the fact that pure platinum metal electrode revealed only redox waves and no deposition of platinum on to platinum surface was observed, as the carbon surface converted to a platinum surface, the completely coated electrode functioned just as the pure platinum surface does.

The current method of electrodeposition needs to be compared with other electrochemical methods. In an excellent article, Litster and McLean [1] have recently reviewed the performance of PEM fuel cell electrodes including those prepared by electrochemical depositions. Reddy et al. [16,17] have described electrodeposition of platinum by utilizing electrodeposition methodology in chloroplatinic acid baths. This patented technology exhibited comparable performance of the fuel cell even with 10-fold reduced platinum loading. Verbrugge [15]

has also utilized electrodeposition methodology in loading platinum; his methodology differed from Reddy's in its use of sulfuric acid, starting platinum substrate, and the application of a membrane (not nafion). In this method, currents of magnitude of a couple of amps were used in a 10 mM $\text{Pt}(\text{NH}_3)_4^{2+}$ solution. This author [15] commented that the voltage during this high pulse current application reached several volts. Certainly, this method requires ultrapure platinum solutions since almost all metals can be reduced on the surfaces due to the large change in voltage during the pulse current applications. As the concentrations of platinum decrease due to the progression of the coating process, larger potential change is required to maintain the constant pulse current. Other researchers have reduced platinum compounds by first adsorbing platinum cations on nafion membranes or carbon surfaces followed by electrochemical reduction by applying appropriate voltage [18–20]. Our method seems to be simple because the catalytic process accelerates the deposition of platinum with a relatively low cut-off voltage. Furthermore, since the catalytic activity of platinum depends on the structures and particle sizes [20,21], our method may afford different structures with variable particle size than those obtained by the pulse current method. The reason for this is that in the pulse current technology, platinum is forced to deposit on the carbon surface by applying a large electromotive force and therefore there is no control over the surface structure. In our method, natural crystal growth may be accomplished due to catalytic nature of the growth process. Also, the deposition seems to be uniform and can be controlled at any level until saturation. Finally, the active surface area obtained from this method with ultra-low platinum coating is much larger than other electrodes either commercially available or reported in the literature [22]. This technology is currently being used in our laboratory to prepare membrane electrode assembly for both membrane exchange and phosphoric acid fuel cell. The structure and adsorption processes of the platinum substrate, platinum phosphate blue, might also be helpful in creating a structural lattice that may be responsible for the higher active surface area. It is interesting to note that Bouwman et al. [23] recently reported that the electrocatalytic activity of oxygen reduction by platinum was enhanced in the presence of dispersed iron phosphate. It remains to be seen whether such enhancement was aided by the phosphate ligand or by the different oxidation states of platinum center.

Acknowledgements

The initial work of this project was carried out at Kent State University. Funding of this research by Department of Transportation (ABB) and Kent State University (RNB) is gratefully acknowledged. We also thank to Dr. Y. Ito and B.D. Armstrong for taking electron microscopy images, and Mr. R. Balan for assisting in the figure preparation.

References

- [1] S. Litster, G. McLean, J. Power Sources 130 (2004) 61.
- [2] M.K. Williams, H.R. Kunz, J.M. Fenton, J. Power Sources 135 (2004) 122.
- [3] D.J. Myers, J.F. Krebs, D.J. Carter, R. Kumar, M. Krumpelt, Am. Chem. Soc., Preprint of Symposia, Division of Fuel Chemistry, 47, (2002) 671.
- [4] R.N. Bose, R.E. Viola, R.D. Cornelius, J. Am. Chem. Soc. 106 (1984) 3336.
- [5] R.N. Bose, R.D. Cornelius, R.E. Viola, Inorg. Chem. 23 (1984) 1181.
- [6] R.N. Bose, R.D. Cornelius, R.E. Viola, Inorg. Chem. 24 (1985) 3989.
- [7] T.G. Appleton, R.D. Berry, J.R. Hall, Inorg. Chim. Acta 64 (1982) L229.
- [8] P.K. Mascharak, I.D. Williams, S.J. Lippard, J. Am. Chem. Soc. 106 (1984) 6428.
- [9] R.N. Bose, M. Sarkar, Platinated Carbon Electrode, U.S. Provisional Patent Application No. 60/437,391.
- [10] R.N. Bose, A. Bose, Metal Coated Carbon Surfaces for Use in Fuel Cells, Pending, Application No. PCT/US2003/041521.
- [11] S.C. Dhara, Ind. J. Chem. 8 (1970) 193.
- [12] B. Fonkeng, R.N. Bose, G. Barr-David, R.P. Farrell, R.J. Judd, P.A. Lay, D.F. Sangster, J. Am. Chem. Soc. 118 (1996) 7139–7144.
- [13] F. Guarr, F.C. Anson, J. Phys. Chem. 91 (1987) 4037–4043.
- [14] P. Denisevich, K. Willman, R.W. Murray, J. Am. Chem. Soc. 103 (1981) 4727.
- [15] M.W. Verbrugge, J. Electrochem. Soc. 141 (1994) 46–53.
- [16] N.R.K.V. Reddy, E.B. Anderson, E.J. Taylor, U.S. Patent No. 5,084,144 (1992).
- [17] E.J. Taylor, E.B. Anderson, N.R.K.V. Reddy, J. Electrochem. Soc. 139 (1992) 45.
- [18] K.H. Choi, H.S. Kim, T.H. Lee, J. Power Sources 75 (1998) 230.
- [19] S.D. Thompson, L.R. Jordon, M. Forsyth, Electrochim. Acta 46 (2002) 1657–1663.
- [20] F. Gloaguen, J.-M. Leger, C. Lamy, J. Appl. Electrochem. 27 (1997) 1052.
- [21] M. Arnez, J.J. Schmidt, K. Wandelt, P.N. Boss, N.M. Markovic, J. Phys. Chem. B 107 (2003) 9813–9819.
- [22] A. Bose, X. Wang, D. Thati, R. Balan, R. Shaik, unpublished results, Northern Illinois University.
- [23] P.J. Bouwman, W. Dmowski, J. Stanley, G.B. Cotton, K.E. Swider-Lyons, J. Electroanal. Soc. 151 (2004) A1989–A1998.