

Synthesis of Carbon Aerogel Supported Co-based PEMFC Catalysts Using Supercritical Ammonia

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ABSTRACT

Chemical treatment of four different Co-containing macrocycles impregnated into the carbon aerogel (CA) structure was performed in supercritical ammonia (scNH₃). The XPS and XRD results indicated chemical changes of the CA support and Co-containing macrocycles. XPS spectra of unmodified CA demonstrated a presence of two oxygen O(1s) groups and five carbon C(1s) groups in deconvoluted spectra. Chemical acidic (HNO₃) or basic (NH₄OH) treatment revealed nitrogen N(1s) which had a 1.5eV higher binding energy than nitrogen introduced supercritically in the temperature range of 140-200°C and 2000psi.

Among four studied Co-containing macrocycles only (1R,2R)-(-)-1,2-Cyclohexanediamino-N,N'-bis(3,5-di-t-butylsalicylidene)cobalt(II) showed solubility in scNH₃. However, chemical changes of the macrocycle structure after scNH₃ treatment were revealed for all four compounds. Sintering of CA impregnated with Co-methoxy-tetra-phenylporfirin (Co-MTOP) at 700 and 900°C in N₂ demonstrated a presence of Co-metal nano particles with 20nm in diameter. HRTEM and diffraction patterns of the Co nano-particles showed a β-Co FCC structure with {111} <110> micro-twins. The electrochemical properties of the Co-based CA supported catalysts sintered at 900°C and tested in sulfuric and perchloric acid solutions were evaluated by rotating disc electrode (RDE) and demonstrated catalytic activity in hydrogen oxidation and oxygen reduction reactions.

INTRODUCTION

The challenge of decreasing the cost of PEMFC is directly related to the cost of the PGM cathode where the ORR takes place. In PEMFC the reduction of oxygen goes through multiple steps and participates in four electron transfer electrochemical reaction with the formation of oxygen ions. Due to the slow ORR kinetics, the cathode catalyst layer needs sufficient amount of expensive Pt Group Metal (PGM). To reduce the cost of the catalyst a few different approaches are currently active and among them the non-noble metal catalyst synthesis. Considering the non-noble metal either in the form of a stabilized cation or in the form of a metal, major attention should be paid to the carbon support structure and morphology which is known to improve the catalytic activity of the metal-based catalysts [1, 2, 3].

Carbon support [4] is known to perform an important role in overall catalytic behavior by changing the Galvani potential of the system, increasing the electronic density and the Fermi level of the deposited metal. The morphology of the carbon support influences the mass transport

of O₂/air, water management, and polymer electrolyte impregnation. However, carbon tends to corrode in humidified fuel cell environment. To improve the corrosion resistance, graphitization of carbon support was performed that also increased the strength of π -sites (sp²-hybridized carbon) helping to anchor PGM nanoparticles and impede metal sintering [5]. Heat-treatment of carbon up to 1400°C in presence of B doped transition metals, e.g. Co, B, Ni, Ti or Fe can also improve carbon graphitization [6].

Carbon functionalization with nitrogen [7, 8] that can be achieved by chemical treatment of carbon with liquid ammonia is another way to impede the CA corrosion. It was reported [9] that sub-monolayers of nitrogen improve durability because of the enhanced π -bonding and high Lewis basicity due to the strong electron donor behavior of nitrogen. In this case both N atoms and π -bonds contribute to the basicity of carbon thus increasing metal-to-carbon interaction [10,11] and decreasing metal sintering. In this case the presence of nitrogen suppress the dissolution and nano-particles migration due to the intermediate strong C-N and N-Me bonds [12].

In addition to carbon support the second important component of the PEMFC cathode catalyst layer is the catalyst itself. Regarding non-noble metal catalysts, the approach using metal nitrides and transition metal macrocycles either in non-sintered form or after heat-treatment is the most active. Catalytic properties of transition metal nitrides, such as Co, Fe, and Re exhibiting catalytic activity and the noble-metal behavior were extensively studied [13]. Many of these studies were performed using ammonothermal synthesis [14] either in the stream of NH₃ at elevated temperatures or using supercritical ammonia as reducing agent [15]. The properties of transition metal nitrides were explained by the vacancies in the metal lattice and in the surface layer [16]. However, they are easily oxidized in presence of oxygen and cannot be used as PEMFC ORR catalysts.

In comparison to transition metal nitrides, central metal ion phthalocyanines and porphyrins demonstrate less catalytic activity, but due to the extensive π -system are stable and can be used as ORR catalysts with the highest catalytic activity reported for Co-containing macrocycles [17]. It is assumed that catalytic activity for transition metal macrocycles is explained by the presence of unpaired electrons and unfilled d orbitals which are available to form bonds with corresponding support in axial positions.

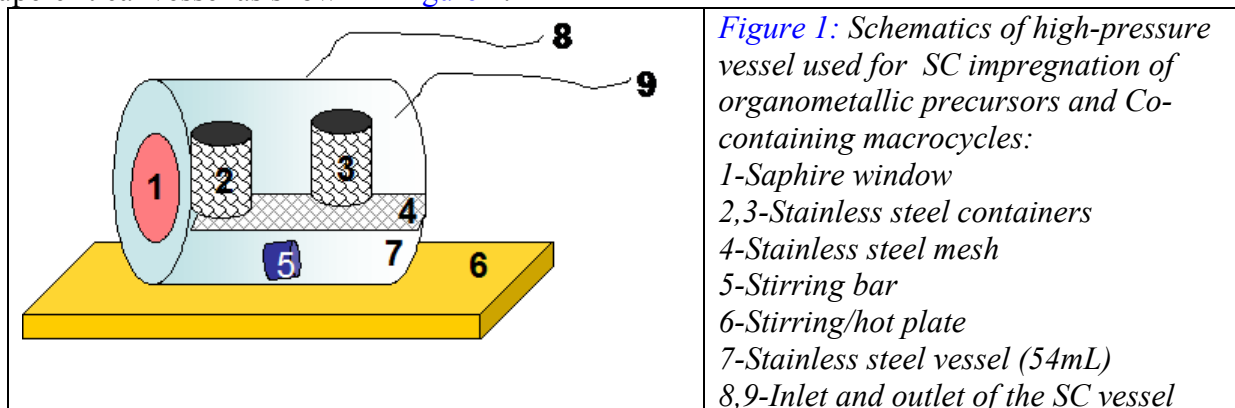
The goal of this work was to perform a preliminary evaluation of the chemical changes in the carbon aerogel structure after exposing it to scNH₃ in comparison to the chemical acid or base treatment reported earlier [18]. As the second part of this work the scNH₃ modification of four different macrocycles was performed and analyzed from the point of crystal structure and stability in scNH₃ at elevated temperatures (140-200°C) and pressures (2000psi). After heat treatment CAs impregnated with Co-macrocycles demonstrated catalytic activity in hydrogen oxidation and oxygen reduction reactions.

EXPERIMENTAL PROCEDURES

Polyimide carbon aerogels (CAs) from Aspen Aerogels either grinded or in the form of monoliths were used for synthesis of the Co-based PEMFC catalysts. Carbon aerogel surface modification was performed in three different ways, such as by chemical treatment with either nitric acid or liquid ammonia at room temperature and ambient pressure or by chemical treatment in supercritical ammonia at elevated temperatures starting from 200°C and pressures exceeding 2000 psi.

Different Co-containing macrocycles (Table 1) were chosen regarding Co- coordination, polarity and their potential solubility in scNH₃. Impregnation of CAs with Co-containing

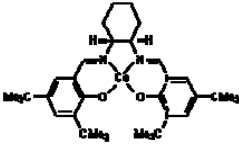
macrocycle from solution was performed by mixing CAs in the form of a powder or immersing CA monoliths into 0.25M solutions prepared by dissolving Co-macrocycles in THF. After impregnation the CAs were dried at 80°C in air and exposed to $scNH_3$. In another approach the samples of CA and Co-macrocycle were placed in a separate stainless steel containers inside the supercritical vessel as shown in [Figure 1](#).



The surface morphology and chemical composition of the synthesized samples was analyzed using HRTEM JEOL 2010 FastEM equipped with EDAX Phoenix system. The crystal structure of the Co-containing macrocycles before and after chemical treatment was evaluated by X-ray diffraction (XRD) using a Bruker D5005 X-Ray Diffractometer, with Cu $K\alpha$ radiation ($\lambda=1.54\text{\AA}$). The surface analysis was performed by using VG X-ray Photoelectron Spectrometer that allow for spectra recording in the range of 1400-0eV. Deconvolution of the overlapping carbon and nitrogen peaks was performed using a mixed Gaussian-Lorentian fit program.

Table 1: Co-containing macrocycles used in this work:

Name and abbreviation	Abbreviation	Wt.%Co	Chemical formula
Cobalt(II) phthalocyanine	Co-PC	10.3	
Cobalt(II) meso-tetraphenylporphine	Co-MTPP	8.9	
Cobalt(II) meso-tetramethoxyphenylporphine	Co-MTOP	7.4	

(1R,2R)-(-)-1,2-Cyclohexanediamino-N,N'-bis(3,5-di- <i>t</i> -butylsalicylidene)cobalt(II)	Co-CCBC	9.8	
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RESULTS AND DISCUSSION

Chemical Modification of Carbon Aerogel Surface

Ammonia treatment is known to remove the acidic functional groups introducing pyridinic basic groups on the carbon surface. On the contrary, acidic treatment allows increasing the number of negative groups on the carbon surface [19].

The XPS spectra for untreated and chemically modified aerogels using different types of modification, specifically NH_3 , HNO_3 and scNH_4 treatments are presented in Figures 2 and 3. It can be seen that the original CA aerogel does not have any nitrogen in its structure and the corresponding XPS spectra of CA show only broad carbon and oxygen peaks (Figure 2). The oxygen peak at 532.16eV represents C-OH or C=O groups and at 536.67eV - chemisorbed oxygen/carboxylic groups and /or water [20, 21]. The carbon peaks which were observed in the binding energy range from 280 to 292eV can be attributed to several carbon-based surface functional groups with different binding energies. The deconvoluted C(1s) peak indicates a presence of different species that were assigned to C-C or carbon bonded to hydrogen, at 284.8eV, C-O-R or C-NR₂ at 286.6eV, -C=O at 288.5eV, O-C=O at 290.2eV and carboxyl, CO₃²⁻ or ester group at 292.5eV. Thus it was concluded that at least four functional groups are present on the surface of carbon aerogel in addition to C-C bonds.

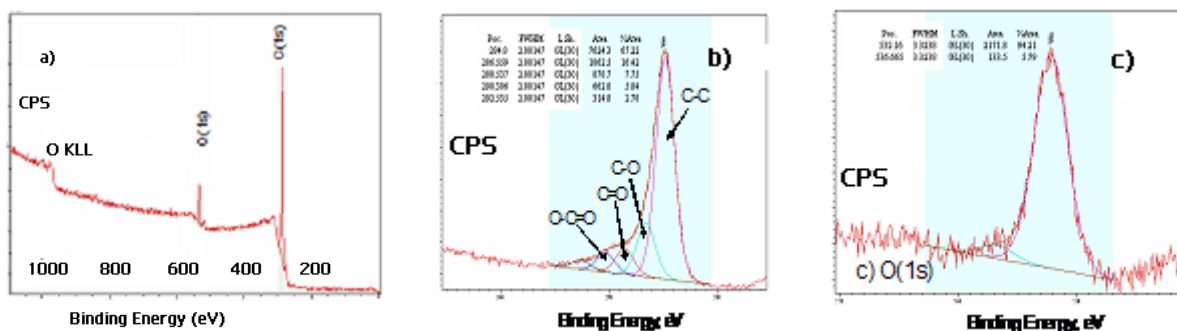


Figure 2: High resolution XPS spectra of untreated CA: (a) wide spectra; b) deconvoluted C(1s) peaks and (c) O(1s) peaks.

Chemical modification with HNO_3 and ammonia solutions introduced nitrogen atoms into the CA structure. The electronic state of nitrogen (N 1s) in the case of HNO_3 and ammonia was similar and revealed only one binding energy at 405.57eV for NH_4OH and 405.52eV for HNO_3 treated CA that can be attributed to the formation of nitro-type complexes rather than nitrate ions that usually appear at higher energies ca. 408eV [22]. However, the bonding energy of nitrogen

that was introduced supercritically was found at 404.00eV and in comparison to HNO₃ and NH₄OH was shifted towards lower energies by 1.5eV that could indicate formation of pyridine-N-oxide.

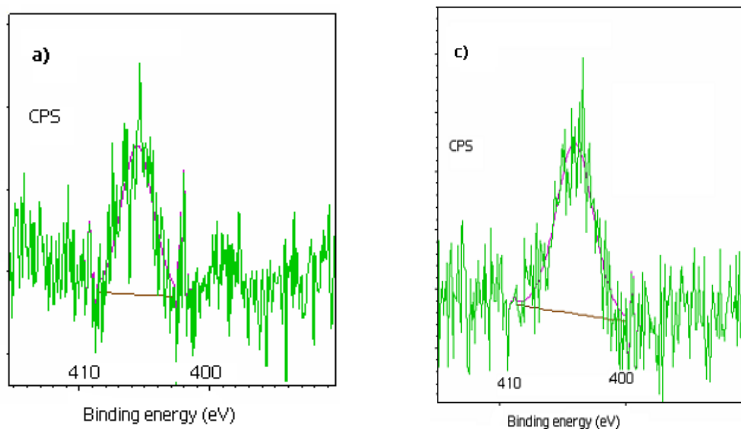
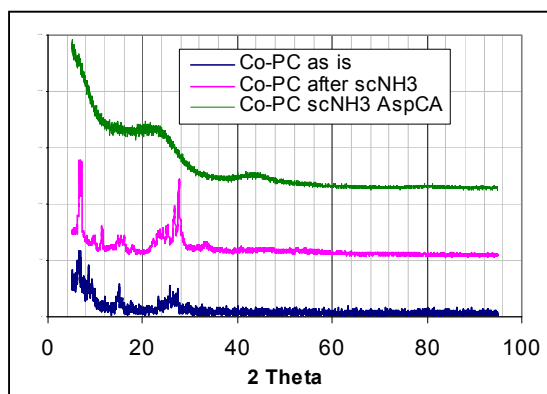


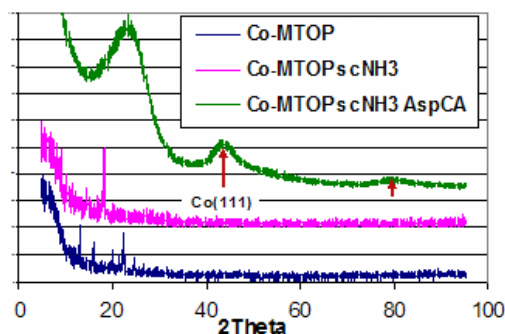
Figure 3: High resolution N1s spectra of CA treated with a) HNO₃ (405.52eV); b) NH₄OH (405.57eV)-not shown, and c) with scNH₃ (404.00eV).

Macrocyclic compounds treated with scNH₃

Phthalocyanines belong to chemically and thermally stable organic semiconductors. However, comparison of XRD spectra before (blue) and after (pink) scNH₃ treatment indicate significant changes in the structure of Co-macrocycles. It can be seen that XRD spectrum for Co-PC that is considered to be the most stable among the chosen macrocycles (Table 1) is significantly changed after scNH₃ treatment (Figure 4a). Some of the original large peaks in the 27<2θ(°)<29 region that match well with the previously reported α-crystallite values [23] disappeared, some of them changed their relative intensity or were shifted indicating the change in crystal structure. In the case of Co-MTOP and Co-MTTP the XRD spectra after scNH₃ did not match the initial spectra (Figure 4b,c) and Co-CCBC was not found in the SS mesh container after exposing it to scNH₃ that indicated either its solubility or decomposition in scNH₃.



a)



b)

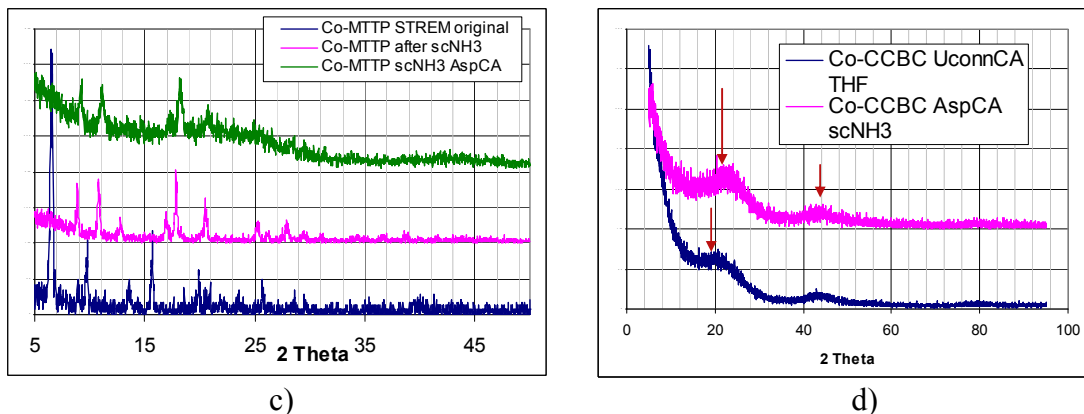


Figure 4: XRD spectra of Co-containing macrocycles before scNH_3 treatment and after 12hrs scNH_3 treatment at 140°C and 2000psi.

The XRD spectra of CA impregnated with Co-macrocycle and exposed to scNH_3 showed either chemically modified macrocycle in the case of Co-MTTP (Figure 4c) or Co/CoN deposited on the surface of carbon aerogel in the case of three other macrocycles (Figure 4a,b,d).

After thermal treatment at 900°C in N_2 flow of CAs impregnated with Co-macrocycle in the form of THF solution, XRD spectra show a characteristic diffraction peak at $2\Theta=44.3^\circ$ which is assigned to the (111) plane of $\beta\text{-Co}$ (Figure 5). Two other diffraction peaks at 51.6 and 76.0° of $\beta\text{-Co}$ were also observed which is in correlation with the earlier work of Faubert et al., who detected Fe and Co phases in heat-treated Co-tetraphenylporphyrins adsorbed on carbon black. In the sintered sample Co is present in FCC cubic ($\text{Fm}3\text{m}$) configuration (PDF#15-0806). Carbon in aerogel support indicates rhombohedral configuration; however the peaks of carbon in comparison to PDF# 26-1079 and #41-1481 are shifted in the direction of angle decrease such as $2\Theta=42.808$ vs. 43.452 and $2\Theta=25.593$ vs. 26.605 indicating complicated nature of carbon which is probably involved in additional interaction with adjacent atoms. TEM images (Figure 6) show that cobalt particles of about 20nm size with the distinct Moiré fringes due to $\{111\}\langle 110\rangle$ micro-twins are evenly distributed on the surface of carbon aerogel that was also observed earlier by Baumann [24].

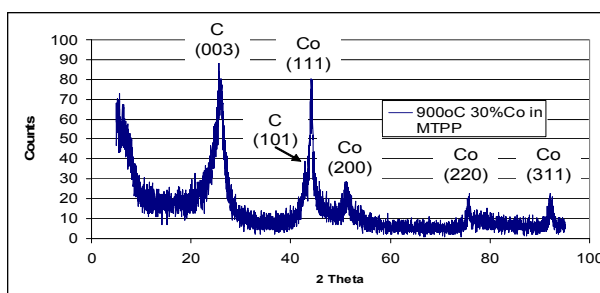


Figure 5: XRD spectrum of Co-MTTP-aerogel catalyst sintered at 900°C in N_2 for 3hrs.

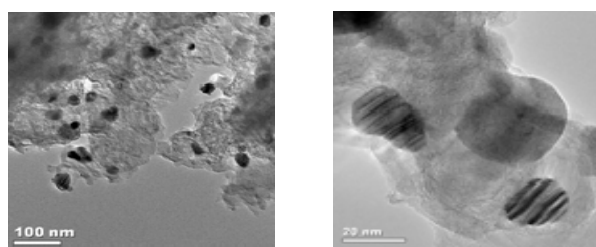


Figure 6: HRTEM images of the carbon aerogel impregnated with Co-MTOP and sintered at 900°C in N_2 flow.

HRTEM images and diffraction patterns taken along the $[110]$ direction (Figure 6) show that Co particles exhibit an f.c.c $\beta\text{-Co}$ structure.

The XPS Co2p spectra of untreated and scNH_3 treated Co-MTTP are presented in Figure 7. The relative intensities of spin-orbit duplet peaks for untreated Co-MTTP are given by the ratio of the duplet $\text{Co}(2p_{3/2})$: $\text{Co}(2p_{1/2}) = 2:1$ with a splitting energy of 15.35eV. For the scNH_3 treated sample, in addition to the existing Co2p peaks a duplet at 788.587eV; 804.578eV was detected with the splitting energy of 15.99eV exceeding the theoretical number by 0.94eV.

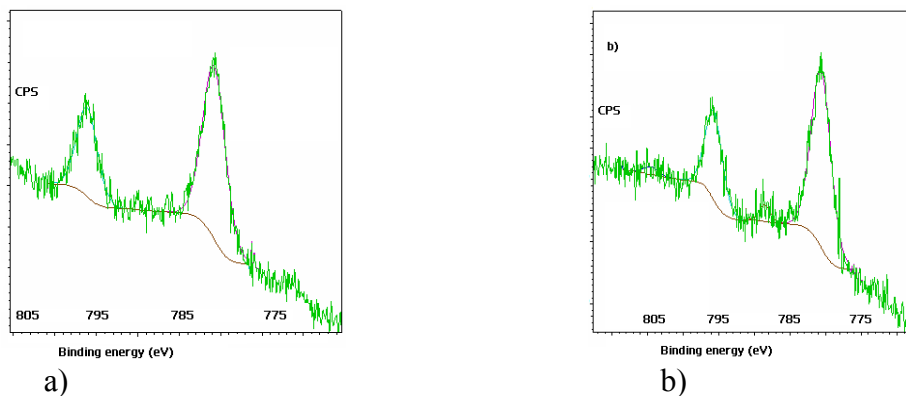
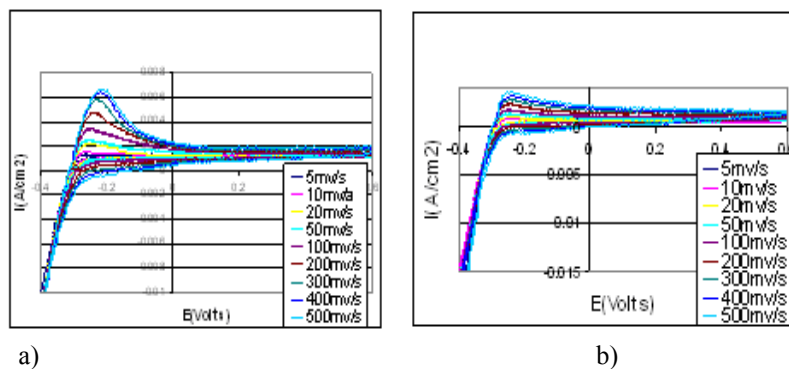


Figure 7: High-resolution XPS Co 2p spectra of Co-MTTP:
a) Untreated sample: $\text{Co}2p_{3/2}$ (780.773eV) and $\text{Co}2p_{1/2}$ (796.119eV);
b) ScNH_3 treated: $\text{Co}2p_{3/2}$ (780.654eV); $\text{Co}2p_{1/2}$ (795.699eV); 788.587eV; 804.578eV.

The results of electrochemical testing of sintered at 900°C and unsintered Co-MTOP samples in O_2 -free acidic solution are presented in Figure 8. As expected, in the case of sintered samples (Figures 8a,b) the maximum current density is gradually increasing with the scan rate reaching 0.003 mA/cm^2 in H_2SO_4 and twice as much (0.006 mA/cm^2) in HClO_4 confirming the properties of HClO_4 as a low adsorbing electrolyte. Less expected results were obtained for non-sintered Co-MTOP/aerogel samples (Figure 8c,d) that could be related to different properties of SO_4^{2-} and ClO_4^- anions regarding their interaction with Co-MTOP macrocycle.

The electrochemical testing in presence of O_2 (Figure 9) demonstrated catalytic activity in ORR for both sintered and unsintered samples, however further work should be done for understanding the difference in catalytic activity mechanisms.



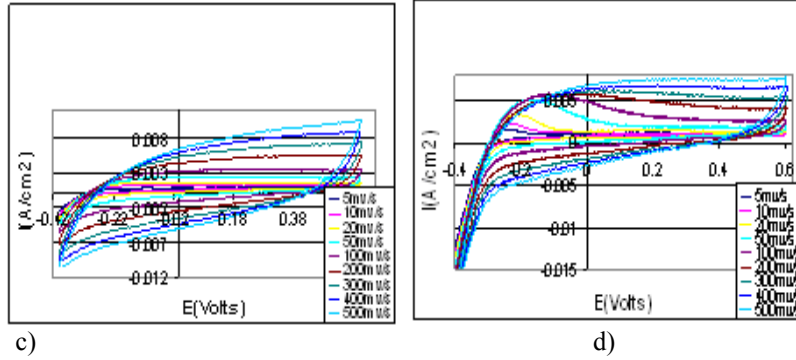


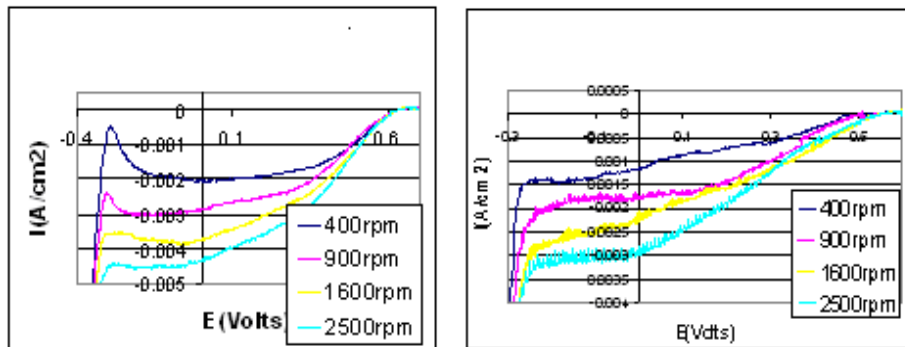
Figure 8: Cyclic voltammetry in 0.5M HClO₄ (a) and 0.5M H₂SO₄ (b) solutions for Co-MTTP samples sintered at 900°C in comparison to the unsintered samples in 0.5M HClO₄ (c) and 0.5M H₂SO₄ (d)

CONCLUSIONS

In this study the surface of carbon aerogels was chemically modified and tested to evaluate its ability to form charged active groups, such as carboxyl, quinone, hydroxyl, carbonyl and others induced on the carbon surface using supercritical ammonia or traditional basic (NH₄OH) or acid (HNO₃) treatment. This approach will be used further for nitrogen enrichment of the carbon surface that will allow for deposition and chemical stabilization of the transition metal porphyrin-like macro-cycles responsible for ORR catalytic activity.

One-step chemical modification of carbon aerogels as efficient supports for fuel cell catalysts was performed. Chemical treatment with NH₄OH or HNO₃ solutions introduced nitrogen into the structure of aerogel that will be used for our future work.

Co-MTOP incorporated into the structure of untreated aerogel samples showed promising results in terms of catalytic activity. Cyclic voltammetry indicated catalytic activity of the samples and allowed to calculate the electrochemical surface areas involved in the HOR. In ORR conditions both sintered and unsintered samples demonstrated catalytic activity, however these results should be evaluated in terms of mass and specific activity. Linearity of Koutecky-Levich plots and Tafel slope values indicated thermodynamic reversibility of the ORR that takes place on the surface of both sintered and un-sintered catalysts. Future work will address the differences in the mechanism of the catalytic activity of sintered and un-sintered carbon aerogel based Co-MTTP samples and samples treated with scNH₃.



a)

b)

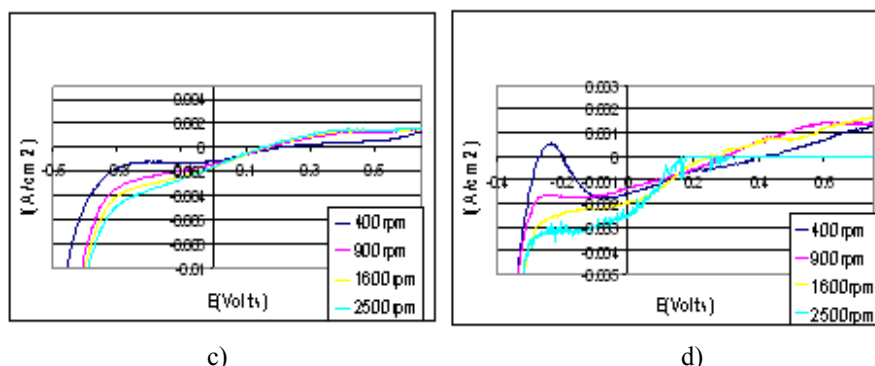


Figure 9: Potentiodynamic tests in 0.5M HClO₄ (a) and 0.5MH₂SO₄ (b) solutions for Co-MTOP sintered at 900°C and un-sintered samples in 0.5MHClO₄ (c) and 0.5MH₂SO₄ (d).

ACKNOWLEDGEMENTS

Financial support from the National Science Foundation (Project # 0736111) and UTC Power is gratefully acknowledged.

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