

Investigation of Activity of Sputtered Transition-Metal (TM)–C–N (TM = V, Cr, Mn, Co, Ni) Catalysts for Oxygen Reduction Reaction

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Variations with heat-treatment temperature of the structure and the electrocatalytic activity of sputtered transition-metal (TM)– C–N (TM = V, Cr, Mn, Co, and Ni) films for the oxygen reduction reaction (ORR) in acid and alkaline electrolytes were studied. The films prepared were all originally amorphous. At a critical heat-treatment temperature (T_c , different for each composition) substantial nitrogen release occurred and the films transformed to a heterogeneous N-containing carbon structure with either Cr₃C₂, Co, Ni, V₈C₇, or Mn₇C₃, depending on the TM used. In acid electrolyte, heat-treated $Cr_xC_{1-x-y}N_y$, films showed little or no activity for ORR in acid electrolyte for all temperatures studied. However, all of the heat-treated $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) films showed oxygen reduction activity in alkaline electrolyte even when heated to temperatures below T_c . Because all the $TM_xC_{1-x-y}N_y$, films heated above T_c contained N-containing carbon, the activity of heat-treated sputtered $C_{1-x}N_x$ and C films, as well as graphite powder, were studied for comparison. Their activities were much lower in acid electrolyte than those of the $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$ films heat-treated at the same temperatures. $C_{1-x}N_x$ null $N_xC_{1-x-y}N_y$ films. The choice of TM and the heat-treatment temperature played important roles in determining the activity of the sputtered $TM_xC_{1-x-y}N_y$ films. The choice of TM and the heat-treatement temperature should go passivation against corrosion. (© 2007 The Electrochemical Society. [DOI: 10.1149/1.2803519] All rights reserved.

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The increasing need for polymer electrolyte membrane fuel cells (PEMFCs) as power sources for residential and transportation applications has intensified research on the oxygen reduction catalysts used in these cells. So far, Pt and Pt–alloy catalysts are the best electrocatalysts for the oxygen reduction reaction (ORR) due to their ability to reduce oxygen efficiently to water in a four-electron reduction. However, Pt is expensive and of limited availability. The replacement of Pt by non-noble metal catalysts could lead to significant cost reduction in PEMFCs and is desirable, provided that similar area-specific catalytic activity can be obtained.^{1,2}

Comprehensive reviews on the development of non-noble catalysts for PEMFCs have been published recently.²⁻⁴ Heat-treating carbon-supported transition-metal (TM) and nitrogen-containing complexes⁵⁻¹³ or TM salts¹⁴⁻¹⁶ in inert gas, ammonia, or acetonitrile vapor has led to promising ORR electrocatalysts. Dodelet and coworkers proposed that FeN₂/C and FeN₄/C or CoN₄/C active sites exist in Fe-based¹⁷ and Co-based catalysts,¹⁸ based on time-of-flight secondary ion mass spectrometry (TOF SIMS) results. Recently, Ozkan et al.¹⁹⁻²¹ and Stevenson et al.²² proposed that a metal site is not needed for ORR and that the active sites are located on the edge planes of nitrogen-containing carbon. Popov et al.²³ proposed that active sites with pyridinic nitrogen are responsible for the catalytic ORR activity. Although the nature of the active sites for ORR is not yet clear, the choice of TM, the nitrogen content, the carbon type, and the preparation method are all believed to influence the formation of the active sites and thus the activity of the catalysts.

The influence of the central metal ion of N₄-phthalocyanines on ORR activity was reported to vary as Fe > Co > Ni > Cu \approx Mn.²⁴ Chu and Jiang investigated the ORR catalytic activity of a series of heat-treated TM (V, Mn, Fe, Co, Ni, Cu, and Zn) tetraphenylporphyrin (TPP) and binary TM TPP (V/Fe, Co/Fe, Ni/Fe, and Cu/Fe). All of these heat-treated TM TPP showed high activity except for metal-free TPP and ZnTPP. Heat-treated FeTPP/CoTPP was shown to be the best ORR catalyst.²⁵ Dodelet et al. studied the ORR activity of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Mo-based catalysts prepared by adsorbing various TM hydroxides or acetates on carbon blacks or perylenetetracarboxylic diahydride (PTCDA) followed by

pyrolysis in acetonitrile vapor or ammonia at elevated temperature. The activity of Cr, Mn, Fe, and Co-based catalysts decreased according to the following sequence: Fe > Co > Cr > Mn. The other metal-based materials showed little activity.^{26,27} Recently, carbon-supported Ru-chelate and Ru-based bimetallic electrocatalysts that produced only 2–3% H₂O₂ were reported by Popov and co-workers, which suggests that the central metal plays an important role in the catalytic activity.^{28,29}

Active Fe-C-N and Co-C-N thin-film electrocatalysts prepared by combinatorial magnetron sputter deposition method in our lab showed excellent ORR activity in acid electrolyte after heat-treatment in inert gas.³⁰⁻³³ In our previous work,³⁰⁻³³ the effect of heat-treatment temperature on the composition, structure, and ORR catalytic activity of sputtered Fe-C-N (acid electrolyte) and Co-C-N (acid and alkaline electrolyte) was studied in detail. In this paper, the effect of TM choice and heat-treatment temperature on the catalytic activity in acid and alkaline electrolytes and corrosion stability of sputtered TM-C-N (TM = V, Cr, Mn, Co, and Ni) films are reported. Results for TM = Fe are not included here because the sputtered Fe-C-N and Co-C-N catalysts showed similar trends in the variation of the ORR activity with the metal (Fe or Co) content and the heat-treatment temperature, which was reported in a previous paper.³¹ Comparisons to the activities of sputtered Co, $C_{1-x}N_x$, and C films, as well as powdered graphite, are made as well in this paper.

Experimental

Deposition of thin-film samples.— The V, Cr, Mn, and Co sputtering targets (2.00 in. diameter, 0.250 in. thick, and 99.95% pure) were obtained from Williams Advanced Materials (Buffalo, NY). The Ni target (2.00 in. diameter, 0.039 in. thick, and 99.99% pure) was obtained from Advent Research Materials (Eyansham, Oxford, U.K.). The C sputtering target (2.00 in. diameter, 0.250 in. thick, and 99.999% pure) was obtained from Kurt J. Lesker Co. (Clairton, PA). All targets, with the exception of Ni, were mounted on 0.125 in. thick copper backing plates using SilverTech PT-1 silver epoxy from Williams Advanced Materials. The Ni target was held in place on the copper backing plate by the magnetic field from the magnetron itself. V, Cr, Mn, Co, Ni, and C were sputtered using MDX-1K DC (Advanced Energy) power supplies with powers of 41, 33, 15, 15, and 150 W, respectively. Specially designed

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masks were positioned in front of each target to produce the desired composition variations, while the substrate table was rotated. More details about the production of binary and pseudo-binary composition spreads using our equipment can be found elsewhere.³⁴ For the constant composition samples, "constant" masks³⁴ were used in front of both C and TM targets. For the composition spread libraries produced, a constant mask was used for the carbon target and a "linear out" mask was used for the TM target.³⁴

Nitrogen was incorporated into the libraries by sputtering in an Ar/N₂ gas mixture.³⁰⁻³³ Gas flows were independently controlled using mass-flow controllers (MKS Instruments, Inc.). Ultrahighpurity Ar (99.999%) and N₂ (99.999%) were supplied at constant flow rates during the sputtering. One composition spread and one constant composition sputtering run was completed for each TM–C–N system. The composition-spread run for each TM–C–N system was sputtered under 7.5 sccm Ar and 2.0 sccm N₂, which corresponds to a total pressure of 0.277 Pa (2.10 mTorr) with N₂/Ar = 20:80. The constant composition run for each TM–C–N system was sputtered under 4.5 sccm Ar and 3.0 sccm N₂, which corresponds to a total pressure of 0.224 Pa (1.70 mTorr) with N₂/Ar = 40:60.

The constant composition $C_{1-x}N_x$ film was sputtered under 4.5 sccm Ar and 3.0 sccm N₂. The constant composition C film was sputtered under 7.2 sccm Ar, which corresponds to a total pressure of 0.224 Pa (1.70 mTorr). For the purpose of comparison of activities in alkaline solution, a constant composition Co film was also sputtered under 6.6 sccm Ar, which corresponds to a total pressure of 0.216 Pa (1.64 mTorr).

The composition-spread and constant composition samples for each TM–C–N system were deposited onto a number of 80 × 15 mm SiO₂-coated Si(100) wafer strips (500 nm thick layer of SiO₂) for heat-treatment, grazing incidence X-ray diffraction (XRD) measurements (constant composition sample only), electron microprobe analysis, and film thickness determination and a number of 5 mm diameter glassy carbon (GC) disks (Tokai Carbon Co.) for electrochemical measurements using the rotating ring-disk electrode (RRDE) technique. Similar sputtering-table layouts were used for the C_{1-x}N_x, C, and Co films. The TM–C–N composition spread was also deposited onto 80 × 10 mm quartz substrates for heattreatment and corrosion testing. More details about the various substrates mounted on the substrate table as well as a projection of the targets and their associated masks on the substrate table can be found elsewhere.³²

The $TM_xC_{1-x-y}N_y$, $C_{1-x}N_x$, and C films deposited on the SiO₂-coated Si(100) wafer strips, GC disks, and quartz substrates were heat-treated at different temperatures in Ar using a Modular Process Technology RTP-600S rapid thermal processor (RTP). The samples were heated at 5°C s⁻¹ in flowing Ar (2 L min⁻¹) and held at the target temperature for 5 min before cooling.

Composition of the sputtered samples.— The composition of the sputtered samples was measured using a JEOL JXA-8200 superprobe electron microprobe system equipped with one energy dispersive (EDS) spectrometer and five wavelength dispersive (WDS) spectrometers. The standards used were: (Si_3N_4) for N; V, Cr, and Ni metals for V, Cr, and Ni, respectively; MnO₂ for Mn; a Mn-Co alloy (Mn:Co = 30:70 by weight) for Co; and pyrolitic graphte for C. Overlap of the N(K α) and Co[L_{β}(2)] lines was carefully considered and accommodated. TM (V, Cr, Mn, Co, and Ni), N, and C atomic compositions were all determined by WDS detectors. An accelerating voltage of 3 kV was employed to eliminate the effect of the substrate on the measurement. The analysis spot size was 50 µm. The composition was measured every 2 mm along the 76 mm long composition-spread samples before and after various heat-treatments. The composition of the as-sputtered composition-spread and constant composition samples are reported in Table I.

Thickness of the sputtered samples.— The thickness of the composition-spread and constant composition samples sputtered on Si wafers was determined using a Dektak 8 Advanced Development Profilometer (Veeco Instruments Inc.). The film thickness was found to increase linearly with increasing TM content across the $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) films. The thicknesses of the composition-spread and constant composition samples are reported in Table I.

Grazing incidence XRD for the constant composition sample.— The crystallographic structure of the constant composition films after heat-treatment to various temperatures was determined by grazing incidence XRD using a Siemens D5000 diffractometer equipped with a grazing incidence attachment. Cu K α radiation was used at an incidence angle of 0.5° and with divergence slits set to 0.1°. Such conditions lead to an illuminated spot of 40 × 12 mm in the center of the 80 × 15 mm constant-composition specimen. A Soller slit box in front of the detector was used to ensure that the scattered X-rays from this large illuminated sample area that entered the detector all had the same scattering angle. Data were collected over a scattering angle range of 10–80° at 0.05° intervals. Total scan times varied from 8 to 12 h.

Electrochemical characterization.— The $\text{TM}_x C_{1-x-y} N_y$ (TM = V, Cr, Mn, Co, and Ni), $C_{1-x} N_x$, C, and Co films were sputtered directly on GC disks as described in the Deposition of thin-film samples section. The loading of $V_x C_{1-x-y} N_y$, $Cr_x C_{1-x-y} N_y$, $\text{Mn}_x C_{1-x-y} N_y$, $\text{Co}_x C_{1-x-y} N_y$, $\text{Ni}_x C_{1-x-y} N_y$, $C_1 C_1 N_x$, C, and Co films on the GC disks were 79, 75, 67, 56, 63, 50, 42, and 24 µg cm⁻², respectively. The electrochemical properties of a graphite powder sample (Fluka, 50870 graphite) were also measured for comparison. An ink of graphite was prepared by mixing 10 mg of powder, 95 µL of Nafion solution (5% wt from Aldrich), and 350 µL of ethanol, followed by ultrasonicating for 40 min. Seven µL of ink was pipetted onto a GC disk, resulting in a graphite powder loading of 780 µg cm⁻².

The electrocatalytic activity for the ORR of the samples on the GC disks was studied with the RRDE technique using a Pine Electrochemical system (AFMSRX rotator and AFCBP1 bipotentiostat). The RRDE electrode consisted of a catalyst film-coated GC disk (5 mm diameter) surrounded by a Pt ring (7.5 mm inside diameter and 8.5 mm outer diameter). The electrochemical measurements were made in a one-compartment cell. The electrolyte was either a 0.1 M HClO₄ solution or a 0.1 M KOH solution prepared from double-distilled HClO4 (GFS Chemicals, Inc.) or KOH (GFS Chemicals, Inc.) and 18 MΩ Barnstead NANOpure water. A Pt-wire counter electrode and Koslow Hg/Hg₂SO₄ reference electrode (used in 0.1 M HClO₄ solution) or Ag/AgCl reference electrode (Bioanalytical Systems, Inc., used in 0.1 M KOH solution) were used for the measurements. The potential of the Hg/Hg₂SO₄ and Ag/AgCl reference electrodes were calibrated vs the reversible hydrogen electrode (RHE). The potentials reported in this study all refer to that of the RHE potential.

The samples on the GC disks were first electrochemically cleaned by sweeping the potential between 0 and 1.0 V (vs RHE) at 50 mV s⁻¹ in an Ar-saturated 0.1 M HClO₄ solution or 0.1 M KOH solution until steady-state cyclic voltammograms (CVs) were obtained. For each catalyst tested, a CV was first collected in Arsaturated 0.1 M HClO₄ solution or 0.1 M KOH solution from 1.0 to 0.05 V at 5 mV $\ensuremath{\text{s}^{-1}}$ to determine the nonfaradaic current. The CVs during oxygen reduction in 0.1 M HClO_4 or 0.1 M KOH solution were performed between 1.0 and 0.05 V at 5 mV s^{-1} with the electrode stationary and with the electrode rotated at 900 rpm. O_2 gas was purged into the solution at a rate of 1 L min⁻¹. The faradaic current was determined by subtracting the CV in Ar-saturated 0.1 M HClO₄ or 0.1 M KOH solution from that obtained in O₂-saturated 0.1 M HClO₄ solution or 0.1 M KOH solution. The onset potential, at which the current for oxygen reduction is first observed,⁴ was determined by the point of intersection of two tangent lines, one

drawn parallel to the baseline (i.e., from 0.9 V to approximately 0.8 V) and the second parallel to the increasing current signal. For all the measurements, the ring potential was held at 1.2 V vs RHE in order to oxidize any $H_2O_2^{35}$ produced in acid solution and HO_2^{-36} produced in alkaline solution. The % H_2O_2 produced in acid solution (or % HO_2^- produced in alkaline solution) was calculated using the following equation^{11,35,37}

%
$$H_2O_2 = 100 \frac{2I_R/N}{I_D + (I_R/N)}$$
 [1]

where I_D is the faradaic current at the disk, I_R is the faradaic current at the ring, and N = 0.2 is the RRDE collection efficiency.

Corrosion testing.— Thin-film composition-spread samples of $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) on quartz strips heated at 700, 800, and 1000°C were immersed in 0.5 M H₂SO₄ (reagent, analytical grade) at 25°C for 1 week. Separate $Cr_xC_{1-x-y}N_y$ composition-spread films heated at 700, 800, and 1000°C were immersed in 0.5 M H₂SO₄ solution at 80°C for 1 week. After treatment, the samples were rinsed with NANOpure water and dried in air for further study. The composition as a function of position was measured and compared to the composition measured before acid treatment.

Results

Composition of the thin-film $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) libraries.— The N content vs TM content in the assputtered $TM_xC_{1-x-y}N_y$ films and those heat-treated subsequently at 700, 800, or 1000°C is shown in Fig. 1. For the as-sputtered $TM_xC_{1-x-y}N_y$ films, the atomic fraction of N varies smoothly from 0.186 to 0.406 for $V_xC_{1-x-y}N_y$, from 0.225 to 0.461 for $Cr_xC_{1-x-y}N_y$, from 0.254 to 0.445 for $Mn_xC_{1-x-y}N_y$, from 0.184 to 0.320 for $Co_xC_{1-x-y}N_y$, and from 0.189 to 0.362 for $Ni_xC_{1-x-y}N_y$. The variation of N content with heat-treatment temperature in these $TM_xC_{1-x-y}N_y$ films shows one striking feature: the N content decreases as heat-treatment temperature increases. However, the amount of nitrogen lost depends on both the choice of TM and the heat-treatment temperature.

 $V_xC_{1-x-y}N_y$, $Cr_xC_{1-x-y}N_y$, and $Mn_xC_{1-x-y}N_y$ do not lose much nitrogen when heated to 700°C. The N content decreases sharply at about 1.2% with respect to Co for $Co_xC_{1-x-y}N_y$ and at about 1.5% with respect to Ni for $Ni_xC_{1-x-y}N_y$ heated to 700°C. $V_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ libraries still retain significant nitrogen when heated to 800°C, with $Mn_xC_{1-x-y}N_y$ retaining more nitrogen than $V_xC_{1-x-y}N_y$. $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ lose nitrogen, in a "knee-shaped" transition when heated to 800°C, at about 3.8% with respect to Cr for the $Cr_xC_{1-x-y}N_y$ film, 0.7% with respect to Co for the $Co_xC_{1-x-y}N_y$ film, and about 1.5% with respect to Ni for the $Ni_xC_{1-x-y}N_y$ film. The thermal stability of the sputtered $TM_xC_{1-x-y}N_y$ libraries decreases in the order of $Co < (\approx)Ni$ < Cr < V < Mn.

Electrocatalytic activity of the sample that showed the highest activity in each $TM_xC_{1-x-y}N_y$ library after heat-treatment.— Fifteen GC disks, as three repeats for five different compositions, were included in each preparation of the composition-spread $TM_xC_{1-x-y}N_y$ libraries. One group of five disks was heated to 700°C, one group of five disks was heated to 800°C, and the final group of five disks was heated to 1000°C. The activity of the sputtered films on all 15 disks (15 disks for each of the five choices of TM = a total of 75 disks) was measured in acid solution. The composition of the most active GC disk sample for a given TM is indicated by circles in Fig. 1.

Figure 2 shows the CVs of the sample on the GC disk that showed the highest activity in each $TM_xC_{1-x-y}N_y$ film after heattreatment measured in O₂-saturated 0.1 M HClO₄ solution at 25 °C. No other data is shown in order to limit the amount of data presented in this paper to a manageable level. The TM content (shown



Figure 1. (Color online) Atomic % N vs atomic % TM for $TM_xC_{1-x-y}N_y$ library before and after heat-treatment at 700, 800, and 1000°C. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The balance of the composition is carbon. The circle-shaped data points indicate the compositions of the sample that showed the highest activity for ORR in acidic electrolyte in each $TM_xC_{1-x-y}N_y$ library.

on each panel in Fig. 2) for the most active compositions in the samples varied only between 10.0 and 11.8%. The heat-treatment temperature for the most active sample was 800°C for $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ and 1000°C for $V_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ and $Mn_xC_{1-x-y}N_y$ only lose substantial N when heated above 800°C, whereas the Cr, Co, and Ni-based libraries had already lost substantial N when heated to 800°C. For all TMs tested, the most active sample was found to be that with the highest metal content of the disks tested and after heating to a temperature at which substantial N loss had occurred. The activity of the samples toward ORR decreases in the order of Co > Cr > Ni > Mn > V. V_{11.3}C_{88.6}N_{0.1} shows little or no activity. The onset potential of $Co_{10.0}C_{87.3}N_{2.7}$ is about 0.76 V vs RHE.

In order to investigate the dependence of the activity of the $TM_xC_{1-x-y}N_y$ films on the heat-treatment temperature in detail, constant-composition $TM_xC_{1-x-y}N_y$ films with nominally the same value of x (x = 0.10) were prepared and heat-treated at a closely spaced series of temperatures. The atomic TM content, shown in Table I, in the as-sputtered films was measured to lie between 9.2 and 11.4%. Constant-composition $C_{1-x}N_x$ (composition included in Table I) and C films were also prepared for comparison.

Electrocatalytic activity of the constant-composition $TM_xC_{1-x-y}N_y$, $C_{1-x}N_x$ and C samples heat-treated at different temperatures.— Figures 3-7 show the variation with heat-treatment temperature of the N content, onset potentials, and the current densities at fixed potentials (vs RHE) for the ORR measured in O₂-saturated 0.1 M HClO₄ and/or O₂-saturated 0.1 M KOH solution at 25°C for the constant composition TM–C–N films. The potentials for comparing the current densities vs heat-treatment temperature were selected to be about 0.1 V below the onset potential of the best sample for each TM.

The data for the constant-composition V–C–N film presented in Fig. 3 shows that there is a dramatic decrease in the N content at $T_c = 825$ °C. The onset potential of the film in alkaline electrolyte does not change significantly with heat-treatment temperature between 650 and 1000 °C, although the maximum occurs for the sample heat-treated at 900 °C. The current density in alkaline solution at 0.6 V increases slightly between 650 and 825 °C (T_c) and then increases significantly above T_c , with the maximum around 900 °C. The significant increase in activity above T_c could be caused by the porosity induced by the N loss at T_c that would increase the surface area. The constant-composition V–C–N film shows little or no activity in acid solution before or after heat-treatment.

There is a dramatic decrease in N content at $T_c = 850^{\circ}$ C for the Mn–C–N film (Fig. 4). The onset potential in alkaline electrolyte increases with heat-treatment temperature between 600 and 900°C, with the maximum occurring for the sample heat-treated at 900°C. The current density at 0.6 V increases slightly between 600 and 850°C (T_c) and then increases significantly above T_c with the maximum occurring at 900°C. The constant-composition Mn–C–N film shows little or no activity in acid solution before and after heat-treatment, which is similar to the V–C–N film.

For the constant-composition Cr–C–N film (Fig. 5), there is a dramatic decrease in N content at $T_c = 800$ °C. The onset potential



Figure 2. Disk current densities for the samples on GC disks that showed the highest activity in an acidic environment for ORR in the $TM_xC_{1-x-y}N_y$ libraries. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The measurement was performed in O₂-saturated 0.1 M HClO₄ at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm. The average composition of the film on each disk is indicated in each panel.



Figure 3. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the $V_x C_{1-x-y} N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

for ORR in acid solution increases with the heat-treatment temperature between 775 and 850°C, as the catalyst becomes active above $T_c = 800$ °C. The onset potential decreases slightly with heat-treatment temperature above 850°C. The film begins to show activity at a lower temperature (700°C) in 0.1 M KOH solution than in 0.1 M HClO₄ solution. The onset potential measured in 0.1 M KOH solution increases with heat-treatment temperature between 700 and 800°C and then does not change much, although the maximum occurs for the sample heat-treated at 900°C. The current density at 0.6 V in acid electrolyte is strongly dependent on the heat-treatment temperature, reaching a maximum for the sample heat-treated at 850°C. The current density at 0.6 V in the alkaline electrolyte increases between 700 and 800°C and then does not change significantly, although, as with the testing in acid, the maximum occurs for the sample heat-treated at 900°C.

There is a dramatic decrease in N content at $T_c = 725$ °C for the constant-composition Co–C–N film (Fig. 6). The onset potential for ORR in acid increases with the heat-treatment temperature between 700 and 800 °C, as the catalyst becomes active above $T_c = 725$ °C. The maximum onset potential occurs for the film heat-treated at 800 °C. The samples begin to show activity at a lower heat-treatment temperature (650 °C) in 0.1 M KOH solution than in 0.1 M HClO₄ solution. The maximum onset potential in alkaline solution occurs for the sample heat-treated at 850 °C. The current density at 0.7 V in acid electrolyte is strongly dependent on the heat-treated at 800 °C. The maximum for the sample heat-treated at 800 °C. The sample heat-treated at 850 °C. The observation that the Co–C–N film starts to show activity at T_c in acid solution and below T_c in alkaline solution is similar to that seen for the Cr–C–N film.

For the constant-composition Ni-C-N film, there is a dramatic



Figure 4. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the $Mn_xC_{1-x-y}N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

decrease in N content at $T_c = 725$ °C. The onset potential for ORR in acid increases with the heat-treatment temperature between 700 and 850°C, as the catalyst becomes active above $T_c = 725$ °C. The maximum onset potential and current density at 0.5 V in acid solution occurs for the film heat-treated at 850°C. The maximum onset potential and the current density at 0.6 V in alkaline solution occurs for the film heat-treated at 900°C; however, the film begins to show activity at a lower temperature (650°C), i.e., below T_c , in 0.1 M KOH solution than in 0.1 M HClO₄ solution. In addition, the ORR activity of the film in alkaline solution is much higher than that in acid solution. This is similar to the behavior of the Co-C-N and Cr–C–N films. In our previous work on the activity of sputtered Co–C–N films in acid and alkaline solutions, we noted 33 that there were samples heated to just below T_c that were active in alkaline solution but not in acid solution. We speculated that small pores created by N loss above T_c are too small for the adsorption of acidic species that block catalytic sites, so the films become active above $T_{\rm c}$ in acid. We further speculated that the sites are not blocked by ions in the alkaline solution regardless of whether or not the samples have been heated through T_{c} .

The activity for the ORR, the optimum heat-treatment temperature, and the composition of the most active sample in the constantcomposition TM–C–N (TM = V, Cr, Mn, Co, and Ni) films in acid and alkaline solution are summarized in Table II. In 0.1 M HClO₄ solution, the activity of the most active heat-treated sample in TM– C–N (TM = Cr, Co, and Ni) follows the order Co > Cr > Ni. In 0.1 M KOH solution, the activity of the most active heat-treated sample in TM–C–N (TM = V, Cr, Mn, Co, and Ni) follows the order Co > Ni > Mn > V > Cr.

Figure 8 shows the CV and the percentage of HO_2^- (% HO_2^-) produced at the disk electrode vs the disk potential for the most



Figure 5. (a) N content, (b) onset potential, and (c) current density at 0.6 V for ORR in 0.1 M HClO₄ and 0.1 M KOH solution vs heat-treatment temperature of the $Cr_xC_{1-x-y}N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

active heat-treated V–C–N and Mn–C–N samples, whose compositions are given in Table II, measured in O₂-saturated 0.1 M KOH solution at 25°C. No well-defined diffusion-limited current is reached, although there is a plateau between 0.4 and 0.6 V in the CV curves in both cases. For V–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential decreases and reaches 95.0% at 0.60 V and then decreases with the disk potential. For Mn–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential decreases as the disk potential decreases as the disk potential. For Mn–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential. For Mn–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential decreases as the disk potential. For Mn–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential decreases as the disk potential. For Mn–C–N, the percentage of HO₂⁻ (% HO₂⁻) first increases as the disk potential decreases and reaches about 55% at 0.50 V, and then does not change much with the disk potential. The fraction of per-oxide produced is very large.

Figure 9 shows the CVs and the percentage of H_2O_2 (% H_2O_2) (in acid solution) and HO_2^- (% HO_2^-) (in alkaline solution) produced at the disk electrode vs the disk potential for the most active heattreated Cr-C-N, Co-C-N, and Ni-C-N samples, whose compositions are given in Table II, measured in O₂-saturated 0.1 M HClO₄ solution and in O2-saturated 0.1 M KOH solution at 25°C. No welldefined diffusion-limited current is reached for ORR over the potential range measured in the CV curves in acid and alkaline solution for the Cr-C-N, Co-C-N, and Ni-C-N samples. For Cr-C-N, the activity in acid and alkaline solution are similar. The % HO₂ (about 85% between 0.6 and 0.3 V) produced in alkaline solution is higher than the % H_2O_2 (about 65% between 0.6 and 0.3 V) produced in acid solution. For Co-C-N, the CV curve in acid solution shows two clear reduction waves. The % H₂O₂ in acid is between 22 and 50% between 0.80 and 0.05 V and increases as the disk potential decreases, which correlates to the two steep reduction waves in the CV curve. The Co-C-N CV curve in alkaline solution shows a relatively well-defined current plateau, which indicates that the activity in alkaline solution is higher than that in acid solution. The % HO₂



Figure 6. (a) N content, (b) onset potential, and (c) current density at 0.7 V for ORR in 0.1 M HClO₄ and 0.1 M KOH solution vs heat-treatment temperature of the $Co_x C_{1-x-y} N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

increases as the disk potential decreases, reaching 55% at 0.60 V, and then decreases slightly for lower disk potentials. The % HO₂⁻ is between 40 and 55% between 0.70 and 0.05 V, which is slightly higher than the % H₂O₂ produced in acid solution. For Ni–C–N, the activity in alkaline solution is much higher than in acid solution. The onset potentials measured in acid and alkaline solution are 0.60 and 0.84 V, respectively. The % HO₂⁻ (about 60–90% between 0.80 and 0.05 V) produced in alkaline solution is higher than the % H₂O₂ (about 40–55% between 0.60 and 0.05 V) produced in acid solution. All of these thin-film catalysts produce large amounts of peroxide.

Grazing incidence XRD of the constant-composition $TM_{x}C_{1-x-y}N_{y}$ samples heat-treated at different temperatures. Figures 10-14 show grazing incidence XRD spectra for the constantcomposition TM-C-N films heat-treated to a range of different temperatures between 650 and 1000°C. In all the cases, at a critical temperature (T_c) , the film transforms to a heterogeneous mixture of N-containing carbon and V₈C₇ (Fig. 10), Cr₃C₂ (Fig. 11), Mn₇C₃ (Fig. 12), Co (Fig. 13), or Ni (Fig. 14). The observed phases in the XRD pattern of the heat-treated TM-C-N (TM = V, Cr, Mn, Co, and Ni) films and the equilibrium phases in the TM–C (TM = V, Cr, Mn, Co, and Ni) binary-phase diagrams³⁸ are summarized in Table III. Previous studies on Co–C–N samples³³ have shown that T_c decreases with TM content and increases with N content in the films. Even though the constant-composition samples were designed to have similar TM and N contents in the as-sputtered state, the variations that exist between the samples (see Table I) make it impossible to rank the five TMs for their effectiveness at catalyzing the transformation at T_c . The observed phases in the heat-treated TM-C-N



Figure 7. (a) N content, (b) onset potential, and (c) current density for ORR at 0.6 V in 0.1 M KOH solution or 0.5 V in 0.1 M HClO₄ vs heat-treatment temperature of the $Ni_xC_{1-x-y}N_y$ samples. The samples were derived from the constant-composition sample described in Table I.

samples are in good agreement with equilibrium-phase diagrams, which indicates that heating above T_c causes a transformation to a nanocomposite of expected equilibrium phases.

In all the cases, the transformation at T_c coincides with a significant loss of N as shown in Fig. 3-7, respectively. The thermal stability of the amorphous constant-composition $\text{TM}_x C_{1-x-y} N_y$ (x = 0.10) films increases in the order of $\text{Co} \approx \text{Ni} < \text{Cr} < \text{V} < \text{Mn}$ based on the value of T_c . This is in agreement with the results for thermal stability obtained for the $\text{TM}_x C_{1-x-y} N_y$ libraries [i.e., $\text{Co} < (\approx) \text{Ni} < \text{Cr} < \text{V} < \text{Mn}$] that can be inferred from Fig. 1.

Comparison of the electrocatalytic activity of heated TM–C–N films to heated $C_{1-x}N_x$ and C films.— The results above show that each of the TM–C–N systems transforms to N-containing graphitic carbon and either TM or a TM-carbide above T_c . Therefore, it is natural to consider the role that the TM plays in the formation of the active sites for ORR in both acid and alkaline solution. Experiments focusing on the case of TM = Co were made. In this case, films of $C_{1-x}N_x$, C, and Co were prepared and studied by XRD and RRDE



Figure 8. Disk current density and $\% \text{HO}_2^-$ produced for the heat-treated $V_x C_{1-x-y} N_y$ and $Mn_x C_{1-x-y} N_y$ constant-composition samples on the GC disks that showed the highest activity for ORR measured in O₂-saturated 0.1 M KOH. The measurements were performed at 25°C with a sweep rate of 5 mV s⁻¹ and rotation speed of 900 rpm. The average compositions of the films on the disks are indicated.

before and after heat-treatment. RRDE of graphite powder was also measured for comparison in alkaline solution. First, the data for the $C_{1-x}N_x$ and C samples are presented and later compared to the heated TM–C–N and Co films (in alkaline solution) in the Discussion section.

Figure 15 shows the variation with heat-treatment temperature of the N content, the onset potential, and the current densities at 0.3 V for the ORR measured in O₂-saturated 0.1 M HClO₄ and the current densities at 0.6 V (vs RHE) in O2-saturated 0.1 M KOH solution at $25\,^{\circ}\text{C}$ for the constant-composition $C_{61.1}N_{38.9}$ film (the composition shown here is for the as-sputtered sample). The N content decreases as the heat-treatment temperature increases. The onset potential for ORR in acid increases with the heat-treatment temperature in the range between 700 and 900°C and then decreases as it is heated to 1000 and 1100°C. The maximum onset potential and current density at 0.3 V in acid solution occurs for the film heat-treated to 900°C. The film begins to show activity at 400°C in 0.1 M KOH solution. The maximum onset potential and the current density at 0.6 V in alkaline solution occurs for the film heat-treated at 1000°C. The ORR activity of the film in alkaline solution is much higher than that in acid solution.

Figure 16 shows the CVs and the percentages of H_2O_2 (% H_2O_2) (in acid solution) and HO_2^- (% HO_2^-) (in alkaline solution) produced at the disk electrode vs the disk potential for the constant-composition $C_{61.1}N_{38.9}$ sample heat-treated at 900°C (i.e., the most active one in acid solution, the composition is $C_{78.6}N_{21.4}$

Table II. The activity for ORR, the optimum heat-treatment temperature, and the compositions of the most active sample in the constant-composition TM-C-N (TM = V, Cr, Mn, Co, and Ni) samples in acid and alkaline solutions.

	Composition of the as-sputtered sample	$T_{\rm c}$ (°C)	Electrolyte	Optimum heat-treatment temperature (°C)	Composition of the most active sample after heat-treatment	Onset potential (V vs RHE)
V-C-N	V _{9.4} C _{47.4} N _{43.2}	825	0.1 M KOH	900	V ₁₃₂ C ₈₃₁ N ₃₇	0.79
Cr-C-N	Cr _{11.4} C _{47.2} N _{41.3}	800	0.1 M HClO ₄	850	Cr _{14.2} C _{80.1} N _{5.7}	0.80
			0.1 M KOH	900	Cr _{14.6} C _{82.0} N _{3.4}	0.78
Mn-C-N	Mn _{9.7} C _{52.7} N _{37.6}	850	0.1 M KOH	900	Mn _{13.3} C _{83.7} N _{3.0}	0.82
Co-C-N	Co _{9.2} C _{57.3} N _{33.5}	725	0.1 M HClO ₄	800	Co _{11.5} C _{82.5} N _{6.0}	0.81
			0.1 M KOH	850	Co _{11.9} C _{82.8} N _{5.3}	0.87
Ni-C-N	Ni _{10.1} C _{50.5} N _{39.4}	725	0.1 M HClO ₄	850	Ni _{13.2} C _{82.7} N _{4.1}	0.60
			0.1 M KOH	900	Ni _{13.4} C _{83.2} N _{3.4}	0.84



Figure 9. Disk current density and % H_2O_2 (% HO_2^- in 0.1 M KOH) produced for the heat-treated $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ constant-composition samples on the GC disks that showed the highest activity for ORR measured in O_2 -saturated 0.1 M HClO₄ and in O_2 -saturated 0.1 M KOH. The measurements were performed at 25°C with a sweep rate of 5 mV s⁻¹ and rotation speed of 900 rpm. The average compositions of the films on the disks are indicated.



Figure 10. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of V–C–N. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.



Figure 11. (Color online) Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Cr–C–N. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

after heat-treatment at 900°C) measured in O₂-saturated 0.1 M HClO₄ solution at 25°C and heat-treated at 1000°C (i.e., the most active one in alkaline solution, the composition is $C_{88.7}N_{11.3}$ after heat-treatment at 1000°C) measured in O₂-saturated 0.1 M KOH solution at 25°C. The onset potentials measured for the sample heated at 900°C in acid solution and for the sample heated at 1000°C in alkaline solution are 0.40 and 0.83 V, respectively. The % HO₂ (about 30–60% between 0.80 and 0.05 V) produced in alkaline solution for the sample heated at 1000°C is lower than the % H₂O₂ (about 60–77% between 0.40 and 0.05 V) produced in acid solution for the sample heated at 900°C.

Figure 17 shows the variation with heat-treatment temperature of the onset potential and the current densities at 0.6 V (vs RHE) for the ORR measured in O_2 -saturated 0.1 M KOH solution at 25 °C for the sputtered C film. The onset potential (0.71–0.73 V) does not change much with heat-treatment temperature in the range between 25 and 900 °C and then decreases to 0.62 V when it is heated to 1000 °C. The current density at 0.6 V increases slightly over the range between 25 and 800 °C and then decreases at 900 and 1000 °C. The C film shows little or no activity in acid solution before and



Figure 12. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Mn–C–N. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.



Figure 13. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Co–C–N. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

after heat-treatment. Recall that the $C_{1-x}N_x$ films heated between 700 and 1100°C are somewhat active for ORR in acid solution as shown in Fig. 16, confirming the importance of N doping on the activity of C in acid solution as reported in the literature.^{39,40}



Figure 14. Grazing incidence XRD measurements showing intensity vs scattering angle for the heat-treated constant-composition sample of Ni–C–N. The heat-treatment was done in flowing N_2 and the heat-treatment temperature is indicated next to each curve. The major Bragg peaks of the phases present are indicated.

Table III. The critical temperature for the phase transformation, the observed phases (from the grazing incidence XRD patterns) in the heat-treated constant-composition samples of TM–C–N (TM = V, Cr, Mn, Co, and Ni), and the equilibrium phases in the TM–C (TM = V, Cr, Mn, Co, and Ni) binary-phase diagrams.³⁶

As-sputtered sample	Critical temperature (T_c) (°C)	Observed phases	Equilibrium phases for TM–C
V _{9.4} C _{47.4} N _{43.2}	825	V ₈ C ₇ , N-carbon	V ₈ C ₇ , carbon
Cr _{11.4} C _{47.2} N _{41.3}	800	Cr ₃ C ₂ , N-carbon	Cr_3C_2 , carbon
Mn _{9.7} C _{52.7} N _{37.6}	850	Mn ₇ C ₃ , N-carbon	Mn_7C_3 , carbon
Co _{9.2} C _{57.3} N _{33.5}	725	Co, N-carbon	Co, carbon
Ni10.1C50.5N39.4	725	Ni, N-carbon	Ni, carbon



Figure 15. (a) N content, (b) onset potential for ORR, and (c) current density for ORR at 0.6 V in 0.1 M KOH solution or 0.3 V in 0.1 M HClO₄ vs heat-treatment temperature of the $C_{1-x}N_x$ samples. The samples were derived from the constant-composition sample described in Table I.

Figure 18 shows the CV and the percentages of HO₂⁻ (% HO₂⁻) produced at the disk electrode vs the disk potential for the C film heat-treated at 800°C (i.e., the most active one) measured in O₂-saturated 0.1 M KOH solution at 25°C. There are two waves in the CV curve, possibly corresponding to two active sites for the ORR, which is consistent with literature experiments on GC, ^{41,42} on the roughened basal plane of graphite⁴³ and on the edge of pyrolytic graphite. ^{44,45} The two waves were also observed in the CV curves of the as-sputtered C film and the C films heated at all temperatures up to 1000°C (not shown here). These results suggest that the assputtered, ^{42,46} which agrees with the XRD measurements on these



Figure 16. Disk current density and % H_2O_2 (% HO_2^- in 0.1 M KOH) produced for the heat-treated $C_{1-x}N_x$ sample on the GC disk that showed the highest activity for ORR measured in O_2 -saturated 0.1 M HClO₄ and in O_2 -saturated 0.1 M KOH at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm. The average compositions of the films on the disks are indicated.



Figure 17. (a) Onset potential and (b) current density at 0.6 V for ORR in 0.1 M KOH solution vs heat-treatment temperature of the C samples. The samples were derived from the constant-composition sample.

films that show no clear Bragg peaks (not shown). The percentage of HO_2^- (% HO_2^-) produced on the C film heat-treated at 800°C is about 60% between 0.60 and 0.05 V.

Stability of the $TM_xC_{1-x-y}N_y$ films heat-treated at different temperatures against corrosion in acid.— Figure 19 shows the difference in the atomic content of TM ($\Delta\%$ TM = % of TM lost) before and after soaking in 0.5 M H₂SO₄ at 25°C for 1 week plotted vs the initial (before acid) atomic content of TM (%TM) in the TM_xC_{1-x-y}N_y libraries heat-treated at 700, 800, and 1000°C. The films with low TM content show relatively good stability with respect to TM dissolution. For initial TM contents, %TM (TM = V,Mn,Co,Ni) = 1.0–1.2% and % Cr = 6.5%, little or no TM is dissolved from the films. More TM is dissolved from the films when the TM concentration is relatively high in the TM_xC_{1-x-y}N_y librar-



Figure 18. Disk current density and % HO_2^- produced for the heat-treated C sample on the GC disk that showed that highest activity for ORR measured in O_2 -saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.



Figure 19. (Color online) The change in TM content ($\Delta\%$ TM = % of transition metal lost) caused by soaking in 0.5 M H₂SO₄ at 25 °C for 1 week vs the initial atomic content of TM (%TM) in the TM_xC_{1-x-y}N_y libraries heat-treated at 700, 800, and 1000 °C. TM = (a) V, (b) Cr, (c) Mn, (d) Co, and (e) Ni. The inset in (b) is $\Delta\%$ Cr before and after soaking in 0.5 M H₂SO₄ at 80 °C for 1 week vs the initial % Cr in the Cr_xC_{1-x-y}N_y library.

ies. The amount of TM dissolved ($\Delta\%$ TM) from the films increases as the heat-treatment temperature increases. Especially for $Co_xC_{1-x-y}N_y$ and $Ni_xC_{1-x-y}N_y$ films heat-treated at 1000°C, Co and Ni are almost completely dissolved from the films at high Co and Ni concentrations as shown in Fig. 19d and e. Interestingly, the $Cr_xC_{1-x-y}N_y$ composition spread is much more stable against corrosion than the $V_xC_{1-x-y}N_y$, $Mn_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ spreads. Only about 1.0% Cr was lost, even at high Cr concentration (12.1% Cr), after acid treatment at 25°C for 1 week, and $\Delta\%$ Cr is only about 1.5% at 12.1% Cr after acid treatment at 80°C for 1 week, as shown in Fig. 19b. This indicates that Cr component in the heated $Cr_xC_{1-x-y}N_y$ film provides passivation against



Figure 20. (Color online) Disk current density of (a) sputtered C heated at 900°C, (b) sputtered C–N heated at 900°C, (c) sputtered C–N heated at 1000°C, (d) sputtered C–N heated at 1100°C, (e) graphite, (f) sputtered V–C–N heated at 900°C, (g) sputtered Cr–C–N heated at 900°C, (h) sputtered Mn–C–N heated at 900°C, (i) sputtered Co–C–N heated at 900°C, and (j) sputtered Ni–C–N heated at 900°C, on the GC disks for ORR measured in Ω_2 -saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.

corrosion in acid solution. The stability of heated $Cr_xC_{1-x-y}N_y$ in acid may arise from the presence of $Cr_3C_2^{\ 47-49}$ in the film.

Discussion

Activity in acid solution.- The results from the previous section are summarized in this section and comparisons between the different samples are made. Heat-treated $\bar{V_xC_{1-x-y}N_y}$ and $Mn_xC_{1-x-y}N_y$ films show little or no activity for ORR in acid electrolyte. The heat-treated $Cr_x C_{1-x-y} N_y$, $Co_x C_{1-x-y} N_y$, and $Ni_x C_{1-x-y} N_y$ films show activity after heating to T_c and above in acid electrolyte. Heattreated $C_{1-x}N_x$ films show much lower activity in acid solution than the $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ films heat-treated at the same temperatures. The as-sputtered and heated C films show little or no activity in acid electrolyte. Therefore, it is clear that activity in acid solutions appears above T_c and for TM–C–N materials with TM = Cr, Co, and Ni. It has also been shown that active materials are produced when samples with TM = Fe are heated above $T_c^{30,31}$ and the activity of the Fe–C–N is a bit higher than that of Co-C-N. Therefore, the activity for ORR in acid solution follows the order $\operatorname{Fe}_{x}C_{1-x-y}N_{y} > \operatorname{Co}_{x}C_{1-x-y}N_{y} > \operatorname{Cr}_{x}C_{1-x-y}N_{y}$ $> Ni_x C_{1-x-y} N_y$. The results show that TM plays an important role in the formation of the active site for ORR in acid solution.

Activity in alkaline solution.— All of the heat-treated $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) films show activity in alkaline electrolyte when heated to some temperature below T_c . Heat-treated $C_{1-x}N_x$ and as-sputtered or heated C films all show activity in alkaline electrolyte. What is the source of this activity?

The situation in alkaline solution is complicated, because GC, 41,42 graphite, $^{42-44}$ and activated carbon⁵⁰ all show significant activity for ORR. In addition, metallic Co and Ni, which convert to hydroxides or oxides in alkaline solution, also show significant activity for ORR. ^{51,52} Because the TM–C–N samples are carbonaceous (though amorphous) before heating and most show evidence of N-containing graphite after heating above T_c , it is possible that their activity in alkaline solution could arise due to their carbon-containing character alone. Because the Co–C–N and Ni–C–N samples clearly contain Co or Ni after heating above T_c , their activity in alkaline solution could arise from the metal content. We acknowledge that it is difficult to be certain which sites (or combina-



Figure 21. (Color online) Disk current density of (a) sputtered Co heated at 900°C, (b) sputtered Co–C–N heated at 900°C and (c) sputtered Co–C–N heated at 900°C and then treated by soaking in 1.0 M H₂SO₄ at 25°C for one month and at 80°C for one month on the GC disks for ORR measured in O₂-saturated 0.1 M KOH. The measurement was performed at 25°C. The sweep rate was 5 mV s⁻¹ and the rotation speed was 900 rpm.

tions of sites) are active for ORR in alkaline solution in these samples. Nevertheless, some comparison graphs of the data presented in the Results section are useful.

Figure 20 compares the activities in alkaline solution of sputtered C heated at 900°C, sputtered $C_{1-x}N_x$ heated at 900, 1000, and 1100°C, powdered graphite, and sputtered $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, Ni) heated at 900°C. Results for graphite are included because graphitic carbon appears in the XRD patterns of the sputtered $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, Ni) films after heating above T_c (Fig. 10-14). The onset potentials of sputtered $C_{1-x}N_x$ heated at 900, 1000, and 1100°C (curves b, c, and d in Fig. 20) are higher than that of sputtered C heated at 900°C (curve a in Fig. 20). The onset potentials of $C_{1-x}N_x$ heated at 1000 and 1100°C are also higher than that of graphite (curve e in Fig. 20). These results suggest that N doping can improve the activity of C in alkaline solution as well as in acid solution.

The activity of activated carbon for ORR in alkaline solution reported in Ref. 50 is better than the $C_{1-x}N_x$ samples and comparable to those of the TM–C–N samples. Note that when N is lost from $TM_xC_{1-x-y}N_y$ and $C_{1-x}N_x$ samples during heating, it is likely that some porosity, similar to the porosity in activated carbon, may form. Thus, the correlation of the increased activity with TM type or N content in the heated films may be a result of increased porosity or increased numbers of particular surface functional groups formed on surfaces which become exposed through N loss.

The samples that show the highest activity in Fig. 20 are the $Co_x C_{1-x-y} N_y$ and $Ni_x C_{1-x-y} N_y$ samples (curves i and j) heated to 900°C. These samples contain metallic Co and metallic Ni as shown in Fig. 13 and 14. It is, therefore, extremely important to compare their activity to the activity of the metals alone. Ni hydroxide⁵¹ and Co hydroxide⁵² are electroactive for ORR in alkaline solution. Pourbaix diagrams show⁵³ that Ni and Co are passivated by an oxide or hydroxide layer above ca. 0.20 and 0.15 V (vs RHE) in an alkaline solution having pH > 9, respectively.

Figure 21 shows CVs in oxygen-saturated alkaline solution for a sputtered Co film and for two samples of $Co_xC_{1-x-y}N_y$. The $Co_xC_{1-x-y}N_y$ samples were a film heated at 900°C (from the constant-composition sample described in Table II) and an identical film (also heated to 900°C) that was soaked in 1.0 M H₂SO₄ at 25°C for 1 month and then at 80°C for another month to dissolve any exposed Co in the film. The activity of the heated $Co_xC_{1-x-y}N_y$ film is higher than that of heated Co film and does not change significantly after the Co is dissolved away, indicating that other active sites account for the improved activity of the heated $Co_xC_{1-x-y}N_y$ film (and the Ni_xC_{1-x-y}N_y film as well).

The results in Fig. 20 show that the onset potentials for ORR in alkaline solution follow the order $\text{Co}_x\text{C}_{1-x-y}\text{N}_y > \text{Ni}_x\text{C}_{1-x-y}\text{N}_y > \text{Mn}_x\text{C}_{1-x-y}\text{N}_y > C_{1-x}\text{N}_x$ heated at 1000°C > V_xC_{1-x-y}N_y

 $> Cr_x C_{1-x-y} N_y$. The difference between the activity of $C_{1-x} N_x$ and $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) suggests that the TM may play a role in the formation of the active site for ORR. Apparently, Co, Ni, and Mn are beneficial while V and Cr are not useful in the formation of active sites for ORR in alkaline solution.

To summarize, the results in this paper and in the literature suggest that the choice of TM is important in the formation of the active sites for ORR both in acid and alkaline solution. As mentioned earlier, the trends in the activities of heat-treated $Cr_{r}C_{1-r-\nu}N_{\nu}$, $Co_x C_{1-x-y} N_y$, and $Ni_x C_{1-x-y} N_y$ films in acid and alkaline solutions are different from the trends shown by heat-treated $V_x C_{1-x-y} N_y$ and $Mn_xC_{1-x-y}N_y$ films. Heat-treated $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ films begin to show activity at T_c in acid electrolyte and show activity in alkaline electrolyte when heated to a temperature below T_c . Heat-treated $V_x C_{1-x-y} N_y$ and $Mn_x C_{1-x-y} N_y$ films show little or no activity for ORR in acid electrolyte but show activity in alkaline electrolyte when heated.

For noble-metal catalysts, the pH effect for ORR on Pt⁵⁴ and on Ag⁵⁵ is basically attributed to the adsorption of spectator species that either block the active sites required for adsorption of ORR intermediates or that lower the adsorption energy of the reaction intermediates. In our previous work on the activity of sputtered Co-C-N films in acid and alkaline solutions, we noted³³ that there were samples heated to just below T_c that were active in alkaline solution but not in acid solution. We speculated that small pores created by N loss above T_c are too small for the adsorption of acidic species that block catalytic sites, so the films become active above T_c in acid and the sites are not blocked by ions in the alkaline solution regardless of whether the samples have been heated through $T_{\rm c}$.

An alternative explanation for the trends observed could be based on the onset of microporosity above T_c . The detailed studies in this work show that carbon, graphite, and CN_x are all active for ORR in the alkaline solution. More active sites appear above T_c for TM-C-N, which increase the activity in alkaline solution. Dodelet and co-workers⁵⁶ argue that microporosity is essential for the formation of MN_x catalytic sites within slit-shaped pores in carbon that are active in acid solution. Therefore, the activity in acid solution above T_c could result from the porosity created by N loss above T_c , i.e., micropores are essential to obtain catalytic activity in acid solution.56

Heat-treated $V_x C_{1-x-y} N_y$ and $Mn_x C_{1-x-y} N_y$ films show little or no activity for ORR in acid electrolyte and show activity in alkaline solution. Apparently, V and Mn seem to show little or no ability to create the sites which are active in acid above T_c . These samples behave similarly to the heated carbon films, and it is therefore believed that their activity arises primarily from the carbon in the samples. For carbon catalysts, the pH effect is attributed to the adsorption of ORR intermediates that block the active sites at low pH.5

Conclusion

Sputtered $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) films transform from an amorphous structure to a nanoscale mixture of N-containing carbon and V₈C₇, Cr₃C₂, Mn₇C₃, Co, or Ni when heated above $T_{\rm c}$. The transformation temperature, $T_{\rm c}$, of the sputtered $TM_xC_{1-x-y}N_y$ (x = 0.10) films increases in the order of Co \approx Ni < Cr < V < Mn. No obvious structure changes were observed in the XRD patterns measured on $C_{1-x}N_x$ and C films after heat-treatment.

The activity of the heat-treated sputtered $TM_xC_{1-x-y}N_y$, $C_{1-x}N_x$, and C films for ORR depends on the N doping, TM type, heattreatment temperature, and electrolyte. Heat-treated $V_x C_{1-x-y} N_y$ and $Mn_xC_{1-x-y}N_y$ films show little or no activity for ORR in acid electrolyte. Heat-treated $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and $Ni_xC_{1-x-y}N_y$ films begin to show activity in acid electrolyte at T_c . Heat-treated $C_{1-x}N_x$ films show some activity in acid solution but their activities are much lower than that of the $Cr_xC_{1-x-y}N_y$, $Co_xC_{1-x-y}N_y$, and

 $Ni_xC_{1-x-y}N_y$ films heat-treated at the same temperatures. The assputtered and heated C films show little or no activity in acid electrolyte.

All the heat-treated sputtered $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) films show activity in alkaline electrolyte when heated to a temperature below T_c . Heat-treated $C_{1-x}N_x$ and as-sputtered or heated C films all show activity in alkaline electrolyte. Because disordered carbons, graphite, and transition metals all show activity for ORR in alkaline electrolyte, it is difficult to make conclusive statements about the results in alkaline electrolyte. However, heattreated Co-C-N samples which were acid-etched for 2 months still showed equivalent ORR to fresh heat-treated samples, suggesting the Co metal, formed after heating above T_c , is not involved in the most active sites.

Corrosion-stability experiments on the heat-treated $TM_xC_{1-x-y}N_y$ (TM = V, Cr, Mn, Co, and Ni) libraries showed that the heat-treated $Cr_x C_{1-x-y} N_y$ libraries show good passivation against corrosion, which is believed to be provided by the Cr component. This suggests that combining Cr into $TM_xC_{1-x-y}N_y$ (TM = Fe or Co) films may improve the stability of the films against corrosion and could increase catalyst lifetime in PEMFC applications.

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