

Voltammetric Studies of the Mechanism of the Oxygen Reduction in Alkaline Media at the Spinels Co₃O₄ and NiCo₂O₄

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The mechanism of O_2 reduction at the spinels, Co_3O_4 and $NiCo_2O_4$, in KOH electrolyte is probed using voltammetry at rotating disc and rotating ring-disc electrodes by examination of the rotation rate dependent limiting currents. The analysis shows that the products and mechanisms at the two spinels are quite different. At the cobalt spinel, a substantial amount of the $2e^-$ reduction product, H_2O_2 , is formed while at $NiCo_2O_4$ the $4e^-$ reduction strongly predominates. In terms of both the overpotential for reduction and its limiting current density, the mixed spinel is a substantially better electrocatalyst. It is proposed that the differences arise from an enhanced rate of O-O bond cleavage early in the reduction process at $NiCo_2O_4$.

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Electrocatalysts that can support both oxygen reduction and oxygen evolution at high current densities are critical components of proposed metal/air secondary batteries and reversible fuel cells. The development of such electrocatalysts (and gas diffusion electrodes) provides additional challenges to electrodes designed for only one of these electrode reactions (as in fuel cells and water electrolysers respectively). Spinels and perovskites have been widely proposed as bifunctional oxygen electrocatalysts in concentrated alkaline solutions.^{1–5}

In general, of course, cathodic oxygen reduction is a widely studied reaction.^{1,6} It is clearly a multistep reaction and both the products and the overpotential for the reaction depend strongly on the cathode material. It is accepted that the reduction can occur by a number of pathways, see Figure 1.7,8 The direct 4e⁻ reduction pathway is envisaged to result from mechanisms where there is cleavage of the O-O bond early in the reaction sequence, while the alternative pathways involve 2e⁻ steps with hydrogen peroxide either as the final product or as an intermediate further reduced or undergoing chemical disproportionation. The rate of the further reduction and chemical decomposition of hydrogen peroxide depends strongly on the cathode and reaction conditions. For energy storage applications, it is important that oxygen undergoes the full 4e⁻ reduction because (a) the equilibrium potential of the O2/H2O couple is positive to that for the O_2/H_2O_2 couple leading to a higher battery voltage, (b) the current density at any potential is twice as large, and (c) the energy storage capability/mole of oxygen is double. However the observation of a 4e⁻ reduction alone does not distinguish two reaction pathways, the direct $4e^-$ reduction and the $2 \times 2e^-$ reduction where further reaction of H₂O₂ is rapid.

In contrast to oxygen evolution, studies of oxygen reduction at Co_3O_4 and $NiCo_2O_4$ are not extensive. Moreover, in most papers graphitic carbon powder is present in the catalyst composition^{9–15} and this can confuse studies of O_2 reduction since graphitic carbon offers an alternative reaction surface and it is known to influence the response.^{9–11} It is also not a viable component of bifunctional oxygen electrodes because of possible corrosion in the conditions of oxygen reduction. Three recent papers from our group^{16–18} report oxygen reduction at GDE based on NiCo₂O₄ catalyst without graphitic carbon. A number of papers have also reported the behavior of nanostructured Co_3O_4 and NiCo₂O₄ for oxygen reduction^{12,13,19–32} but the assessment of these data is often hampered by the absence of data at 'standard' surfaces, such as Pt, graphitic carbon, or the uncoated glassy carbon surface, for comparison. The inclusion of such standard surfaces enables accurate comparison of the limiting currents and onset potentials

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for the reactions and eliminates the variability related to the use of different reference electrodes.

An exploration of the literature, however, shows that there are a number of issues related to oxygen electrochemistry at Co_3O_4 and $NiCo_2O_4$ catalysts, especially in regards to the reduction of oxygen, that have not been fully addressed and these will influence the performance of electrodes with spinels or perovskites as catalysts during battery operation. The aim of this paper is to address these issues using rotating disc electrode experiments with the spinels, Co_3O_4 and $NiCo_2O_4$, through analysis of the rotation dependent limiting currents for oxygen reduction and hydrogen peroxide oxidation and reduction. The catalysts are investigated using bound films on an inert (vitreous carbon) rotating disc electrode (RDE)³³ and the results are compared to those obtained at the standard Pt and graphitic carbon electrodes mentioned above.

Experimental

Instrumentation.—All electrochemical experiments were carried out with Autolab PGSTAT instruments with NOVA and GPES software packages. The rotation rates of the electrodes were controlled by Pine Instrument Rotators, type CPR or MSR. Scanning electron microscopy (SEM) images of the deposits were obtained with a Philips XL30 ESEM environmental scanning electron microscope operating in the wet mode with a secondary electron (SE) detector and fitted with an EDAX International Phoenix 2 EDX. Transmission electron



Figure 1. Pathways for cathodic O_2 reduction in aqueous alkaline media, based on References 7 and 8.

Table I. Summary of XRD structure refinement of the patterns shown in Figure 2.

Powder	Crystal system	Space group	Lattice constant a=b=c (Å)	V (Å ³)	
Co ₃ O ₄	cubic	fd3m	8.09	530	
NiCo ₂ O ₄	cubic	fd3m	8.11	533	

microscopy (TEM) images were recorded on either an FEI Tecnai 12 (Co_3O_4) or JEOL JEM-2100 (NiCo₂O₄) microscope using samples drop coated onto a Cu grid (1000 mesh holey carbon, VWR) and an accelerating voltage of 200 kV. X-ray diffraction data were collected on a Bruker D2 (Cu-K α , 1.5418 Å) with a fluorescence filtering detector. Structural refinement of the XRD data (Table I) was completed using the Rigaku PDXL and Rietveld analysis was conducted using the GSAS software packages. Brunauer, Emmett and Teller (BET) surface area measurements employed a Micromeritrics – Gemini instrument.

Electrochemical cells and electrolyte.- Experiments with rotating disc and ring disc electrodes were carried out in beaker cells (volume $\sim 200 \text{ cm}^3$) with a polymer cover and a water jacket through which water with a known temperature (generally 298 K) was passed. The counter electrode was a Pt gauze in the same compartment and the reference electrode a laboratory fabricated Hg/HgO/KOH (1M) electrode (potential + 866 mV vs NHE) inside a Luggin capillary. The glassy carbon rotating disc electrode (area 0.2 cm^2) was a Pine Instruments AF3M electrode. The rotating ring disc electrode had a glassy carbon disc and Pt ring (Pine Instruments AFE7R9GCPT) with a collection efficiency of 0.37. Prior to each experiment, the electrodes were polished on microcloths (Buehler) with alumina slurries of 1.0 μm then 0.05 μm particle size. Unless otherwise stated, the electrolyte was 1 M KOH pre-saturated with oxygen (BOC) prior to each measurement, which included repeating the saturation between measurements at different rotation rates. A blanket of $O_2(g)$ was maintained over the electrolyte during the measurements and data for at least three replicates of each measurement were obtained. The reproducibility between measurements was $\pm 2\%$ of the measured current densities.

Preparation of spinels and electrode coatings.—Co₃O₄ - 5 g Co(NO₃)₂6H₂O (Sigma Aldrich) was dissolved in 20 cm³ of deionized water. The solution was evaporated to dryness and heated at 378 K for 3 hours. The residue was ground and then calcined at 673 K for 12 hours. The resulting black solid was reground and then sieved through a 53 μ m sieve. NiCo₂O₄ – 29 g Co(NO₃)₂.6H₂O (Sigma Aldrich) and 14.5 g Ni(NO₃)₂.6H₂O (Sigma Aldrich) were dissolved in 100 cm³ of deionized water to give a deep red solution. 56 g KOH (Sigma Aldrich) and 53.9 g NaHCO₃ (Fisher Scientific) were dissolved in 1500 cm³ of deionized water and the Ni(II)/Co(II) solution was slowly added drop wise to this solution with vigorous stirring. After complete addition, the solution was heated at 353 K for 20 hours. The green opaque suspension was filtered through a 0.02 µm polyamide filter (Whatman) and dried at 373 K. It was then ground before being calcined at 648 K for 4 hours. The resulting black solid was reground and then sieved through a 53 μ m sieve.

The spinel structure of both samples was confirmed by XRD (Fig. 2) and the structural parameters are reported in Table I. Elemental analysis of the NiCo₂O₄ showed the Ni:Co ratio of 1:2. SEM (Fig. 3) images indicated that the solids were made up of irregular particles with dimensions of $10 - 50 \ \mu m$ while both TEM (Fig. 4) and width of the peaks in the XRD suggest that these particles were, in fact, masses of much smaller crystallites or particles with typical particle size of $10 - 20 \ nm$. The surface areas measured by BET were $30 \ m^2 \ g^{-1}$ for Co₃O₄ and 68 m² g⁻¹ for NiCo₂O₄.

The spinel electrocatalysts were formulated as inks. 2 mg spinel was added to 6 cm^3 of deionized water and the suspension placed in an



Figure 2. XRD patterns of spinels Co₃O₄ (bottom) and NiCo₂O₄ (top).



Figure 3. Scanning electron microscope (SEM) of Co₃O₄ (left) and NiCo₂O₄ (right). Scale bar is 10 micron.

ultrasonic bath (Fisherbrand FB15046) for 30 minutes followed by 2 minutes shear force stirring in a homogenizer (Fisher Powergen 1000). The ink was applied to the glassy carbon discs (0.2 cm^2) in $3 \times 15 \mu$ l aliquots with drying with an IR heat lamp between applications. Finally, a thin film of Nafion was drop cast over the catalyst layer using 15 μ l of 1 wt% Nafion in water (prepared from aqueous Nafion solution, 10% solids (Ion Power GmbH)) and the coating again dried. This final layer was found to greatly enhance the stability of the coating and to improve the reproducibility of experimental data. In contrast to many papers in the literature, these spinel catalyzed layers do not contain graphitic carbon powder. Voltammograms of the Co₃O₄ and NiCo₂O₄ catalysts used in this study in nitrogen purged 1 M KOH have been previously reported.¹⁸

For comparison purposes, coatings were prepared either with Pt black (Fuel Cell Grade) from E-TEK or XC-72R carbon powder



Figure 4. Transmission electron microscopy (TEM) of Co_3O_4 (left) and $NiCo_2O_4$ (right). Scale bar: 100nm (left) and 20 nm (right).



Figure 5. Voltammograms at coated glassy carbon RDE in O_2 saturated 1 M KOH. (a) Pt black (b) XC-72R Carbon powder (c) Co_3O_4 (d) Ni Co_2O_4 (e) Bare GC electrode. Temperature 298 K. Rotation rate 400 rpm. Potential scan rate 5 mV s⁻¹.

replacing the spinel catalyst, but otherwise prepared by the same procedure. In all cases, the catalyst loading was $\sim 75 \ \mu g \ cm^{-2}$.

Results

Rotating disc electrode (RDE) studies of oxygen reduction.-Figure 5 compares voltammograms for O₂ reduction in 1 M KOH at a temperature of 298 K at four catalyst layers and an uncoated glassy carbon disc, each recorded with a rotation rate of 400 rpm. With each electrode, a well-formed sigmoidal reduction wave is obtained but the overpotentials and limiting currents differ significantly, see Table II. Reduction of oxygen does occur at the uncoated glassy carbon disc, as has been previously reported in the literature^{34–36} but it is immediately apparent that the spinel coatings lead to a positive shift in the reduction potential and, in some cases, a large increase in limiting current density. The voltammogram at the Pt black coated electrode is included to allow comparison with the response of a catalyst known to yield the 4e⁻ reduction of O₂. Although the spinel catalyzed coatings in our programe do not contain carbon powder, the response at XR-72 is important to this work as it defines the response at a particle-based coating supporting a 2e⁻ mechanism³⁷ similar to the spinel coating studied in this paper. High area carbon, which is often added to the catalyst ink to improve conductivity and/or the gas diffusion characteristics of the catalyst layer, may influence the response and this is often unrecognized in papers in the literature.

A number of important aspects should be noted:

i Pt black is the best catalyst for O_2 reduction in these conditions but the overpotential at NiCo₂O₄ is larger only by ~110 mV at low current densities (i.e. at potentials where a gas diffusion electrode would be expected to operate); values of the potential for a current density of - 0.1 mA cm^{-2} are reported in Table II.

- ii The fuel cell grade XC-72 carbon powder based layer (without other catalyst) shows only a moderate increase in overpotential compared to Pt black but with a limiting current density half that for the Pt black coating. The response of the XC-72 stresses the importance of checking the activity of any carbon component in all studies that employ catalyst layers that contain graphitic carbon as well as that of the electrocatalyst. The graphitic carbon can contribute to the current and there is the possibility of parallel reaction pathways on the graphitic carbon and catalyst surfaces. This is the reason, along with the likelihood of carbon corrosion in the conditions for O_2 evolution, why in this study, carbon powder was not added to the spinel catalyst layers.
- iii The limiting current densities vary with the catalyst layer. It is to be expected that the Pt black will support full $4e^-$ reduction and the XC-72 mainly a $2e^-$ reduction (fuel cell electrodes based on carbon have been used for the production of hydrogen peroxide in NaOH with a charge efficiency of ~ $80\%^{37}$) and the ratio of the limiting currents is consistent with this expectation. The limiting currents at the spinels differ strongly. At NiCo₂O₄, the limiting current is only slightly less than that at Pt black while that at Co₃O₄ is similar to that at XC-72. However, this voltammetry alone does not allow one to determine whether this limiting current results from a $2e^-$ reduction or a strongly kinetically limited $4e^-$ reduction, as will be explored further below.

The rotation rate dependence of the voltammograms at the coated discs was further investigated. For all four coatings, well-formed reduction waves were observed at all rotation rates. With Pt black and XC-72 catalyzed coatings, the limiting current densities were proportional to the square root of the rotation rates although the slopes of the Levich plots differed by a factor of two, consistent with n = 2at carbon and n = 4 at Pt black. Figure 6 reports the rotation rate dependences of the responses at the two spinel catalyzed coatings. At all rotation rates, a limiting current density is observed and their values are much lower at Co₃O₄ than at NiCo₂O₄. In a limiting current plateau region, the rate determining step in the electrode reaction can be either mass transport or a chemical step (NOT electron transfer since this would make the current density dependent on potential as in the rising part of the voltammogram). The limiting current densities at both spinel coatings increase with rotation rate but the reduction of oxygen is not fully mass transport limited since plots of limiting current densities versus the square root of rotation rate (not shown) are clearly non-linear.

As the limiting current densities, j_L , are partially limited by a chemical step, they were further analyzed using the Koutecky-Levich (K-L) equation:

$$\frac{1}{j_L} = \frac{1}{nFkc_{o_2}} + \frac{1}{0.62nFD^{2/3}v^{-1/6}c_{o_2}\omega^{1/2}}$$

where *n* is the number of electrons/O₂ transferred during reduction, *F* the Faraday constant, c_{O_2} the concentration of oxygen in the electrolyte, *D* the diffusion coefficient of O₂, v the kinematic viscosity of the electrolyte and ω the rotation rate of the disc. *k* is the rate constant for the chemical step in the reduction mechanism. Thus, the

Table II. Comparison of catalyst materials RDE and RRDE data. O₂ saturated 1 M KOH. 298 K. 400 rpm. § data taken for voltammograms recorded at 400 rpm. Slopes and intercepts for all materials shown in the table are only from first three points, corresponding to rotation rates of 100, 400 and 900 rpm).

	RDE data §			Koutecky-Levich		RRDE data
Catalyst	$E_{-0.1 \text{ mA cm}^{-2}}$ vs Hg/HgO/ mV	$E_{3/4} - E_{1/4}/ \ mV$	$j_{\rm L}/{ m mA~cm^{-2}}$	Slope/mA ⁻¹ cm ² rpm ^{-1/2}	Intercept/mA ⁻¹ cm ²	$\% H_2 O_2{}^{\S}$
Pt black	+ 50	-53.7	$-1.6 (\pm 0.1)$	$-11.0(\pm 0.1)$	$-0.06(\pm 0.01)$	<1
XC-72R C	-137	-63.3	$-1.0 (\pm 0.1)$	$-17.0(\pm 0.3)$	$-0.16(\pm 0.02)$	57 (± 3)
Co ₃ O ₄	-149	-75.8	$-1.0 (\pm 0.1)$	$-13.1 (\pm 0.5)$	$-0.32(\pm 0.03)$	36 (± 2)
NiCo ₂ O ₄	-61	-117	$-1.5 (\pm 0.1)$	$-10.2 (\pm 0.3)$	$-0.16(\pm 0.02)$	$6 (\pm 0.3)$

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Figure 6. Rotation rate dependence of the voltammograms for the reduction of O_2 in 1 M KOH at Co_3O_4 and $NiCo_2O_4$ electrodes. Rotation rates (a) 100 rpm (b) 400 rpm (c) 900 rpm (d) 1600 rpm and (e) 2500 rpm. Temperature 298 K. Potential scan rate 5 mV s⁻¹. The surface area of glassy carbon disc is 0.2 cm².

comparative values of the slopes provide information about the number of electrons involved in the reduction while the intercepts reflect the rate of the chemical step.

Figure 7 shows plots of $1/j_L$ vs $1/\omega^{1/2}$ for the four coated electrodes and the slopes and intercepts from these plots are reported in Table II. The K-L plots for the Pt black and XC-72 carbon catalyzed coatings are linear and have only a small intercept on the $1/i_L$ axis, but have different slopes, as expected. This is consistent with mass transport limited currents but different values of n. The linear fit through the data points at low rotation rates for Co₃O₄ and NiCo₂O₄ shown in Figure 7 goes through the first 3 or 4 points, but there is deviation to this linear fit at high rotation rates (small values of $1/\omega^{1/2}$), which is particularly marked for Co₃O₄ at high rotation rates. The slopes of these linear fits at low rotation rates are similar to that obtained for Pt black, confirming that the reduction at the spinels involve 4e⁻. For both spinels, the lines have a clear non-zero intercept on the $1/j_L$ axis confirming a component of kinetic control to the limiting currents. The intercept for Co_3O_4 is substantially larger than that for $NiCo_2O_4$, indicating that the chemical step is slower at this spinel. The deviation

at high rotation rates is probably due to a greater involvement of a $2e^{-}$ mechanism as also evident by the increase in slope (Table II).

Rotating ring disc electrode (RRDE) studies of oxygen reduction: The extent of hydrogen peroxide formation as an intermediate in oxygen reduction was also investigated with catalyst coated glassy carbon disc/Pt ring (RRDE) electrodes (collection efficiency 0.37). The potential of the disc was scanned through the potential range for O_2 reduction while the ring potential was held at + 200 mV vs Hg/HgO, a potential where the oxidation of hydrogen peroxide is mass transport controlled on Pt.³⁸ Figure 8 shows sets of responses for Co_3O_4 and $NiCo_2O_4$ catalyzed disc electrodes while the data for these electrodes as well as XC-72 and Pt black are summarized in Table II by reporting the % of the reduction current that leads to hydrogen peroxide. While some hydrogen peroxide is detected with both spinel catalyzed electrodes, the magnitudes of the ring currents with the two spinels are very different. With NiCo₂O₄, hydrogen peroxide collected at the ring represents a very low current efficiency for hydrogen peroxide, 6% at 400 rpm. Indeed, SEM images of the edges of the coated discs (not shown) revealed that in some cases there



Figure 7. Koutecky-Levich plots for O_2 reduction in 1 M KOH with Co_3O_4 , Ni Co_2O_4 , carbon powder (XC-72R), Pt black coatings on glassy carbon. Data taken at – 500 mV vs Hg/HgO, in the plateau regions of the voltammograms. 1 M KOH. Temperature 298 K. Scan rate 5 mV s⁻¹. Lines shown are best fits through only the three lowest rotation rates (100, 400, and 900 rpm), as discussed in the text.



Figure 8. Disc and ring responses for O_2 reduction at Co_3O_4 and $NiCo_2O_4$ coated glassy carbon discs. The potential of the discs is scanned while the Pt ring electrode is held at + 200 mV vs Hg/HgO. Rotation rates as shown. O_2 saturated 1 M KOH. Temperature 298 K. Potential scan rate 5 mV s⁻¹. The disc area: 0.25 cm²; The ring area: 0.19 cm². The collection efficiency of the RRDE is 0.37.

was uncovered glassy carbon close to the PTFE surround, and such exposed substrate could easily account for the small amount hydrogen peroxide formation observed. In contrast, at the Co_3O_4 based coating, hydrogen peroxide formation at the catalyst particles on the disc becomes a significant contributor to the disc current, 36% at 400 rpm.

The results with XC-72 and Pt black are consistent with the literature. The formation of hydrogen peroxide is a very minor contribution at the Pt black thin film electrode (<1%), while with the XC-72R carbon it becomes the major reaction; for the carbon electrode 57% of the charge at the disc leads to H_2O_2 and this is to be expected from the known performance of C based GDEs³⁷

RDE studies of hydrogen peroxide oxidation and reduction.— Figure 9 compares the voltammograms at Co_3O_4 and $NiCo_2O_4$ catalyzed disc electrodes for a solution of hydrogen peroxide in 1 M KOH. At both electrodes, both reduction and oxidation of hydrogen peroxide is observed but the current densities for reduction are smaller than for oxidation (both oxidation to oxygen and reduction to hydroxide involves $2e^-$ and the mass transport controlled current densities



Figure 9. Voltammograms at glassy carbon RDE coated with (a) Co₃O₄ (b) NiCo₂O₄ for ~10 mM H₂O₂ in N₂ purged, 1 M KOH. Temperature 298 K. Rotation rate 400 rpm. Potential scan rate 1 mV s⁻¹.

would be equal). Even the oxidation limiting currents are not mass transport controlled (the limiting currents are not proportional to the square root of rotation rate) and all the currents are low compared those expected for the estimated concentration of hydrogen peroxide. The limiting current for the reduction is almost independent of the rotation rate of the disc confirming the strong kinetic limitation to the reduction of hydrogen peroxide at these spinels. Clearly, with a slow rate for the reduction of H₂O₂ at the spinel coatings, a $2e^- + 2e^-$ mechanism for a $4e^-$ reduction is unlikely.

Discussion

Transition metal oxide electrocatalysts have been subjected to substantial study as alternative catalysts to precious metals for O_2 reduction.^{1-6,33} Many such oxides are easy to prepare from cheap starting materials and they can be conductive and sometimes show electrocatalytic activity for O_2 reduction. The spinels, Co_3O_4 and NiCo₂O₄, are both conductive and straightforward to prepare from aqueous nitrate solutions. They may also be formulated into catalyst layers free of graphitic carbon powder on an inert RDE.

In our studies, Co₃O₄ and NiCo₂O₄ in alkaline electrolytes show very different properties as O₂ reduction electrocatalysts. NiCo₂O₄ is an effective catalyst; it supports the full 4e⁻ reduction (as Pt) at a rate approaching mass transport control, although with a slightly larger overpotential than Pt. In contrast, the Co₃O₄ coating is a poor catalyst for O₂ reduction. The voltammetry also suggests a 4e⁻ reduction in some mass transport conditions, but it also implies a slow step in the 4e⁻ pathway (presumably the initial cleavage of the O-O bond) allowing the 2e⁻ pathway to compete particularly at high rates of convection. Thus at Co₃O₄ coatings, the limiting currents are substantially below those for a mass transfer controlled 4e⁻ reaction and then only with a higher overpotential while RRDE studies confirm a substantial fraction of the charge passed leads to hydrogen peroxide. Literature reviews¹⁻⁵ agree that the cobalt spinel is a poor O_2 reduction catalyst and, indeed, a review of cobalt spinel electrocatalysts² makes no mention of the parent cobalt spinel in the section on oxygen reduction. On the other hand, Heller-Ling et al.¹⁴ conclude that a Co₃O₄ coating catalyzed the full 4e⁻ reduction and imply a limiting current indicating mass transfer control; the reason for the discrepancy with the work reported herein is not clear. In addition, several recent papers^{22-24,30,32} report studies on electrode coatings containing nanostructured Co₃O₄ and some show good oxygen reduction activity. The recently reported activity of Co_3O_4 nanochains³² is particularly impressive. But all these coatings contain an active carbon, a graphitic carbon powder or graphene, and, in general, papers do not define the role of these additional materials. It remains possible, however, that the nanostructured Co₃O₄ can have a high density of the actual catalyst sites promoting the cleavage of the O-O bond.

As noted in the Introduction, the full 4e⁻ reduction can occur by two types of pathway, one not involving H₂O₂ and probably involving the early cleavage of the O-O bond and another where H₂O₂ is formed but rapidly converted to hydroxide by reduction or disproportionation on the catalyst surface. The two reaction pathways will always compete with the more rapid dominating.

With the NiCo₂O₄ catalyst, the RDE data is generally consistent with O₂ reduction in a full 4e⁻ reduction and the RRDE experiments show, at most, only a very low formation of H₂O₂. The sluggish cathodic reduction of H2O2 at NiCo2O4 seems to rule out reaction pathways for O₂ reduction where H₂O₂ is formed and rapidly further reduced. Hence, we believe that at NiCo₂O₄, O₂ reduction occurs via a mechanism where the O-O bond is cleaved in an initial step. The Levich and Koutecky-Levich plots confirm that O₂ reduction is never fully mass transport controlled and even in the limiting current plateau it is partially kinetically controlled by the rate of this O-O cleavage reaction. The use of high rotation rates will put more pressure on the chemical step leading to cleavage of the O-O bond and this will lead to an increased opportunity for electron transfer as the first step and hence for the formation of H₂O₂ in a 2e⁻ step and the slight deviation from linearity in K-L plot for this spinel. The voltammetry at XC-72 carbon shows that electron addition to O2 occurs at potentials only slightly negative to those for catalytic mechanism.

The responses with Co₃O₄ are consistent with a similar mechanism, but correspond to a system where the chemical step is much slower. Hence, the 2e⁻ has a greater role. The RRDE experiment shows substantial H₂O₂ formation and the Koutecky-Levich plot has a larger intercept. The K-L plot for the limiting currents at lower rotation rates also suggest a 4e⁻ reduction but there is a larger deviation of the slope toward that for a 2e⁻ reduction at higher rotation rates.

Thus it appears that two reaction pathways for O₂ reduction occur in parallel and at intermediate rate constants for the chemical step, the relative importance of the two mechanisms changes with mass transport conditions; increasing the rate of convection will put greater pressure on the chemical step in the direct 4e⁻ reduction. It is tempting to propose, more generally, that electron transfer is the "default mechanism" when the rate of O-O cleavage is slow. The potentials for electron addition to O_2 are only slightly negative to that for the direct 4e⁻ reduction initiated by a chemical step such as O-O bond cleavage; the potential of direct 4e⁻ reduction will, of course, depend critically on the electrocatalyst and the kinetics of the chemical step on its surface. Certainly, with catalytic layers containing both active carbon powder and another catalyst, it is possible that the two mechanisms occur in competition with the relative importance of the two routes depending on the rate of O-O cleavage at the other catalyst.

Further investigations are necessary. From the literature and unpublished studies in our laboratory, we are aware that spinel catalysts prepared by different routes and using different conditions within a single route show some variation in the rate of O₂ reduction but the reasons cannot be deduced from the information available (perhaps a result of different crystallite sizes or small variations in Ni/Co/O ratios, etc.). For this reason, we would stress that it must be recognized that the literature on each spinel with nominally the same composition in fact represents the behavior and performance of a related family of materials. Perhaps an even more important question is why the overpotential and limiting current for O₂ reduction are sensitive to choice and ratio of transition metals in the spinel. Both questions are the subject of further study.

Conclusions

The reduction of oxygen at cathodes catalyzed by NiCo₂O₄ occurs predominantly by a 4e⁻ reaction leading to water without the intermediate formation of hydrogen peroxide. The rate limitation is controlled by a chemical step, most likely the cleavage of the O - O on the surface of the spinel. The reduction at Co₃O₄ occurs with lower current densities. The rate of the cleavage reaction and hence the 4e⁻ reduction is much slower and this leads to a significant contribution from a competing mechanism, initial electron transfer to the oxygen molecule; almost half the charge passed leads to hydrogen peroxide formation. The literature shows that some nanostructured Co₃O₄ materials are more active for the 4e- implying a much higher density of active sites on those materials.

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