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

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The mechanism of O2 reduction at the spinels, Co3O4 and NiCo2O4, in KOH electrolyte is probed using voltammetry at rotating disc and rotating ring-disc electrodes. The products and mechanisms at the two spinels are quite different. At the cobalt spinel, a substantial amount of the 2e- reduction product, H2O2, is formed while at NiCo2O4 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 NiCo2O4.

1. Introduction

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 electrocatalysts (and gas diffusion electrodes) that will support both oxygen reduction and oxygen evolution at high rates 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 alkali.[1-5] An exploration of the literature, however, shows that there are a number of issues related to their electrochemistry, especially 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. This paper seeks to address these issues using experiments with the spinels, Co3O4 and NiCo2O4. The catalysts are investigated using bound films on an inert (vitreous carbon) rotating disc electrode (RDE).[6]

In general, of course, cathodic oxygen reduction is a widely studied reaction.[1,7] 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. 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 as the final product or 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 O2/H2O2 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 x 2e- reduction where further reaction of H2O2 is rapid.

In contrast to oxygen evolution, studies of oxygen reduction at Co3O4 and NiCo2O4 are not extensive. Moreover, in most papers carbon powder is present in the catalyst composition [8-14] and this can confuse studies of O2 reduction since carbon offers an alternative reaction surface and it is known to influence the response.[8-10] It is also not a viable component of bifunctional oxygen electrodes because of possible corrosion in the conditions of oxygen evolution. Two recent papers [15,16] report oxygen reduction at GDE based on NiCo2O4 catalyst without carbon components. A number of papers have also reported the behaviour of nanostructured Co3O4 and NiCo2O4 for oxygen reduction [11,12,17-30] but the assessment of these data is often hampered by the absence of data at ‘standard’ surfaces for comparison.

**Experimental**

* 1. 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 microscopy (TEM) images were recorded on a Jeol JEM-2100 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 was collected on an Agilent Supernova diffractometer with a Mo Kα X-ray source. Rietveld analysis was run on the data using the GSAS software package. Brunauer, Emmett and Teller (BET) surface area measurements employed a Micromeritrics – Gemini instrument.

* 1. Electrochemical Cells and Electrolyte

Experiments with disc and ring disc electrodes were carried out in beaker cells (volume ~ 200 cm3) 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 cm2) 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 KOH (1 M) pre-saturated with oxygen (BOC).

* 1. Preparation of Spinels and Electrode Coatings

Co3O4 - 5 g Co(NO3)26H2O (Sigma Aldrich) was dissolved in 20 cm3 of deionised 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 μm 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 deionised water to give a deep red solution. 56 g KOH (Sigma Aldrich) + 53.9 g NaHCO3 Fisher Scientific) was dissolved in 1500 cm3 of deionised water and the Ni(II)/Co(II) solution was slowly added drop wise 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 μm sieve.

The spinel structure of both samples was confirmed by XRD (SI Fig 1) and elemental analysis of the NiCo2O4 showed the Ni:Co ratio of 1:2. SEM (SI Fig 2) images indicated that the solids were made up of irregular particles with dimensions of 10 – 50 μm while both TEM (SI Fig 3) and analysis of the XRD peak shape confirmed that these particles were, in fact, masses of much smaller particles with typical particle size of 10 – 20 nm. The surface areas measured by BET were 30 m2 g-1 for Co3O4 and 68 m2 g-1 for NiCo2O4.

Electrode Coating - The spinel electrocatalysts were formulated as an ink. 2 mg spinel was added to 6 cm3 of deionised water and the suspension placed in an ultrasonic bath (Fisherbrand FB15046) for 30 minutes followed by 2 minutes shear force stirring in a homogeniser (Fisher Powergen 1000). The ink was applied to the glassy carbon discs (0.2 cm2) in 3 x 15 μl 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 μl 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 catalysed layers do NOT contain carbon powder.

For comparison purposes, coatings were prepared with Pt black (Fuel Cell Grade) from E-TEK and XC-72R carbon powder replacing the spinel catalyst but otherwise prepared by the same procedure. In all cases, the catalyst loading was ~ 75 μg cm-2.

There is an uncertainty associated with the geometric area of all such coated electrodes; with the technique used, the coating may not quite cover all the vitreous carbon disc or it may just spill over the polymer surround. We estimate this as + 10 %.

1. RESULTS
	1. Rotating Disc Electrode (RDE) Studies of Oxygen Reduction

Figure 2 compares voltammograms for O2 reduction in 1 M KOH at a temperature of 298 K at four catalyst layers, each recorded with a rotation rate of 400 rpm. The voltammogram at Pt/C is included to show the response at a state-of-the-art O2 reduction catalyst. Although the spinel catalysed coatings in our programme do not contain carbon powder, the response at XR-72 is important to this work as it defines the response at a surface supporting a 2e- mechanism [31]. The role of high area carbon is often unconsidered in papers in the literature.

With each electrode, a well-formed sigmoidal reduction wave is obtained but the overpotentials and limiting currents differ significantly, see table 1. A number of important conclusions should be noted:

1. Pt black is the best catalyst for O2 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 1.
2. The fuel cell grade XC-72 carbon powder based layer (without other catalyst) also supports O2 reduction with only a moderate increase in overpotential compared to Pt black. In fact, the overpotential for O2 reduction at carbon depends strongly on the carbon surface. For example, at uncoated, polished glassy carbon, no reduction current is observed positive to -500 mV vs Hg/HgO. 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 carbon as well as that of the electrocatalyst. The carbon surface can contribute to the current and there is the possibility of parallel reaction pathways on the carbon and catalyst surfaces. This is the reason, along with the likelihood of carbon corrosion in the conditions for O2 evolution, why in this study, carbon powder was not added to the spinel catalyst layers.
3. 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 % [31]) 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. 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.

The rotation rate dependence of the voltammograms was investigated. For all four coatings, well-formed reduction waves were observed. With Pt black and XC-72 catalysed 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 = 2 at carbon and n = 4 at Pt black. Figure 3 reports the rotation rate dependences of the responses at the two spinel catalysed 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.

The limiting current densities are partially limited by a chemical step. The limiting current densities, *jL*, were further analysed using the Koutecky-Levich (K-L) equation:

where *n* is the number of electrons/O2 transferred during reduction, *F* the Faraday constant, the concentration of oxygen in the electrolyte, *D* the diffusion coefficient of O2, *ν* 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. The 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 4 shows plots of 1/*jL* vs 1/*ω1/2* for the four coated electrodes and slopes and intercepts from these plots are reported in table 1. The K-L plots for the Pt black and XC-72 carbon catalysed coatings are linear and have only a small intercept on the 1/*jL* axis but have different slopes. This is again consistent with mass transport limited currents but different values of n. The plots for Co3O4 and NiCo2O4 appear to be linear at low rotation rates but there is deviation (particularly marked at Co3O4) at high rotation rates. At low rotation rates, the K-L plot has the same slope as the data for Pt black confirming that the reduction at the spinels involve 4e-. For both spinels, the lines have a clear intercept on the 1/*jL* axis confirming a component of kinetic control to the limiting currents. The intercept for Co3O4 is substantially larger than for NiCo2O4 indicating that the chemical step is slower at this spinel. The deviation at high rotation rates is probably due to a greater involvement in a 2e- mechanism (note the increase in slope).

 **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 electrodes (collection efficiency 0.37). The potential of the discs were scanned through the potential range for O2 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.[32] Figure 5 shows sets of responses for Co3O4 and NiCo2O4 catalysed disc electrodes while the data for these electrodes as well as XC-72 and Pt black is summarised in table 1 by reporting the % of the reduction current that leads to hydrogen peroxide. While some hydrogen peroxide is detected with both spinel catalysed 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, of the disc current while at Co3O4, hydrogen peroxide formation at 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 Pt black catalysed disc (< 1 %), while with the XC-72R carbon it becomes the major reaction; 57 % of the charge at the disc leads to H2O2 and this is to be expected from the known performance of C based GDEs.[31]

* 1. RDE Studies of Hydrogen Peroxide Oxidation and Reduction

Figure 6 compares the voltammograms at Co3O4 and NiCo2O4 catalysed 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 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. Also the limiting current for the reduction is almost independent of the rotation rate of the disc. Clearly, the reduction of hydrogen peroxide is kinetically limited at both spinels although even more strongly at Co3O4. With a slow rate for the reduction of H2O2, a 2e- + 2e- mechanism for a 4e- reduction is unlikely.

1. DISCUSSION

Transition metal oxide electrocatalysts have been subjected to substantial study as alternative catalysts to precious metals for O2 reduction.[1-7**]** Many such oxides are easy to prepare from cheap starting materials and they can be conductive and sometimes show electrocatalytic activity for O2 reduction. The spinels, Co3O4 and NiCo2O4, are both conductive and straightforward to prepare from aqueous nitrate solutions. They may also be formulated into catalyst layers free of carbon powder on an inert RDE.

In our studies, Co3O4 and NiCo2O4 in alkaline electrolytesshow 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, voltammetry with Co3O4 coatings is indicative of a strong kinetic limitation in the 4e- reduction; the limiting currents are substantially below those for a mass transfer controlled reaction and then only with a higher overpotential while RRDE studies confirm a substantial fraction of the charge passed leads to hydrogen peroxide. The conclusion concerning Co3O4 differ starkly from those of Heller-Ling et al [13] who concluded that it catalysed the full 4e- reduction with a limiting current indicating mass transfer control. In addition, several recent papers [20-22, 28, 30] report studies on electrodes based on nanostructured C3O4 and some show good oxygen reduction activity. The recently reported activity of Co3O4 nanochains [30] is particularly impressive. The reviews [1-5], however, imply that Co3O4 is a poor O2 reduction catalyst and a review of cobalt spinel electrocatalysts [2] makes no mention of the parent cobalt spinel in the section on oxygen reduction. The reasons for these discrepancies are not clear especially as most active catalyst compositions include carbons or graphene. Clearly, present knowledge implies a key role for the nanostructured Co3O4 presumably increasing the density of the actual catalyst sites and/or a role for carbon but a definitive conclusion must await further studies.

 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 reactions 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 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 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 towards 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. 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 O2 are slightly negative to that for O-O bond cleavage where, of course the potential of the latter step will depend on the electrocatalyst. Certainly, with catalytic layers containing both 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 unpublished results, we are aware that NiCo2O4 prepared by different routes and using different conditions show some variation in the rate of O2 reduction but the reason is not clear (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 recognised that the literature on each spinel with nominally the same composition in fact represents the behaviour 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.

1. **CONCLUSION**

The reduction of oxygen at cathodes catalysed 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 these materials.

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**Legends for Figures**

**Figure 1.**

Pathways for cathodic O2 reduction in aqueous alkaline media.

**Figure 2.**

Voltammograms at coated glassy carbon RDE in O2 saturated 1 M KOH. (a) Pt black (b) XC-72R carbon powder (c) Co3O4 (d) NiCo2O4. Temperature 298 K. Rotation rate 400 rpm. Potential scan rate 5 mV s-1.

**Figure 3.**

Rotation rate dependence of the voltammogram for the reduction of O2 in 1 M KOH Co3O4 and NiCo2O4. 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 0.25 cm2

**Figure 4.**

Koutecky-Levich plots for O2 reduction in 1 M KOH with Co3O4, NiCo2O4, 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.

**Figure 5.**

Disc and ring responses for O2 reduction at Co3O4 and NiCo2O4 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. O2 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.

**Figure 6.**

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.



**Figure 1** Pathways for cathodic O2 reduction in aqueous alkaline solutions.



**Figure 2.** Voltammograms at coated glassy carbon RDE in O2 saturated 1 M KOH. (a) Pt black (b) XC-72R carbon powder (c) Co3O4 (d) NiCo2O4. Temperature 298 K. Rotation rate 400 rpm. Potential scan rate 5 mV s-1.

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**Figure 3.** Rotation rate dependence of the voltammogram for the reduction of O2 in 1 M KOH Co3O4 and NiCo2O4. 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 0.25 cm2

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**Figure 4.** Koutecky-Levich plots for O2 reduction in 1 M KOH with Co3O4, NiCo2O4, 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.

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**Figure 5.** Disc and ring responses for O2 reduction at Co3O4 and NiCo2O4 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. O2 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.



**Figure 6.** 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.

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| **Catalyst** | **RDE data§** | **Koutecky-Levich** | **RRDE data** |
| **E -0.1 mA cm-2vs****Hg/HgO/ mV** | **E3/4 – E1/4/ mV** | **IL/****mA cm-2** | **Slope/****mA-1 cm2 rpm-1/2** | **Intercept/****mA-1 cm2** | **% H2O2§** |
| Pt black | + 50 | - 55 | - 1.64 | - 11 | - 0.06 | < 1 |
| XC-72R C | - 135 | - 65 | - 0.97 |  - 18 | - 0.13 | 57 |
| Co3O4 | - 150 | - 75 | - 1.01 | - 13 | - 0.36 | 36 |
| NiCo2O4 | - 60 | - 115 | - 1.47 | - 10 | - 0.18 | 6 |

Table 1. Comparison of catalyst materials base on 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 Co3O4 and NiCo2O4 are from the points for two lowest rotation rates(100 rpm and 400 rpm).