Dimensionally Stable Anodes (DSA®) for Electrochemical Water Splitting: Redox Properties, OER Kinetics and Mechanism at RuO$_2$/NiO Modified Electrodes in Aqueous Base.

I.J Godwin, M.E.G Lyons

School of Chemistry, Trinity College Dublin, College Green, Dublin 2, Ireland

The RuO$_2$/NiO electrode was found to be extremely effective as a water oxidation catalyst in alkaline conditions. Addition of 25 mol % of RuO$_2$ to a NiO electrode lowered the oxygen evolution reaction (OER) overpotential by ca. 30 %. Based on kinetic data obtained we have proposed a mechanism for both RuO$_2$ and NiO utilizing the surfacial group concept which envisages water oxidation occurring at hydrated interlinked oxy-metal surface active groups.

Introduction

Dimensionally Stable Anodes (DSA®) consist of an underlying electrochemically inert valve metal substrate such as titanium, coated usually with an oxide or mixed oxides of platinum group metals (PGM). DSA® electrodes have been employed in many industrial processes such as the chlorine evolution reaction$^{[1]}$, electrowinning of metal ores$^{[2]}$ and as an anode in water electrolyzers$^{[3]}$. Herein, we focus attention on the latter use in an alkaline environment. DSA® electrodes currently exhibit the lowest overpotential for the oxygen evolution reaction (OER), which is said to be the ‘bottleneck’ or rate determining step in a water electrolyzer cell at standard operating currents. PGM oxide mixtures such as IrO$_2$/RuO$_2$ as studied by Lyons$^{[3, 4]}$, Trasatti$^{[5-7]}$ and others on Ti exhibit extremely low OER overpotentials (ca. 0.20-0.25 V) and display long term stability in strong alkaline conditions required for an alkaline water electrolyzer setup. However, the main drawback in fully utilizing PGM oxide based DSA® electrodes is in the high cost associated with these metals, and thus, significant international research is being currently focused on finding cheaper alternatives which still display relatively low overpotentials. This paper focuses on minimizing the amount of PGM oxides, RuO$_2$ in this case, required by combining them with low cost NiO which displays relatively low overpotentials for the OER$^{[8-10]}$ but at a significantly lower cost as shown in fig. 1. A range of mole fractions of RuO$_2$/NiO will be studied. The effect of varying the relative mole percent of each oxide on the redox properties, reaction order and OER kinetics and mechanism will be studied using cyclic voltammetry and steady state Tafel plots.

The OER in an alkaline environment proceeds according to (1).

$$4\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 4\text{e}^- \quad (1)$$

The driving potential needed for water oxidation can be written as
\[ E(i) = E_{e,cell} + |\eta_c| + \eta_A + iR \]  

(2)

where \( E(i) \) is the overall potential required to drive the reaction, \( E_{e,cell} \) is the thermodynamic reversible potential, \( |\eta_c| \) is the overpotential associated with the hydrogen evolution reaction at the cathode, \( \eta_A \) is the OER overpotential at the anode and \( iR \) is the ohmic drop in the cell.

Experimental

All experiments were conducted in a conventional three electrode cell kept at 25°C connected to a Gamry 600 potentiostat. All metals and metal salts used were supplied by Alfa Aesar > 99.99% metals basis. A graphite rod was used as the counter electrode and Hg/HgO (CH instruments) was employed as the reference electrode. The \( iR \) drop was calculated using high frequency potentiostatic impedance spectroscopy and all electrochemical data reported has been corrected accordingly. All measurements conducted in 5 M NaOH unless otherwise indicated. The RuO\(_2\)/NiO films were made up by making separate 0.2 M solutions of RuCl\(_3\).xH\(_2\)O and Ni(NO\(_3\))\(_3\).6H\(_2\)O in butanol. These solutions were then mixed in the desired ratios and the resulting solution was painted onto the exposed Ti wire electrode. The electrodes were dried at 80°C for 5 min to evaporate off excess solvent and further annealed at 425°C for 10 minutes for conversion to the oxide. This process was repeated several times until a sufficiently thick loading was obtained. The electrode was finally annealed at 425°C for approx. 3 hours to ensure complete conversion to the oxide.

Results

All references to the relative mole fractions will be described as additions of RuO\(_2\) to a NiO electrode i.e. 0 mol % RuO\(_2\) electrode describes a 100 mol % NiO electrode while a 25 mol % RuO\(_2\) electrode describes a 75% NiO electrode and so on. The effect of varying the relative mole fraction of RuO\(_2\) on the voltammetric response can be seen in fig. 2(a) shows a typical cyclic voltammogram of an RuO\(_2\) electrode in 5 M NaOH showing the characteristic Ru(VI/VII) redox peaks while a 0 mol % in fig.2 (d) shows a very sluggish

![Graph showing cost comparison of iridium, ruthenium, and nickel](image-url)
Ni(II/III) oxidation peak which almost coincides with the OER. As shown in fig 2 (c), even relatively small additions of RuO₂ display a characteristic ‘ruthenium like’ behaviour indicating that the voltammetric response is dominated by RuO₂.

The effect of varying the relative mol % of RuO₂ on the double layer capacitance was also studied. The capacitance of the mixed oxide electrode was found to increase linearly with additions of RuO₂ as seen in fig. 3. The capacitance value was determined by picking a fixed potential window on the cyclic voltammogram, 100 mV in this case, where there is no faradaic activity and integrating the area which gives the charge. This charge is divided by the potential which gives a capacitance. The capacitance values are normalized for the varying material on each electrode by dividing by q*, which is the total anodic charge, and is found by integrating the area between the fixed lower potential limit up to the OER onset potential.

Fig. 2 Typical cyclic voltammograms of (a) 100 (b) 50 (c) 25 (d) 0 mol % RuO₂ added to a NiO electrode on a Ti substrate in 5 M NaOH. Scan rate: 40 mV s⁻¹. Potentials quoted against Hg/HgO

Fig. 3 Charge normalised capacitance values vs. mol % RuO₂. Charge values taken in 5 M NaOH.
OER kinetics

Fig. 4 below shows steady state polarization curves for varying mole fractions of RuO$_2$/NiO electrodes. Interestingly, one can see a near linear trend in Tafel slope from *ca.* 40 mV dec$^{-1}$ for a 100 mol % RuO$_2$ electrode to *ca.* 120 mV dec$^{-1}$ for a 0 mol % RuO$_2$ electrode at low overpotentials. The observed Tafel slopes for both materials prepared in this manner have been widely reported previously in the literature. Using classical theory, a Tafel slope of 40 mV dec$^{-1}$ is characteristic of the second electron transfer step in a multistep reaction being the rate determining step (RDS) while a 120 mV dec$^{-1}$ Tafel slope is indicative of the first electron transfer step being rate determining. This near linear trend in Tafel slope for varying mole fractions would suggest a linear superposition type behavior of the two mixed oxides i.e. two different but parallel OER pathways are occurring at discrete sites of each oxide. This near linear trend in Tafel slope for varying mole fractions would suggest a linear superposition type behavior of the two mixed oxides i.e. two different but parallel OER pathways are occurring at discrete sites of each oxide with each material acting independently. This linear behaviour in the Tafel slope was mirrored for various concentrations (0.5-5 M) of NaOH and can be seen in fig. 5

Fig. 4 Steady state polarisation curves of (a) 100 (b) 75 (c) 50 (d) 0 mol % RuO$_2$ added to a NiO electrode on a Ti substrate. Electrolyte is 5 M NaOH. Scan rate: 1 mV s$^{-1}$. Potentials quoted against Hg/HgO
Conversely, and more interestingly, the dependence of the OER overpotential on increasing addition of RuO$_2$ displays a decreasing non-linear behaviour. Fig. 6 below shows a law of diminishing return behaviour with increasing additions of RuO$_2$. The overpotential drops by 0.13 V or ~30 % with the addition of 25 mol % RuO$_2$ while additions of RuO$_2$ after 50 mol % have little effect of further lowering the overpotential. Thus additions of RuO$_2$ seem to lower the OER activation barrier for the entire mixed oxide system which suggests some degree of interaction between the two oxides rather than them acting independently as stated previously. This dual behaviour is currently being investigated and will be elucidated in a future more detailed study.

Fig. 5 Effect on the Tafel slope by varying the mole fraction of RuO$_2$ on a NiO electrode for several NaOH concentrations (0.5-5 M).

Conversely, and more interestingly, the dependence of the OER overpotential on increasing addition of RuO$_2$ displays a decreasing non-linear behaviour. Fig. 6 below shows a law of diminishing return behaviour with increasing additions of RuO$_2$. The overpotential drops by 0.13 V or ~30 % with the addition of 25 mol % RuO$_2$ while additions of RuO$_2$ after 50 mol % have little effect of further lowering the overpotential. Thus additions of RuO$_2$ seem to lower the OER activation barrier for the entire mixed oxide system which suggests some degree of interaction between the two oxides rather than them acting independently as stated previously. This dual behaviour is currently being investigated and will be elucidated in a future more detailed study.

Fig. 6 The dependence of the oxygen evolution reaction overpotential in 5 M NaOH on the mole fraction of RuO$_2$ added to a NiO electrode on a Ti substrate.

Reaction order studies $m_{OH^-} = \frac{\partial \log i}{\partial \log a_{OH^-}}$ were also carried out for a variety of mole fractions of RuO$_2$ as seen in fig. 7 below. A reaction order was obtained by measuring the current at a fixed overpotential in a wide variety of aqueous NaOH solutions, typically in the concentration range 0.5 M – 5 M. Concentrations were converted to activities using the required activity coefficients to accurately reflect the non-ideal nature of NaOH.
Reaction orders of ca. 0.5 were obtained for additions of ≥ 25 mol % RuO$_2$ and remained relatively invariant with further additions of RuO$_2$. A reaction order of near unity was obtained for a 0 mol % RuO$_2$ electrode or a NiO electrode. A reaction order of unity has been reported previously for NiO prepared in this fashion and indeed for other nickel oxides and hydroxides prepared using different methodologies.

Fig. 7 Reaction order plots for several mole fractions of RuO$_2$.

**OER mechanism**

Using the kinetic data obtained, we propose a possible OER mechanism at NiO and RuO$_2$ surfaces. We have previously reported a proposed mechanism for the OER at metal oxides based on the surfao group concept [11-13]. The mechanism has been applied to various forms of iron, nickel, ruthenium and iridium oxide, and has the advantage of enabling a direct relationship to molecular water catalysis. The proposed catalytic cycle for the OER for NiO is shown below. Our experimental kinetic data shows a Tafel slope of ca. 120 mV dec$^{-1}$ or 2(2,303RT/F) and $m_{OH^{-}}$ of unity. To accommodate these observations we propose step A.II as being rate determining. Step A.I is considered a pre-equilibrium step. The complete reaction can therefore be written schematically as follows

$$SOH_2 + OH \rightarrow SOH + H_2O \quad (A.I)$$

$$SOH \rightarrow SOH + e^- \quad (A.II)$$

$$SOH + OH \rightarrow SO^- + H_2O \quad (A.III)$$

$$SO^- \rightarrow SO + e^- \quad (A.IV)$$

$$SO + OH \rightarrow SOOH + e^- \quad (A.V)$$

$$SOOH + OH \rightarrow SO_2 + H_2O + e^- \quad (A.VI)$$
$SO_2 + OH \rightarrow SOH + O_2$ \hspace{1cm} (A.VII)

where S represents a surfaquo group attached to the bulk NiO. The surfaquo group concept proposed envisages hydrated interlinked oxy-metal surface active groups, hence the term surfaquo group, which facilitate the OER at the surface. We are likening the OER behaviour of NiO prepared by this thermal decomposition method to other nickel oxides/hydroxides formed by potential multicycling in base\textsuperscript{12}, electroprecipitation\textsuperscript{14} and by cathodic deposition\textsuperscript{15}. The nickel cations at the surface tend to undergo some degree of hydration i.e. become coordinated to surrounding water molecules, in the basic environment. The coordinated water molecules are therefore the source of the discharged hydroxide ion in step I. This hydration of thermally prepared NiO is therefore not unreasonable to expect. The surfaquo group concept attempts to bridge the link between these heterogeneous electrocatalysts and homogeneous molecular catalysts for water oxidation which is an area of current intense study by groups such as Llobet and coworkers\textsuperscript{16, 17}. The OER catalytic cycle can be seen pictorially in fig. 8 which shows the octahedrally coordinated surfaquo group attached to the bulk NiO.

We can now conduct a kinetic analysis of the mechanism shown in the scheme above. The total flux for the reaction can be written as

$$f_E = k'_2 \Gamma_{SOH^-}$$ \hspace{1cm} (3)

where $f_E$ is the total flux, $k'_2$ is the rate constant for the forward reaction in step II and $\Gamma_{SOH^-}$ is the surface coverage of the indicated species. The total flux for step I can be written as

$$f_1 = k_1 \Gamma_{SOH^-} a_{OH^-}$$ \hspace{1cm} (4)

Assuming pseudo-equilibrium conditions where $f_2 = f_1 = f_{-1} = f_2$ with the reverse of $f_1$ being given by

$$f_{-1} = k_{-1} \Gamma_{SOH^-} a_{H2O}$$ \hspace{1cm} (5)

therefore we can write the surface coverage of the SOH$^-$ species as

$$\Gamma_{SOH^-} = \frac{k_1}{k_{-1}} \Gamma_{SOH^-} a_{OH^-} a_{H2O}^{-1}$$ \hspace{1cm} (6)
which gives the total reaction flux as

$$f_\Sigma = k'_2 \Gamma_2 SOH^- = k'_2 K_1 \Gamma_2 SOH^- a_{OH^-} a_{H_2O}^{-1} \exp \left[ \frac{\beta F \eta}{RT} \right]$$  \hspace{1cm} (7)

Where $\eta$ is the overpotential, $\beta$ is the symmetry factor and $F$, $R$ and $T$ have their usual meanings. Assuming $\beta = 1/2$, this predicts a Tafel slope of $2(2.303RT)/F$ which is approximately $120$ mV dec$^{-1}$ and a reaction order of unity. Our experimental Tafel slope of $124 \pm 3$ mV dec$^{-1}$ and reaction order of $0.89 \pm 0.04$ agrees excellently with theory. The kinetic data obtained for 100 mol % RuO$_2$ electrode can also be incorporated into a proposed mechanism for the OER. The following mechanism was previously proposed by Lyons and Floquet$^4$ and has been adapted for use here and, similarly to scheme A, starts with the initial discharge of a hydroxide ion. A more in depth analysis of the mechanism can be found in an extensive review of the OER at metal oxides published recently by our group$^{18}$. This hydroxide discharge is then thought to be followed by a structural rearrangement to a more energetically favourable arrangement to accommodate the extra hydroxide ion. Subsequent to this rearrangement, a second electron discharge occurs forming an unstable Ru (VIII) species which acts as a precursor to the generation of oxygen.

$$(-O-)_2 RuO'(OH)_3 + OH \leftrightarrow (-O-)_2 Ru. O'(OH) + H_2O + e^- $$ \hspace{1cm} (B.I)

$$(-O-)_2 RuO.O'(OH) \rightarrow (-O-)_2 RuO_2(OH) + e^- $$ \hspace{1cm} (B.II)

$$(-O-)_2 RuO_2(OH) + 2OH \rightarrow (-O-)_2 RuO_2 + 2H_2O + O_2 + 2e^- $$ \hspace{1cm} (B.III)
$$(-O-)_2\text{RuO}_2 + OH^- + H_2O \rightarrow (-O-)_2\text{RuO'}(OH)_3$$  \hspace{1cm} (B.IV)

An observed Tafel slope of 40 mV dec$^{-1}$, shown in fig. 4, indicates that the second electron transfer step B.II will be rate determining at low overpotentials. A Tafel slope of 120 mV dec$^{-1}$ was observed, though not shown in fig. 4, indicating that the RDS switches to the first electron transfer step B.I at higher overpotentials. Scheme B is represented pictorially in fig. 9 below.

Lyons and Floquet arrive at a theoretical expression for the total flux given by

$$f_\Sigma = \frac{k_1^0 k_2^0 \Gamma_s a_{OH^-} \exp[\beta \eta]}{k_1^0 a_{H_2O} \exp[-\eta] + k_2^0}$$  \hspace{1cm} (8)

and at low overpotentials assuming $k_2^0 \ll k_{-1}^0$ (8) reduces to

$$f_\Sigma = K^0 a_{H_2O}^{-1} \Gamma_s a_{OH^-} \exp[(1 + \beta)\eta]$$  \hspace{1cm} (9)

which predicts a reaction order of unity and a Tafel slope of 40 mV dec$^{-1}$. The Tafel slope for the theoretical analysis agrees with our experimental Tafel slope of 39±2 mV dec$^{-1}$. However, our observed reaction order of 0.5 for RuO$_2$ is at difference to the predicted value of 1 and indeed experimentally seen by Floquet and Lyons despite the synthesis condition being identical. One possibility is that the electrode undergoes some ageing.

Fig. 9 Pictorial representation of the OER cycle for RuO$_2$ in base.
type processes upon successive potential multicycling regimes, polarization etc. which will affect the surface morphology and hence the reaction order as noted by Trasatti\cite{19}. Indeed, the prior usage history of the electrode can drastically affect the measured properties. For example, the Tafel slope was found to vary between 40 and 60 mV dec\textsuperscript{-1} depending on the prior polarization regime applied before the measurement was taken. The degree of interaction between the hydroxide ions and the surfaceto sites will be morphology dependent and hence if this access is somehow restricted one would expect to see a lower reaction order than unity even though the OER mechanism remains as is. The reaction order did however remain relatively invariant after extended OER polarization regimes. SEM images are being prepared at the time of writing to monitor the surface morphology with electrode use and will be published in future work.

Another facet of the reaction order studies is to rationalize the domination on the behaviour of RuO\textsubscript{2} on the value of m\textsubscript{OH}\textsuperscript{-} for even minor additions to a NiO film. As noted in the previous section, NiO seems to have little or no influence on the mixed oxide system. One possibility for this is that RuO\textsubscript{2} is found primarily at the surface and it is largely the RuO\textsubscript{2} that experiences the majority of the interaction and hence the m\textsubscript{OH}\textsuperscript{-} value will be largely ‘ruthenium like’. Again, SEM and EDX analysis are currently being carried out to test this suggestion and will be reported in the near future.

Conclusion

In conclusion, we have shown that the RuO\textsubscript{2}/NiO mixed oxide electrode is extremely effective at catalyzing water oxidation. Small additions \textasciitilde25 mol % of RuO\textsubscript{2} added to an inexpensive NiO electrode drastically lowers the OER overpotential by 0.13 V or ca. 30%. Further additions > 50 mol % RuO\textsubscript{2} gave diminished returns in this regard. Furthermore, we have also obtained kinetic data pertaining to the OER for both RuO\textsubscript{2} and NiO and proposed an OER mechanism based on this data while incorporating previous work by Lyons and Floquet and others. We have used the surfaceto group concept which consists of surface active sites on the bulk oxide film where the OER is suggested to occur. This surfaceto group concept attempts to bridge the link between heterogeneous electrocatalysis and molecular water oxidation catalysts. Further work is needed to rationalize the reaction order of 0.5 observed which contradicts previous studies reported in the literature on RuO\textsubscript{2} electrodes prepared in the same manner.

Acknowledgments

The Authors are grateful for the financial support of the Trinity Trust and Science Foundation Ireland (SFI) under grant number SFI/10/IN.1/I2969.

References