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Ru\textsubscript{x}Nb\textsubscript{1-x}O\textsubscript{2} catalyst for the oxygen evolution reaction in proton exchange membrane water electrolysers

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\textbf{ABSTRACT}

Bimetallic catalyst system of ruthenium oxide (RuO\textsubscript{2}) and niobium oxide (Nb\textsubscript{2}O\textsubscript{5}) was prepared using the Adams method and the hydrolysis method. Physical and electrochemical characterizations of the catalysts were studied using X-ray diffraction (XRD), Scanning electron microscopy (SEM), cyclic voltammogram (CV) and polarization measurements. Nb\textsubscript{2}O\textsubscript{5} addition to RuO\textsubscript{2} was found to increase the stability of RuO\textsubscript{2}. In Adams method the sodium nitrate was found to be forming complex with Nb\textsubscript{2}O\textsubscript{5} at high temperature reaction. This makes Adams method unsuitable for the synthesis of RuO\textsubscript{2}–Nb\textsubscript{2}O\textsubscript{5} bimetallic system. Hydrolysis method on other hand does not have this problem. But a proper mixture of two oxides was not obtained in hydrolysis method. A lower crystallite size for bimetallic system was obtained with Adams method compared to hydrolysis method. RuO\textsubscript{2} prepared by Adams method had higher activity compared to the hydrolysis counterpart in electrolyzer operation with nafion membrane. A cell voltage of 1.62 V was obtained with RuO\textsubscript{2} (A) at 1 A/cm\textsuperscript{2}. A higher stability for Ru\textsubscript{0.8}Nb\textsubscript{0.2}O\textsubscript{2} (A) compared to RuO\textsubscript{2} (A) was observed in continuous cyclic voltammogram and electrolyzer cell test.

\textbf{1. Introduction}

Current energy demand of the world is satisfied mostly by fossil fuels. Unlimited use of fossil fuels, environmental problems due to emissions from fossil fuel combustions (CO\textsubscript{x}, NO\textsubscript{x}, SO\textsubscript{x}, C\textsubscript{6}H\textsubscript{m}, ashes etc) and increasing global demand for energy has led to the search for alternative clean energy resources such as renewable energy [1,2]. In this respect hydrogen is getting more and more attention recently as its one of the cleanest fuel available and emits nothing but only water on combustion. Hydrogen will play an important role in the future energy scenario to form a sustainable energy carrier. But current hydrogen production is mainly dominated by natural gas reforming and is not eco-friendly as it produces greenhouse gases like CO and CO\textsubscript{2} during the process. Water electrolysis is the most sustainable way for the production of...
hydrogen, but currently only 4% of hydrogen is produced by water electrolysis [3]. Proton exchange membrane water electrolyzer (PEMWE) first developed by General Electric Co. in 1966 is the most attractive and efficient method for the production of hydrogen from water at low temperature [1]. State of the art PEMWE has disadvantages in terms of cost and efficiency. For example higher over-potential for oxygen evolution reaction (OER) and material component cost (PEM, bipolar plates and electrocatalyst) are the major limitation associated with PEM-water electrolyzers.

IrO₂ and RuO₂ are found to be the most active catalyst for the OER [4]. RuO₂ is widely used material in electrochemical capacitors as well and has very high capacitance value of 150–260 μF/cm² [5]. It is widely used in the chlor-alkali industry as dimensionally stable anode (DSA) [6]. The high capacitance value in RuO₂ arises from the pseudo-capacitance by the reaction of proton (H⁺) on the surface of RuO₂ [5]. Low temperature process is normally preferred for the preparation of high surface area and small particle size RuO₂ polycrystalline material [7]. The metal—metal distance and radius of the cations in RuO₂ are such a way that overlapping of inner d orbital is possible and leading to conductivity in the ruthenium oxides [8]. The Adam’s fusion method has been widely used for the preparation of metal oxide since the method was reported in 1923 [9]. Most of the metal oxides reported for electrolysis process are based on DSA technology developed by H. Beer in 1965 for chlor-alkali industry [10].

In DSA type electrodes metal oxides (RuO₂ or IrO₂) are formed on Ti substrates by thermal decomposition of its precursors. However RuO₂ is unstable in the electrolyzer anodic environment and does not have long term stability [11]. Mixtures of RuO₂ and IrO₂ have been studied as anode catalysts and found to have considerable stability and activity [6]. The Ir₀.₆Ru₀.₄O₂ has been found to show best performance by Marshall et al. [12]. RuO₂ and RuO₂ are expensive materials leading to high cost of electrolyzer systems. Various non-noble metal oxides such as SnO₂, TiO₂, Ta₂O₅ were added to the RuO₂ and IrO₂ in view of increasing activity and stability [6,12,14,15]. Depending upon the effectiveness of mixing different outcome can be obtained in mixed oxides [16]. It may either form a solid solution or simply a fine mixture. Increasing the number of components in the catalyst may also lead to a finer morphology because of poor mixing and can increase the surface area [5,17–19]. Metal oxides with similar structure and proper atomic radii to RuO₂ such as SnO₂, TiO₂ may form solid solution with RuO₂ whereas oxides with different crystal structure such as Nb₂O₅ and Ta₂O₅ may not form solid solution. But there are discrepancies in various reports regarding the solid solution formation. This could be because of different conditions used for the preparation. The proper solution formation depends on various factors such as oxidation and precipitation kinetics of two metal ions, solvent used to mix the precursors, heating rate etc [16]. Also in many cases bimetallic system resulted in a surface richer in one composition than other [16].

First DSA electrode containing Nb₂O₅ was developed by Terezo et al. [15] using the polymeric precursor method. It was found that 70:30 mol% ratio of Ti/RuO₂–Nb₂O₅ yielded the highest anodic voltammetric charge (thus higher electrochemical active area) and highest stability among the other compositions studied. RuO₂ and Nb₂O₅ were present as two different crystal structures (rutilic and orthorhombic) at 600 °C calcination temperature and Nb₂O₅ was amorphous at calcination temperatures below 500 °C [15,20]. Crystalline RuO₂ is a good electronic conductor but a very bad proton conductor whereas hydrous Nb₂O₅ on other hand is proton conductor and conductivity depends on the water content [19,21,22]. Adding niobium oxide to RuO₂ will act as network former [19]. Even though the ionic radii of Ru (IV) and Nb (V) are nearly the same its different crystal structural will restrict the formation of solid solution.

Later in a study by Santana et al. [4,23] on DSA type electrode Nb₂O₅ was found to be stabilizing the Ru + Ti + Ce oxide system. They systematically substituted Nb₂O₅ for CeO₂ and found that addition of Nb increased the stability of the catalyst. The effect of calcination temperature, precursor salt, molar ratios of reducing agents of IrO₂–Nb₂O₅ DSA electrode has also been studied by Santana et al. [20]. Recently Marshall et al. [12] studied the effect of Ta₂O₅ addition to the Ir + Ru oxide system prepared by the aqueous hydrolysis method. The particle size and resistivity of the catalyst was found to increase with Ta content in Ir₀.₆Ru₀.₄O₂. They found that approximately 20 mol% of Ta could be added without compromising the activity and stability of catalyst significantly.

This current study is based upon the hypothesis that a solid-state mixture between the active oxide (RuO₂) and the stabilizing oxide (Nb₂O₅) is the best anode catalyst for acid water electrolysis considering both activity and stability. Nb₂O₅ has a good stabilizing effect similar to Ta₂O₅ but cheaper in cost [24]. Most of the studies in literature on RuO₂–Nb₂O₅ catalyst system were carried out as DSA electrode on Ti support whereby effects of TiO₂ on the properties of the catalyst especially on the stability cannot be neglected. As PEMWE uses powder catalyst system, it is important to study OER activity of the catalyst in membrane electrode assembly (MEA). A major focus is on the effect of the addition of niobium on ruthenium in terms of physical and electrochemical properties. Two preparation methods are also compared namely the Adams method and the hydrolysis method, in an attempt to prepare the optimum ruthenium-niobium mixture.

2. Experimental methods

Ru (III) chloride (Ru content 45–55%) and NbCl₅ (99.995 trace metal basis) from Sigma Aldrich were used as Ru and Nb precursors respectively. NaNO₃ (99.5% assay) reagent grade from Merck, 2 propanol from Fischer scientific were used as reagent and solvent respectively.

2.1. Electrocatalyst syntheses

2.1.1. Adams fusion method
RuCl₃ precursor as required by stoichiometry was dissolved in isopropanol (IP) solvent and stirred for 3 h. To this NbCl₅ solution (added as solution in IP) was added as required by the stoichiometry. The total metal concentration was approximately 0.01 M. To this 20 g of finely grounded NaNO₃ was added and stirred well for 4–5 h. The solvent was then evaporated slowly in an air oven at 75 °C. The sample was
transferred to a silica crucible and calcined in a muffle furnace at 500 °C for 1 h. The sample was kept in the furnace until the temperature reached room temperature. During heat treatment the NaNO₃ (melting point = 308 °C) forms a oxidizing melt, dissolves the precursors and react with it to form nitrates as given in Eq. (1) [25]. The excess salt was then dissolved in DI water. The sample was washed and centrifuged using excess DI water and dried in the air oven at 75 °C overnight. Ru,Nbₓ₋ₓO₂ (x = 1, 0.8, 0.6, 0.4, 0) materials were prepared using this procedure by varying the precursor for required molar ratios of Ru and Nb. The reaction taking place in the Adam’s fusion method [9] can be written as, 

\[
\text{RuCl}_3 + 3\text{NaNO}_3 \xrightarrow{\Delta} 3\text{NaCl} + \text{Ru(NO}_3\text{)}_3
\]

(1)

\[
\text{Ru(NO}_3\text{)}_3 \xrightarrow{\Delta} \text{RuO}_2 + 3\text{NO}_2 \uparrow + \frac{1}{2}\text{O}_2 \uparrow
\]

(2)

The advantage of Adam’s fusion method is that two of the bi-products formed are gases (NO₂ and O₂) and are released from the system; only solid bi-product is sodium chloride which can be dissolved in water and is separated easily.

2.1.2. Hydrolysis method

The calculated amount of RuCl₃ and NbCl₅ (as solution in isopropanol) according to the stoichiometry was dissolved in DI water to yield a total metal concentration of 0.01 M. To this, 0.5 M NaOH solution was added. Metal:NaOH molar ratio was maintained as 1:20. This mixture was then heated at 80 °C with stirring for 1 h. A deep blue colored complex was formed on heating and on drying the precipitate completely disappeared. A white jelly precipitate was formed but the precipitate was not very dense and was known but it was assumed to be an aqua-hydroxochloro complex [26]. The solution was stirred overnight, centrifuged and heat treated at 400 °C for 30 min to form an oxide. A temperature of 400 °C was reported to be giving better performance by other groups [27,28]. The precipitate at higher temperatures above 300 °C gives anhydrous RuO₂ [5]. Synthesis of Nb₂O₅ by the same method was also attempted. A white jelly precipitate was formed but the precipitate was not very dense and on drying the precipitate completely disappeared.

The catalysts prepared by the Adams fusion method are represented as RuₓNb₁₋ₓO₂ (A) and those prepared by the hydrolysis method are represented as RuₓNb₁₋ₓO₂ (H) throughout this study. Membrane electrode assembly (MEA) was prepared using these catalysts and tested in PEMWE cell.

2.2. Electro catalyst characterization

2.2.1. Physical characterization

The X-ray diffraction (XRD) analyses of the samples were carried out using a PANalytical X’Pert Pro MPD, (powered by a Philips PW3040/60 X-ray generator and fitted with an X’Celerator) with Cu-Kα radiation (λ = 1.541874 A). The data were collected over a range of 5° to 100° 2θ with a step size of 0.0334° 2θ and nominal time per step of 200 s. All scans were carried out in ‘continuous’ mode using the X’Celerator RTMS detector. Phase identification was carried out by means of the X’Pert accompanying software program PANalytical High Score Plus in conjunction with the ICDD Powder Diffraction File 2 database (1999) and the Crystallography Open Database (September 2011; www.crystallography.net).

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) analyses were carried out in Fei XL30 Esem-Feg (Environmental Scanning Electron Microscope-Field Emission Gun) at 20 kv for elemental analysis on uncoated samples in low vacuum mode and at 10 kv on gold coated samples in high vacuum mode for the images. The EDX system was a Rontec using Quantax software.

2.2.2. Electrochemical characterization

Voltammetry analyses of the catalysts were conducted using a potentiostat/galvanostat (Aultlab) and a homemade tantalum working electrode (4 mm diameter) which was well polished well with SiC paper (1200, 2400 and 4000 grade) before use. A Ag/AgCl (sat. KCl) and a Pt wire were used as reference and counter electrode respectively. The catalyst ink was prepared by dispersing the catalyst in 0.5 ml solvent (3:2 water: ethanol mixture) containing nafion solution (25 wt.%). The mixture was sonicated in an ultrasonic bath for 30 min before drop casting 10 μl on to the electrode using a micropipette. It was then dried in the air and introduced in the three electrode cell containing 0.5 M H₂SO₄ solution. Nitrogen gas was purged for 15 min before the experiment. A preconidion of the electrode was carried out at 100 mV/s for 10 cycles. Cyclic voltammogram (CV) was carried out starting from higher scan rate of 200 mV/s up to a lower scan rate of 5 mV/s. All potentials in this study are denoted with respect to Ag/AgCl electrode.

Powder conductivity of the sample was measured by pressing the sample in between two copper pistons. The thickness of the powder was measured using a standard micrometer. Resistance of the sample was measured at various thicknesses by passing voltage and measuring current. Conductivity was calculated from the resistance vs. thickness plot.

Membrane Electrode Assembly (MEA) with the commercial and the as prepared catalysts were prepared using the Catalyst Coated Membrane (CCM) method with Nafion® 115 membrane. Hispec Pt/C (40%) and as prepared oxide catalyst were used as cathode and anode catalyst layer respectively. Nafion solution (Sigma Aldrich) was used as ionomer. The electrolysis was carried out in a stainless body cell (4 cm² active area) with two titanium porous sinters. Titanium fiber (Bekentit, Japan, thickness 0.3 mm, porosity 60%) and carbon cloth were used as current collector/backing layer on anode and cathode respectively [29]. Pre-heated de-ionized water from the reservoir was pumped to the cell with the aid of a peristaltic pump at atmospheric pressure and the cell temperature was maintained at 80 °C. The polarization curves (V/I) were recorded potentiostatically from +1 V to +2 V using Neware battery testing system (Neware technology Ltd, China).

3. Results and discussion

3.1. Structures and morphologies

The XRD spectra analysis of RuₓNb₁₋ₓO₂(A) is given in Fig. 1. The peaks indicate the rutile structure of the catalysts (JCPDS-
The peaks at 28, 35, 40 and 54° are RuO2 (110), (101), (111) and (211) respectively. Peaks at 22.9, 32.59 and 46.7° started appearing upon Nb2O5 addition. These peaks were identified to be NaNbO3 (JCPDS-19-1221) and are represented as NaNb in Fig. 1. This complex formation was due to the reaction between NaNO3 reagent and Nb2O5 at high temperature as reported for Nb and Mo elsewhere [30,31].

Peaks intensities of NaNbO3 peaks were lower for Ru0.8N-b0.2O2(A) and were due to the low weight% of Nb2O5 in the catalyst. RuO2 peaks were clearly visible even in Nb2O5 rich compositions and thus can be concluded that RuO2 was crystallizing well in our experimental conditions and the presence of niobium oxide did not depress crystallization of RuO2. Crystallinity is higher for RuO2 as it crystallizes before Nb2O5. Since Nb2O5 and Ta2O5 are amorphous at temperatures below 500 °C [13,15,20], it can be confirmed that the peaks associated with Nb2O5 in the XRD are NaNbO3 (which is formed and crystallized at lower temperature) and not Nb2O5. The differences in crystal structure of Nb2O5 and RuO2 will make it difficult to form a solid solution. But in a mixed oxide system, in order to have an influence on catalyst activity, a perfect solid solution formation is not required, but a fine mixing of metals is sufficient [15,32]. In DSA electrodes, IrO2-Ta2O5 catalysts were found to be the best catalysts for OER which cannot be explained based on the solid solution formation between the two metal oxides [13,15]. In fact since the RuO2 and Nb2O5 possess two different crystalline structures a tension between the two species is predominantly present at higher crystallinity and this tension tend to increase on Nb2O5 crystallization in turn decreasing the catalytic activity [15].

The crystallite sizes of the catalysts were determined using the Scherrer’s Eq. (3),

$$t = \frac{0.9 \lambda}{\beta \cos \theta} \quad (3)$$

where ‘t’ is the crystallite size, \(\lambda\) is the wavelength of the X-ray, \(\beta\) is the full width at half maximum and \(\theta\) is the position of the peak. Three major peaks at 28, 35 and 54° were used to calculate the average crystallite sizes. The crystallite sizes of Ru0.8Nb0.2O2(A) calculated from XRD are shown in Table 1. The lowest crystallite size was found to be for RuO2(A) (8–9 nm). A gradual increase in the crystallite sizes was evident on Nb2O5 addition. This is partly because of lack of solid solution formation between Nb2O5 and RuO2 as both have different crystalline structures and partly because of sodium–niobium complex formation. The crystallite sizes of Ru0.6Nb0.4O2(A) and Ru0.4Nb0.6O2(A) were almost similar (~3 nm difference) due to the low Nb2O5 content and thus low NaNbO3. There is a steep increase in crystallite sizes from Ru0.8Nb0.2O2(A) to Ru0.4Nb0.6O2(A) due to the higher content of Na(I) ion which has a very large ionic radii compared to Ru(IV) and Nb(V). Lower crystallite sizes may indicate a higher geometric surface area but do not necessarily lead to electrochemical activity since inert Nb2O5 dilute the RuO2 catalyst [14].

In order to study the effect of Na–Nb complex formation with respect to temperature, Ru0.8Nb0.2O2(A) composition was selected and was prepared at different calcination temperatures. The XRD plots of these compositions were prepared at various calcinations temperatures are shown in Fig. 2. The increased intensity of RuO2 peak with increasing calcination temperature indicates the increase in crystallization at high temperature. Variations in the intensity of the peaks of NaNbO3 were very clear as the calcination temperature was increased from 400 °C to 550 °C. The NaNbO3 peak started to appear above calcination temperature 450 °C and thus it can be concluded that NaNbO3 complex formation occurs only above 400 °C. This behavior is prominent in Adams fusion method as pure NaNO3 is used as oxidizing agent. An increase in crystallite size is also clear with respect to the calcination temperature (Table 2). The increase in crystallite size was smaller from 400 °C to 450 °C, but from 450 to 500 °C a steep increase is observed. This is due to the formation of NaNbO3 complex above 450 °C as previously explained. It can be assumed that the increase in particle size in ruthenium–niobium mixture here is mainly due to the sodium–niobium complex more than that of effect of niobium oxide addition to ruthenium oxide.

The XRD spectrum of Ru0.8Nb0.2O2(H) is given in Fig. 3. The XRD behavior of RuO2(H) was similar to RuO2(A). Both shows well-defined rutile structures; however Nb addition gave different patterns in both methods of preparation.

Table 1 – Average crystallite size of Ru0.8Nb0.2O2(A) calculated using Scherrer equation from XRD.

<table>
<thead>
<tr>
<th>x-Value</th>
<th>t1</th>
<th>t2</th>
<th>t3</th>
<th>taverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.27</td>
<td>9.05</td>
<td>8.345</td>
<td>8.55</td>
</tr>
<tr>
<td>0.8</td>
<td>10.63</td>
<td>14.12</td>
<td>10.38</td>
<td>11.7</td>
</tr>
<tr>
<td>0.6</td>
<td>19.04</td>
<td>22.52</td>
<td>14.635</td>
<td>18.73</td>
</tr>
<tr>
<td>0.4</td>
<td>40.9</td>
<td>37.86</td>
<td>27.89</td>
<td>35.55</td>
</tr>
</tbody>
</table>

Fig. 1 – XRD spectra of Ru0.8Nb0.2O2(A) with x value 1, 0.8, 0.6, 0.4 and 0.
of ruthenium aqua-hydroxide complex intermediates [26]. The peaks of RuO₂ in Fig. 3 showed amorphous nature (broader peak) at high Nb₂O₅ content. Pure Nb₂O₅ was also prepared using hydrolysis method but unfortunately failed as explained in the experimental section. The difficulty in obtaining a precipitate of Nb₂O₅ was reported elsewhere [33]. However the presence of Nb₂O₅ in all other compositions were detected in EDX analyses caused by the precursor of ruthenium acting as a nuclei for the precipitation of Nb₂O₅. Such nuclei are not available when preparing Nb₂O₅. Since in the Adams method no effect on crystallization of RuO₂ was found on Nb₂O₅ addition in XRD, the different hydrolyzing behavior of NbCl₅ and RuCl₃ could be the reason for the amorphous nature at high niobium content in the hydrolysis method. The small peaks which appear only at higher Nb content (Ru₀.₄Nb₀.₆O₂) at around 22 and 33° are associated to sodium niobium complexes formed from the NaOH impurity. Crystallite sizes of the catalysts prepared by hydrolysis method are given in Table 3. The table shows that the crystallite sizes of bimetallic catalyst by Adams method are lower than that of hydrolysis method. The reason for this is not very clear. It cannot be explained based on crystalline nature of the catalyst since hydrolysis method gives more amorphous nature, its crystallite size should be smaller than that in Adams method. Even though in both methods solid solution formation will not occur, a better interaction between the two oxides (or a partial solid solution) is evident in Adams method whereas in hydrolysis method both oxides form simple physical mixtures with lower interaction between them. The large increase in crystallite size for RuₓNb₁₋ₓO₂ above 60% Nb₂O₅ addition in Adams fusion method can be mainly attributed to the presence of sodium in the lattice.

Crystallite sizes were found to increase on Nb₂O₅ addition in hydrolysis method as well. Ru₀.₄Nb₀.₆O₂(H) showed lower crystallite sizes compared to other. The crystallite size of this composition calculated from Scherrer equation may not be accurate since the wide peak in XRD is more likely due to amorphous nature of the material. The XRD analysis confirms the amorphous nature of the catalyst at higher Nb content. The peaks at ~27° and ~35° are not well resolved at high Nb₂O₅ content indicating that niobium oxide crystallization was not complete at 400°C. This was also the case in the Adams fusion method but RuO₂ formation was complete even at 400°C in the hydrolysis method whereby peaks were well resolved unlike in the fusion method. Here a distinction has to be made in both processes as nitrates are the intermediate in the fusion method for decomposition and hydroxides are the intermediates for decomposition in the hydrolysis method. The decomposition of nitrates produces less crystalline RuO₂ [34]. Crystallization in the hydrolysis method was easier than in the fusion method. This could be due to the fact that in the fusion method the oxide formation reaction takes place in many steps, for example (i) dispersion of precursor in NaNO₃

| Table 2 – Average crystallite sizes of Ru₀.₈Nb₀.₂O₂(A) calcined at different temperature. |
|---------|---------|---------|---------|------|
| Calcination temperature (°C) | Crystallite size (nm) |
|        | t₁      | t₂      | t₃      | taverage |
| 400    | 5.31    | 7.5     | 6.07    | 6.29     |
| 450    | 8.62    | 11.11   | 8.93    | 9.55     |
| 500    | 28.23   | 27.77   | 22.89   | 26.23    |
| 550    | 38.98   | 37.86   | 28.79   | 35.21    |

| Table 3 – Average crystallite size of RuₓNb₁₋ₓO₂(H) calculated using the Scherrer equation from XRD. |
|---------|---------|---------|---------|------|
| x-Value | Crystallite size (nm) |
|        | t₁      | t₂      | t₃      | taverage |
| 1      | 13.2    | 13.6    | 11.74   | 12.8    |
| 0.8    | 24.076  | 26.87   | 27.2    | 26.04   |
| 0.6    | 24.805  | 23.14   | 17.5    | 21.815  |
| 0.4    | 6.013   | 10.04   | 10.98   | 9.041   |

![Fig. 2 – XRD spectra of Ru₀.₈Nb₀.₂O₂(A) prepared at different calcination temperatures.](image)

![Fig. 3 – XRD of RuₓNb₁₋ₓO₂(H) with x value 1, 0.8, 0.6 and 0.4.](image)
(ii) melting of NaNO₃ (308 °C) (iii) reaction of the precursor with the melt NaNO₃ to form nitrates (iv) decomposition of nitrates to form their respective oxides by releasing NO₂ gas whereas in hydrolysis the overall mechanism is governed by the thermal decomposition of hydroxide which is formed before the calcination stage. The intermediate steps involved in the hydrolysis method are less than that in the fusion method during the oxide formation.

3.1.1. Morphology

SEM and TEM techniques were used to observe the morphology of the catalysts. The RuO₂ (A) sample showed well crystalline particle structure. Fine particles can be seen in SEM (Fig. 4a and b). It seems that the particles are more dense and agglomerated. Ru₀.₈Nb₀.₂O₂₃ (A) also shows a similar morphology as RuO₂ (A). The hydrolysis method gives more uniform particles compared to Adams method (Fig. 4c and d). The particle size is higher than that of Adams method. The difference in morphology is due to the difference in preparation method. More agglomerated structure in Adams method may be due to the high temperature used for the synthesis. Since temperature used for hydrolysis method here is 400 °C, the formed oxide is likely to contain some amorphous hydrous oxide as well.

3.1.2. Powder conductivity

A linear relationship was observed for the thickness vs. resistance plot (Fig. 5 insert) of the powder sample indicating ohmic behavior of the samples. The powder conductivity of the sample is shown in Fig. 5. The RuO₂(A) exhibited higher conductivity than RuO₂(H). This is mainly due to the higher crystallinity of the catalysts prepared at 500 °C compared to RuO₂ (H) prepared at 400 °C, in other words, a higher crystallinity increases the electronic conductivity of the particle.

However, the electronic conductivity of RuₓNb₁₋ₓO₂ prepared by both methods decreases on Nb₂O₅ addition, a sharp decrease in the conductivity was observed for the catalysts prepared by the Adams method than in the hydrolysis method. The higher decrease for the Adams method is caused by the sodium ion in the catalyst. The electronic conductivity in the catalyst is mainly attributed to the RuO₂ network as Nb₂O₅ is an insulator. The presence of non-conducting particles in the catalyst may restrict the electron conduction path in turn increasing the overall resistance of the catalyst layer. This issue is more severe if the two components do not form a solid solution. If a proper solid solution is formed, the overall resistivity of the catalyst is expected to be lower or similar to the conducting component. An effect of calcination temperature on the powder conductivity of Ru₀.₈Nb₀.₂O₂ (A) is shown in Fig. 6. Contrary to the expected increase, the conductivity values decrease due to the sodium–niobium complex formation. Above 450 °C the sodium–niobium complex starts to form as indicated by XRD (Fig. 2). The conductivity of the compositions prepared at 400 °C and 450 °C were similar.

Fig. 4 – SEM picture of (a) RuO₂(A) (b) Ru₀.₈Nb₀.₂O₂₃(A) (c) RuO₂(H) (d) Ru₀.₈Nb₀.₂O₂₃(H) (magnification 50×K).
4. Electrochemical characterization

4.1. Cyclic voltammetry

The electrochemical performance of the prepared catalyst samples was tested by cyclic voltammetry. CV of RuO₂ (A) is shown in Fig. 7. The RuO₂(A) shows common shape and features of the rutile RuO₂. A similar shape for crystalline RuO₂ is reported elsewhere [30,36] due to the redox charge transition attributed to the Ru(III)/Ru(IV) and Ru(IV)/Ru(V) surface transitions respectively [30,36] due to the redox charge transition between the hydrogen ion (H⁺) and RuO₂ surface [8,37] as shown below,

\[
\text{RuO}_2(OH)_x + \delta H^+ + \delta e^- \rightleftharpoons \text{RuO}_{2-x}(OH)_{x+y}
\]  

(4)

For all compositions current density decreased with scan rate. The characteristic redox peaks of RuO₂ disappeared on Nb₂O₅ addition. A similar behavior was also reported for DSA type electrode [15]. Oxygen evolution currents were also suppressed on Nb₂O₅ addition. The RuO₂(A) and Ru₂₋₈Nb₂₋₈O₂(A) sample potential curves were almost symmetrical around zero current indicating that they act as capacitor. Lower activity above 20% Nb₂O₅ is due to the dilution of RuO₂ by Nb₂O₅ and the sodium–niobium complex formation. Capacitance values were calculated from,

\[
C = i/(dE/dt)
\]  

(5)

where \(i\) is the current and \(dE/dt\) is the scan rate[13]. Since in metal oxide double layer capacitance and pseudo-capacitance coexist, it is difficult to differentiate between the two[13]. Thus the calculated capacitance \(C\) includes both the double layer and pseudo-capacitance contribution. The current density at +0.65 V (vs. Ag/AgCl) where no redox reaction occurs is used to calculate capacitance. Here, it was found that the specific capacitance of RuO₂ (A) and Ru₂₋₈Nb₂₋₈O₂ (A) were similar (50.24 F g⁻¹) for our experimental condition. A similar behavior on Nb₂O₅ addition to RuO₂ was reported by Brumbach et al.[19] whereas Terezzo et al. [15] reported an increase in anodic charge on 30% Nb₂O₅ addition to RuO₂. This was explained to the optimized interconnection of the proton conducting Nb₂O₅ and the electron conducting RuO₂ as well as the morphological changes on Nb₂O₅ addition [15,19]. Since Nb₂O₅ is an electronic insulator the current values in CV is solely due to the RuO₂ network [4,15,19]. As it can be observed from the powder conductivity studies the electronic conduction of Ru₂₋₈Nb₂₋₈O₂ (A) conductivity decreases on Nb₂O₅ addition (Fig. 5) and thus the capacitance behavior can not only be explained on the basis of electronic conduction. The amorphous nature and lower electronic conduction of Nb₂O₅ could be the reason for the asymmetric distortion of the CV curves on Nb₂O₅ addition [19]. The formed Nb₂O₅ partially covers the active RuO₂ sites restricting the proton diffusion which is clear from the CVs as the Faradaic peaks at +0.4 and +0.7 V vs. Ag/AgCl disappear on Nb addition. The distortion of the symmetry of the curves is more pronounced at Nb₂O₅ percentage of above 20%. We assume that an optimized interconnection between the RuO₂ and amorphous Nb₂O₅ (or a partial solid solution formation) gives Ru₂₋₈Nb₂₋₈O₂ (A), the ideal capacitor behavior and similar capacitance to RuO₂(A). Lower RuO₂ content and the presence of sodium ion in the catalyst reduces the specific capacitance of the catalyst above 20% Nb₂O₅ [5].

In order to avoid sodium–niobium complex formation, a hydrolysis method was adopted for synthesis. Since hydroxides are intermediates in hydrolysis method, a lower temperature (400 °C) is used for the calcination. Hydroxides require lower calcination temperature for decomposition as clear from XRD. The CV curve at different composition of Ru₂₋₈Nb₂₋₈O₂(H) prepared by hydrolysis method is given in Fig. 8. The trend of CV curve with respect to composition was same as that in Adams method. Redox peaks of RuO₂ are clear in RuO₂(H) as well. On adding Nb₂O₅, the characteristic peaks are lost as in Adams method. The characteristic redox peaks of RuO₂ are clearer in the Adams method due to higher crystallinity [5]. The rectangular shape obtained for Ru₂₋₈Nb₂₋₈O₂ (A) was not observed in hydrolysis method and may be due to...
the lack of proper interaction between RuO₂ and Nb₂O₅ unlike in Adams method. The lower interaction in hydrolysis method can be either due to the lower calcination temperature or due to the different hydrolyzing behavior of NbCl₅ and RuCl₃. NbCl₅ is an easily hydrolyzing salt compared to RuCl₃ and in a mixture of both, the former hydrolyzes first and the positively charged niobium ions interact with the RuCl₃ preventing the complete oxidation of ruthenium. RuO₂ formed thus will not be crystallized very well at the prepared condition[20].

The specific capacitance of RuO₂(H) and Ru₀.₈Nb₀.₂O₂(H) were 62.8 F/g and 12.56 F/g respectively. As explained by Zhang et al. the capacitance value is higher for RuO₂ prepared at lower calcination temperatures which could explain the higher capacitance of RuO₂ (H) [5]. The difference in capacitance is very high on adding 20% Nb₂O₅ addition unlike in Adams method. This can be due to the lack of proper interaction between RuO₂ and Nb₂O₅ in the catalyst as explained above.

In order to study the effect of calcinations temperature on performance of Ru₀.₈Nb₀.₂O₂ (A), a set of catalyst calcined at different temperature of 400, 450, 500 and 550 °C were prepared. The cyclic voltammogram of which is compared in Fig. 9. The characteristic peaks of RuO₂ starts appearing at calcination temperature of 450 °C and 500 °C. A well-defined redox peaks are clearly seen on the samples prepared at 450 °C and 500 °C. Interestingly a steep change in the shape and active area can be seen for sample prepared at 550 °C. A change in shape of CV curve with respect to calcinations temperature was reported for RuO₂ and IrO₂ [5,38] and a decrease in active area with respect to calcinations temperature was reported. A higher calcination temperature increases the crystallinity and clear peaks were expected. The lower active sites for the samples prepared above 500 °C is partly due to the sintering of particles and partly due to the sodium–niobium complex formation at this temperature which was clear from XRD peak (Fig. 2). Sintering of particle lead to increase in grain size (Table 2) and thus decrease in active area. As explained in Section 3.1 at high temperature both RuO₂ and Nb₂O₅ crystallizes and increased tension between the two decreasing the active area.

5. Stability of the catalyst

The stability of the catalyst was assessed using continuous CV within the potential range +0 to +1.25 V (vs. Ag/AgCl) and data are shown in Fig. 10.

The capacitance as well as the OER current decreases after several cycles of potential scans. This is caused by the dissolution of RuO₂ at high anodic potential to form RuO₄ which dissolves in the solution [36]. The characteristic peaks of RuO₂ are lost after few potential cycles and the decrease in current
is gradual with cycles. The loss of characteristic peaks of RuO₂ after a few cycles clearly indicates the dissolution of the RuO₂. An addition of Nb₂O₅ was found to stabilize the RuO₂ in both synthesis methods. The decrease in oxygen evolution current was lower on Nb₂O₅ addition compared to pure RuO₂. Also the effect of Nb₂O₅ addition to the stability was prominent in Adams method than in hydrolysis (Table 4). This confirms the better mixture formation in Adams method. This clearly indicates the importance of proper mixture (or partial solid solution) formation between RuO₂ and Nb₂O₅ in order to modify the electrochemical properties of the bimetallic system. The higher stability on adding Nb₂O₅ is an interesting feature as the stability of the catalyst during oxygen evolution is an important drawback of RuO₂ catalyst under water electrolysis operations. In this study, an MEA was fabricated in order to investigate the behavior of the catalyst in ‘real’ electrolyzer operations.

### 6. Water electrolysis performance

The MEA performance of the prepared catalyst is shown in Fig. 11. It was found that RuO₂(A) gives the best performance (1.62 V at 1 A cm⁻²) among all the MEA prepared. The lower performance of Ru₀.₈Nb₀.₂O₂ (A) may be due to the complex formation of sodium and niobium and also due to the lower electronic conductivity. It was clear from the powder conductivity data that the difference between conductivity of RuO₂ (A) and Ru₀.₈Nb₀.₂O₂ (A) was more than that of the hydrolysis counterpart. This difference was also shown in the MEA performance. The lower electronic conductivity of the catalyst layer will increase the ohmic drop. No considerable

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**Fig. 8** — CV of RuₙNb₁₋ₙO₂(H) with respect to scan rate. (A) RuO₂ (B) Ru₀.₈Nb₀.₂O₂ (C) Ru₀.₆Nb₀.₄O₂ (D) Ru₀.₄Nb₀.₆O₂ in 0.5 M H₂SO₄.

**Fig. 9** — CV of Ru₀.₈Nb₀.₂O₂(A) prepared at different calcination temperature in 0.5 M H₂SO₄ at 20 mV/s.
difference in performance was found for RuO$_2$ (H) and Ru$_{0.8}$Nb$_{0.2}$O$_2$(H). A difference of 133 mV at 1 A/cm$^2$ was found for RuO$_2$ (A) and RuO$_2$ (H). From XRD and conductivity it was clear that RuO$_2$ (H) has higher crystallite size and lower conductivity than RuO$_2$ (A). This contributes to the lower performance of RuO$_2$ (H).

However the stability of the MEA with Ru$_{0.8}$Nb$_{0.2}$O$_2$ (A) was higher than that of RuO$_2$ (A) after 23 h electrolysis operation using an MEA at 1 A/cm$^2$ current density (Fig. 12). It was also observed that the RuO$_2$ (A) over-potential increases drastically after 20 h of operation whereas Ru$_{0.8}$Nb$_{0.2}$O$_2$ (A) shows relatively better performance. The potential value in Fig. 12 is higher than that given in Fig. 11. The reason for the higher potential is that the MEA was tested after the polarization up to 2 V and the titanium current collector oxidized to non-conducting titanium oxide. This increased the resistance and thus Ohmic voltage drop. But it is still interesting to note that Ru$_{0.8}$Nb$_{0.2}$O$_2$ (A) started at higher potential (~2 V) and maintained that potential almost stable even after 23 h operation whereas RuO$_2$ (A) started at 1.8 V, increases the potential after about 20 h of operation at 1 A/cm$^2$ current density.

Fig. 10 – Stability of the catalysts (A) RuO$_2$(A), (B) Ru$_{0.8}$Nb$_{0.2}$O$_2$(A), (C) RuO$_2$(H), (D) Ru$_{0.8}$Nb$_{0.2}$O$_2$(H).

| Table 4 – The stability of RuO$_2$(A) and Ru$_{0.8}$Nb$_{0.2}$O$_2$(A) from continuous cyclic voltamogram. |
| Catalyst | j(0.4 V) 600th cycle $-$ j(0.4 V) 3rd cycle (A cm$^{-2}$ mg$^{-1}$) | j(1 V) 600th cycle $-$ j(1 V) 3rd cycle (A cm$^{-2}$ mg$^{-1}$) |
| RuO$_2$(A) | $1.674 \times 10^{-2}$ | $1.8261 \times 10^{-2}$ |
| Ru$_{0.8}$Nb$_{0.2}$O$_2$(A) | $6.08 \times 10^{-3}$ | $4.38 \times 10^{-3}$ |
| RuO$_2$(H) | $6.922 \times 10^{-3}$ | $1.225 \times 10^{-2}$ |
| Ru$_{0.8}$Nb$_{0.2}$O$_2$(H) | $2.557 \times 10^{-3}$ | $1.55 \times 10^{-3}$ |

Fig. 11 – MEA performance of Ru$_{x}$Nb$_{1-x}$O$_2$(A) and Ru$_{x}$Nb$_{1-x}$O$_2$(H) as anode catalyst. Nafion-115 membrane, Pt/C(40%) cathode.
A bimetallic RuO$_2$–Nb$_2$O$_5$ catalyst was prepared as an anode catalyst for oxygen evolution reaction using Adams and hydrolysis methods. The Adams method was found to form a sodium–niobium complex during synthesis at temperature above 400 °C. This makes Adams method unsuitable for the synthesis of RuO$_2$–Nb$_2$O$_5$ bimetallic catalyst system. It is assumed that in the Adams method RuO$_2$ forms a better mixture with Nb$_2$O$_5$ (or a partial solid solution) and influence its electrochemical properties. A higher stability was found on adding 20% Nb$_2$O$_5$ to RuO$_2$(A). No enhancement in activity was found due to the dilution of the active component. The increase in stability was more in the Adams method than the hydrolysis method. The hydrolysis method does not have issue of unwanted complex formation, but in this method the Nb intermediate was found to cover the RuO$_2$ active sites during synthesis due to the easily hydrolyzing nature of NbCl$_5$ precursor. A proper solid solution was not formed in hydrolysis method. In both methods an addition of more than 20% Nb$_2$O$_5$ lowered the electronic conductivity and activity of the catalyst. No considerable influence on stability and activity was found on adding 20% Nb$_2$O$_5$ to RuO$_2$ in hydrolysis method. This indicates the importance of partial solid solution (or better mixture) formation between RuO$_2$ and Nb$_2$O$_5$ for modifying the electrochemical properties of RuO$_2$, Ru$_{0.8}$Nb$_{0.2}$O$_2$(A) prepared at different calcinations temperature indicate that sodium–niobium complex formation decrease the activity of the catalyst significantly.

7. Conclusion

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