A process was developed to synthesize ruthenium-based chelate (RuN_x) electrocatalysts for the oxygen reduction reaction, using RuCl₃ and propylene diamine as the Ru and N precursors, respectively. High-temperature pyrolysis has a critical role in the formation of the catalytic Ru–N sites for oxygen reduction. The RuN_x catalyst modified in the presence of nitrogen-containing organic exhibited comparable catalytic activity and selectivity for oxygen reduction to the carbon-supported Pt catalyst in acidic media. The catalyst generates less than 2% hydrogen peroxide during oxygen reduction.

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**Experimental**

Preparation of RuN_x catalysts.—The desired amount of RuCl₃ was dissolved in isopropanol alcohol (100 mL). The solution was refluxed at 80–90°C under stirring conditions. Next, propylene diamine was added into the solution to form Ru–N complexes, followed by the addition of carbon black powders (0.4 g, Ketjen Black). The mixture was refluxed for several hours and then heated under vacuum at 80°C. The resulting powder specimens were heat-treated in an argon atmosphere at various temperatures ranging from 600 to 900°C.

Materials characterizations.—XPS was conducted with a Kratos AXIS 165 high-performance electron spectrometer using a monochromatic Al Kα radiation. Low-resolution survey scans were conducted with a step size of 0.5 eV and a dwell time of 100 ms. Next, high-resolution scans were acquired in N 1s region using a monochromatic Al Kα radiation. The crystal structures of the synthesized catalysts, XRD patterns were recorded with an automated Rigaku diffractometer using Cu Kα radiation over the scanning range of 10–60° at the scan rate of 4° min⁻¹. To determine the particle size of the catalyst, TEM was performed using a Hitachi H-8000 operated at 200 keV.

Electrochemical characterizations.—The RRDE measurements were performed in a three-electrode electrochemical system using a bipotentiostat (Pine Instruments) at room temperature. An RRDE with gold ring (5.52 mm inner diam and 7.16 mm outer diam) and glassy carbon disk (5.0 mm diam) was employed as the working electrode. The catalyst ink was prepared by blending the catalyst powder (8 mg) with isopropanol alcohol (1 mL) in an ultrasonic bath. The catalyst ink (15 μL) was deposited onto the glassy carbon disk, which was previously polished with Al₂O₃ powder. After drying, 10 μL of a mixture of Nafion solution (5 wt %, Aldrich) and isopropyl alcohol was coated onto the catalyst layer to ensure better adhesion of the catalyst on the glassy carbon substrate. The electrolyte was 0.5 M H₂SO₄ solution. A platinum mesh and an Hg/HgSO₄ electrode were used as the counter and reference electrodes, respectively. All potentials in this work were referred to a normal hydrogen electrode (NHE).

In order to estimate the double-layer capacitance, the electrolyte was deaerated by bubbling with N₂, and the cyclic voltammogram was recorded by scanning the disk potential between 0.04 and 1.04 V (NHE) at a rate of 5 mV s⁻¹. Then, the electrocatalytic activity for oxygen reduction was evaluated in the oxygen-saturated electrolyte. The ring potential was held at 1.2 V (NHE) to oxidize H₂O₂ generated during the oxygen reduction reaction.

The Koutecky-Levich equation was used to calculate the kinetically limited current $I_k$.
\[
\frac{1}{I_d} = \frac{1}{I_s} + \frac{1}{I_f} + \frac{1}{nFAC_O Turner 1.5} + \frac{1}{0.2 nFAD_O Turner 2/3 \omega^{1/2} v^{-1/6} C_O Turner 2/3}
\]

where \(I_d\) is the measured disk current, \(I_s\) the diffusion limited current, \(I_f\) the Nafion film diffusion limited current, \(n\) the number of electrons exchanged in the electrochemical reaction, \(F\) the Faraday constant, \(A\) the geometric surface area, \(C_O\) the bulk concentration of oxygen, \(D_O\) the diffusion coefficient of oxygen in the bulk solution, \(\omega\) the rotation rate in rpm, \(v\) the kinematic viscosity of the solution, \(L\) the Nafion film thickness, \(C_f\) the reactant concentration in the Nafion film, and \(D_f\) means the diffusion coefficient of oxygen in the Nafion film. Because the film thickness was reduced to the extent that \(I_f\) becomes significantly larger than \(I_s\) and \(I_f\), the influence of \(I_f\) on the measured current in our experiments was negligible. By plotting \(I_d^{-1}\) vs \(\omega^{-1/2}\) and extending the regression line, the \(y\)-intercept or the inverse of \(I_s\) can be calculated.

**Results and discussion**

Formation of active reaction sites on RuN\(_x\)/C catalysts.— Figure 1 shows polarization curves on the rotating disk electrodes for the RuN\(_x\)/C catalysts pyrolized at 600–900°C. The measurements were performed in 0.5 M H\(_2\)SO\(_4\) solution saturated with oxygen at the potential scan rate of 5 mV s\(^{-1}\) and the rotation speed of 900 rpm.

Figure 1. Polarization curves on the rotating disk electrodes for the RuN\(_x\)/C catalysts pyrolized at 600–900°C. The measurements were performed in 0.5 M H\(_2\)SO\(_4\) solution saturated with oxygen at the potential scan rate of 5 mV s\(^{-1}\) and the rotation speed of 900 rpm.

<table>
<thead>
<tr>
<th>Element</th>
<th>As-refluxed (before heat treatment)</th>
<th>As-pyrolyzed (after heat treatment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru</td>
<td>4.4</td>
<td>1.8</td>
</tr>
<tr>
<td>C</td>
<td>70.3</td>
<td>89.9</td>
</tr>
<tr>
<td>N</td>
<td>18.1</td>
<td>1.8</td>
</tr>
<tr>
<td>O</td>
<td>7.2</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Table 1. Surface compositions of the as-refluxed and as-pyrolyzed RuN\(_x\)/C catalysts determined by XPS.
and the "pyrrolic N," respectively. It is known that the pyridinic N possesses one lone pair of electrons in addition to the one electron donated to the conjugated π bond system, so it provides an orbital in the plane of the graphene layer that is capable for coordinating the metal ions. From the results of RRDE and XPS measurements, it is clear that the high-temperature pyrolysis leads to the formation of Ru clusters coordinated with pyridinic N, and such Ru–N chelate sites are catalytically active for oxygen reduction.

Figure 3 presents the powder XRD patterns of the carbon-supported RuN\textsubscript{x} catalysts which were subjected to pyrolysis at various temperatures. For comparison, the XRD pattern for the as-refluxed catalyst is also shown in Fig. 3, and only a broad diffraction peak resulting from carbon support is observed around 24.5°. The absence of the diffraction peaks from Ru indicates that Ru crystal particles are too small to be detected by the instrument. However, all of the XRD patterns for the as-pyrolyzed catalysts clearly exhibit the characteristic peaks which correspond to crystalline Ru. As indicated in Fig. 3, the diffraction peaks at 38.2, 42.0, and 43.8° are assigned to (100), (002), and (101) planes, respectively.

As the pyrolysis temperature increases from 600 to 800°C, the diffraction peaks of Ru become sharper. That is, the Ru crystallite size gradually increases with increasing pyrolysis temperature, which suggests that lower activity of the as-pyrolyzed catalyst at 800°C results from the agglomeration of Ru crystallite particles. The results also indicated that the pyrolysis temperature plays a critical role in the formation of the active reaction sites. However, higher temperatures than 700 °C cause Ru crystallite particles to agglomerate, resulting in a loss of the catalytic activity.

Effect of nitrogen content on the catalytic activity and selectivity of RuN\textsubscript{x}/C.— Figure 4 shows typical polarization curves on the rotating disk electrodes for the carbon-supported RuN\textsubscript{x} catalysts prepared using different molar ratios of Ru to N in the precursor solution. It is clearly seen that the nitrogen incorporation enhances the catalytic activity toward the oxygen reduction reaction. This fact further confirms that the N-coordinated Ru clusters are catalytically active for oxygen reduction. The catalyst prepared with the Ru/N ratio of 1:20 shows the lowest activation overpotential for oxygen reduction, while the best reduction kinetics is observed on the catalyst with the 1:30 ratio.

The Koutecky-Levich plots obtained at the potential range between 0.5 and 0.7 V (NHE) are presented in Fig. 5 for the catalyst with the Ru/N ratio of 1:20. A linear relationship between \(I_q^2\) and \(\omega^{-1/2}\) is clearly observed and the slope remains nearly constant, regardless of the potential, which indicates that the electrochemical reaction follows a first-order kinetics. The values of \(I_q\) at 0.7 V (NHE) for different Ru/N ratios are listed in Table II. The \(I_q\) value increases with increasing the nitrogen content, which confirms that nitrogen incorporation improves the catalytic activity of RuN\textsubscript{x}/C.

In general, the oxygen reduction reaction proceeds by two pathways as follows:

\[
\begin{align*}
O_2 & \rightarrow O_{2,a}^2 \rightarrow H_2O_{2,a}^3 \rightarrow H_2O \\
\downarrow & 4 \\
H_2O_{2,b} & \rightarrow H_2O
\end{align*}
\]

Figure 3. XRD patterns of the RuN\textsubscript{x}/C catalysts subjected to pyrolysis at 600–800°C. For comparison, the XRD pattern for the as-refluxed catalyst is given in the figure.

Figure 4. Polarization curves on the rotating disk electrodes for the RuN\textsubscript{x}/C catalysts prepared using different molar ratios of Ru to N in the precursor solution.

Figure 5. Koutecky–Levich plots at different potentials measured on the RuN\textsubscript{x}/C catalysts prepared with the Ru/N ratio of 1:20.
Table II. Kinetically limited currents, $I_d$, at 0.7 V (NHE) determined for the RuN$_x$/C catalysts prepared using different molar ratios of Ru to N in the precursor solution.

<table>
<thead>
<tr>
<th>Ru/N</th>
<th>$I_d$ at 0.7 V (NHE) (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:2</td>
<td>0.051</td>
</tr>
<tr>
<td>1:4</td>
<td>0.165</td>
</tr>
<tr>
<td>1:10</td>
<td>0.331</td>
</tr>
<tr>
<td>1:20</td>
<td>0.751</td>
</tr>
<tr>
<td>1:30</td>
<td>0.864</td>
</tr>
</tbody>
</table>

where subscripts $a$ and $b$ denote the species adsorbed on the electrode surface and that in the bulk, respectively. $O_2$ may be directly reduced to $H_2O$ through four-electron transfer (Reaction 1). In parallel, $O_2$ may be reduced to $H_2O_2$ via two-electron transfer (Reaction 2), followed by either reduction of $H_2O_2$ to $H_2O$ (Reaction 3) or transport of the adsorbed $H_2O_2$ to the bulk solution (Reaction 4). In the case of metal-chelate catalysts, $H_2O_2$ is believed to be responsible for the deterioration of electrode performance over time, because it may destroy the active reaction sites by oxidation of nitrogen ligands. In addition, the polymer electrolyte membrane may degrade over time due to attack by peroxide radicals.

Figure 6a presents the ring currents measured for the carbon-supported RuN$_x$ catalysts with different molar Ru/N ratios as a function of the disk potential. The ring current increases with decreasing disk potential, then reaches a maximum value between 0.6 and 0.4 V (NHE), and finally decreases with further decreasing the disk potential. The value of ring current decreases with increasing the N content over the whole potential range, which indicates that the nitrogen incorporation improves the selectivity of the catalyst to four-electron reduction of $O_2$ to $H_2O$.

The percentage of $H_2O_2$ produced was calculated using Eq. 3 and was plotted in Fig. 6b as a function of the disk potential

$$\%H_2O_2 = \frac{200(I_d/N)}{I_d + (I_c/N)}$$

where $I_d$ and $N$ mean the ring current and the collection efficiency, respectively. Here, the value of $N$ was taken as 0.39. The percentage of $H_2O_2$ generated on the cathode decreases with increasing N content. The RuN$_x$/C catalysts with the Ru-to-N ratios of 1:20 and 1:30 generate less than 2% $H_2O_2$ over the whole potential range, which is much lower than that value reported in the literature.

**Surface-modification of RuN$_x$/C catalysts.**— Organic additive, which contains N and O, was incorporated into the precursor solution during refluxing, in an attempt to increase the catalytic activity and selectivity. Figure 7a and b demonstrates polarization curves on the rotating disk electrodes and the percentage of $H_2O_2$, respectively, measured for the RuN$_x$/C catalyst prepared using urea [(NH$_2$)$_2$CO].

It is found that urea has a positive effect on the activation overpotential and the reduction kinetics. The urea-modified RuN$_x$/C catalyst exhibits an onset potential as high as 0.9 V (NHE). Urea chemically modifies the RuN$_x$ catalyst surfaces by providing functional groups of nitrogen and oxygen which contribute to the formation of active reaction sites. Also as presented in Fig. 7b, urea decreases the amount of $H_2O_2$ generated on the cathode.

**Comparative study of Ru-based catalysts synthesized using different methodologies.**— Different types of Ru-based catalysts were synthesized and compared with the RuN$_x$/C catalyst: (i) RuO$_2$/C, (ii) amorphous Mo$_3$Ru$_2$Se$_4$/C, and (iii) Ru–NH$_3$/C. The RuO$_2$/C catalyst was synthesized by a colloidal method developed in our laboratory. The Ru complex colloidal solution was prepared with a slow addition of NaHCO$_3$ into an aqueous RuCl$_3\times$$H_2O$ solution, and then the colloidal particles were adsorbed onto the carbon black under stirring conditions.

The amorphous Mo$_3$Ru$_2$Se$_4$/C catalyst was synthesized by reacting metal carboxyls with Se in xylene at 140°C under stirring and refluxing conditions for 20 h, as described by Solorza-Feria and coworkers. Finally, the Ru–NH$_3$/C catalyst was synthesized by heat-treating Ru$^{III}$-impregnated carbon under an NH$_3$ atmosphere at 800°C for 1 h. Here an NH$_3$ gas was used as the N-precursor instead of propylene diamine.

Figure 8a and b summarizes the polarization curves obtained on the rotating disk electrodes and the percentage of $H_2O_2$, respectively, measured for various Ru-based catalysts. The RRDE data obtained from the commercially available 20 wt % Pt/C catalyst are also given in Fig. 8 for comparison. The urea-modified RuN$_x$/C catalyst shows higher catalytic activity toward the oxygen reduction reaction. As shown in Fig. 8a, the activation overvoltage decreases more than 150 mV when compared with all other Ru-based catalysts.
under study. It produces a smaller amount of \( \text{H}_2\text{O}_2 \) during oxygen reduction, indicating the enhanced catalytic selectivity toward four-electron reduction. The results indicated that RuN\(_x\)/C catalyst modified with urea in this work exhibits comparable catalytic activity and selectivity to the commercial Pt/C catalyst in the RRDE tests. From the TEM analysis, the particle sizes of the RuN\(_x\)/C catalysts were estimated to be ca. 2–4 nm, regardless of the presence and absence of urea, which are about two times smaller than the particle sizes of Mo\(_x\)Ru\(_y\)Se\(_z\)/C and Ru–NH\(_3\)/C (ca. 4–8 nm).

Conclusions

Nanosized Ru–N chelate catalysts were synthesized using RuCl\(_3\) and propylene diamine, followed by heat treatment at 600–900°C. The influence of pyrolysis temperature, nitrogen content, and surface modifier on the catalytic properties has been investigated. XPS and XRD studies showed that the high-temperature pyrolysis plays a critical role in the formation of the active Ru–N sites, but it causes the agglomeration of Ru crystalline particles above 800°C. The RRDE experiments indicated that the nitrogen incorporation improves the catalytic activity and selectivity toward four-electron reduction of molecular oxygen to water. The urea-modified RuN\(_x\)/C catalyst with the particle sizes of 2–4 nm exhibited comparable catalytic activity to the carbon-supported Pt catalyst and generated less than 2% \( \text{H}_2\text{O}_2 \) during oxygen reduction.

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References