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ABSTRACT

We firstly report remarkable stability and performance of non-precious catalyst, nitrogen doped graphene (NG) towards oxygen reduction reaction (ORR) in a protic ionic liquid (N,N-diethylmethylammonium trifluoromethanesulfonate(dema-TfO)) at intermediate temperatures. Our electrochemical results indicate that an enhanced operating temperature has an enhancing effect on ORR activity of NG in dema-TfO. In addition, even after 2000 cycles of potential sweep in the potential range from 1.0 V to 1.5 V vs. RHE at 120°C in dema-TfO, NG keeps the same ORR onset potential with 14% decrease in oxygen reduction current, showing the excellent stability of NG. Whereas commercially available Pt/C (Pt 37.5% in weight) shows 13% negative ORR onset potential shift along with 56% loss of oxygen reduction current during the stability test. TEM and EDS observations taken after durability test were also in agreement with the higher durability of NG over Pt/C at 120°C in dema-TfO. Raman and XPS results taken after the durability test also substantiated the structural stability of NG in dema-TfO at intermediate temperatures. The greater durability and comparable electrochemical activity of NG with Pt/C can unfold the possibilities of non-precious catalyst for intermediate temperature PEFCs.

Keywords: Intermediate Temperature PEFC, Non-precious Catalyst, Ionic Liquid

1. Introduction

It is beyond any doubt that soon we will be completely reliant on renewable energy sources by replacing the finite fossil fuels. In this context, polymer electrolyte fuel cells (PEFCs) have been attracting much attention due to their excellent properties such as high power density, high energy efficiency and wide range of applications in different fields.1–3 However, the use of Pt electrocatalyst and its related issues like cost, efficiency and durability4–6 have been the main challenges which delay the practical application of PEFC to the main stream.7 The development of non-precious catalysts having better durability and excellent electrochemical activity continues to receive significant attention for the last several years. Carbon nanomaterials, especially hetero atom (N, P, S etc.) doped graphene, carbon nanotubes (CNTs) and carbon nanofibers have been widely using as electrocatalysts in various energy devices because of their fascinating properties like high surface area, excellent thermal stability and high catalytic activity.8–11 Particularly, nitrogen doped graphene has got an immense attention because of its promising ability to enhance the oxygen reduction reaction (ORR) in both acidic and alkaline media.7,14–18

Although, there are major advances in the field of electrocatalyst, the other issue facing by the commercialization of PEFC is the selection of electrolyte. The commonly using perfluorinated sulfonic acid polymer electrolytes like Nafion® work only at humidified condition which limits the operating temperature of PEFC below 80°C.19–21 Fuel cells performing at intermediate temperatures (above 100°C) are highly demanded because of the advantages like low CO poisoning,22–25 high electrochemical kinetics26 and ease of heat and water management.24–27 The researchers have been mainly focusing on the fabrication of new proton conducting membranes which can work at elevated temperatures under non-humidified conditions. This includes the development of organic-inorganic composite membranes, acid doped polymer electrolyte membranes, ionic liquids etc.19,24,28,29 Recently, protic ionic liquids, especially N,N-diethylmethylammonium trifluoromethanesulfonate (dema-TfO) has gained considerable attention as an electrolyte for intermediate temperature fuel cells and have shown appreciably high open circuit voltage at elevated temperatures.30–32 These results have triggered the extensive research on dema-TfO based fuel cells with Pt based electrocatalysts to realize the detailed kinetics and mechanistic aspects of oxygen reduction and hydrogen oxidation reactions at high temperatures.33–35 Our group has also focused on dema-TfO and investigated the electrochemical ORR kinetics of Pt in dema-TfO at intermediate temperatures.30,34 Even though CO tolerance and ORR kinetics can be improved at elevated temperatures, the high cost and low durability of Pt are persisting as critical hurdles for wide spread applications of fuel cells. As a consequence, it is essential to explore the possibilities of nonprecious catalysts in ionic liquids at intermediate temperatures.

In this study, we are exploring the possibilities of ORR on non-precious catalyst in dema-TfO and studying the influence of operating temperature on ORR activity along with its stability at intermediate temperatures in order to realize the application of intermediate temperature PEFCs. Here, we synthesized nitrogen doped graphene by simple pyrolysis of urea and graphene oxide (GO) and studied its oxygen reduction activity in dema-TfO from 30°C to 120°C. Interestingly, we have found that the elevated operating temperature has positive effect on electrochemical activity of nitrogen doped graphene in dema-TfO and it exhibits better durability and comparable electrocatalytic activity with commercially available precious Pt/C catalyst at 120°C.

2. Experimental Section

2.1 Materials

Graphene oxide (GO, 4 mg mL−1 dispersion in water) purchased from Sigma Aldrich was used without any purification. Urea was received from Wako chemicals. Nafion® 5 weight% in water was...
purchased from Aldrich. Ultrapure water from Sigma Aldrich was used for all synthesis purposes. N,N-diethylmethylamine (dema) and trifluoromethane sulfonic acid (TfO) were purchased from Tokyo Chemical Industry Co., LTD. (TCI).

2.2 Synthesis of nitrogen doped graphene (NG)

50 mg GO was added to 20 mL ultrapure water and kept stirring for about 30 minute to get uniform dispersion. 2 g urea was added into the GO suspension and then kept stirring at 60°C for drying. The dried powder was loaded on an alumina boat and heat treated at 900°C for 1 h in Ar atmosphere to obtain NG (Scheme 1).

In addition, GO was thermally reduced without urea in the same condition in order to obtain reduced graphene oxide (RGO) for comparison with NG.

2.3 Synthesis of electrolyte (dema-TfO)

Dema-TfO was synthesized according to the previously reported method by the neutralization reaction between equimolar trifluoromethanesulfonic acid (TfO) and N,N-diethylmethylamine (dema) followed by water evaporation. The detailed procedure is as follows. 14.5 g of dema was added to the ultrapure water (100 mL) under stirring and kept cold in ice bath. 25 g of TfO was added slowly by using a dropping funnel. After completing the reaction, all of water was removed using a rotatory evaporator followed by heating at 100°C under vacuum for 48 h before use.

2.4 Characterizations

Thermal stability of prepared catalysts were investigated by thermogravimetric analysis (TA-60WS, Shimadzu) under air atmosphere. Each sample was heated in a platinum pan with a heating rate of 5°C min⁻¹ from room temperature to 800°C. The morphology and elemental composition of samples were analyzed by scanning electron microscopy (SEM) (SEM, JEOL-JSM-6490A) and transmission electron microscopy (TEM) (JEOL-ARM200FCHR) equipped with energy dispersive X-ray spectrometer (EDS). Raman spectra were obtained to measure the extent of graphitization and the defects produced during the heat treatment synthesis, using a spectrometer (NRS-1000, JASCO, excitation at 532 nm). In order to investigate the chemical structure of NG and RGO, X-ray photoelectron spectra (XPS) were measured by Shimadzu Kratos AXIS-NOVA with Al Kα source. The chemical bond energy in XPS spectra was calibrated based on C 1s binding energy (284.6 eV). The spectral fitting was done with CASA XPS software using Shirley background type. Brunauer-Emmett-Teller (BET) specific surface area of NG was measured from the nitrogen adsorption-desorption isotherms at 77 K using Belsorp-mini (BEL Japan, Inc.).

2.5 Electrochemical measurement

Electrochemical measurements were carried out in three electrode system using an electrochemical analyzer ALS 660A BAS Inc. A catalyst coated on a rotating glassy carbon disc (Φ = 5 mm, Pine instruments. Inc.) was used as a working electrode. Pt mesh or graphite rod was used as a counter electrode and a reversible hydrogen electrode (RHE) was used as a reference electrode. RHE was composed of a Pt flag dipped in dema-TfO with continuous hydrogen bubbling and located adjacent to the working electrode by using a Luggin capillary.30,35 The detailed schematic diagram of the electrochemical cell is shown in Scheme 2. Prior to the catalyst loading, the glassy carbon electrode was polished with 0.05 µm polishing alumina powder followed by washing ultrasonically in ultrapure water for 10 minutes. For the preparation of catalyst ink, 1 mg catalyst was ultrasonically dispersed in 1 mL of water-Nafion 9:1 mixture for 2 h. 20 µL of catalyst slurry was coated on a glassy carbon electrode to obtain a total catalyst loading of 0.106 mg cm⁻² on the electrode surface.

The room temperature ORR studies of NG were carried out by linear sweep voltammetry (LSV) in oxygen saturated 0.5 mol dm⁻³ H₂SO₄. Prior to oxygen purging, the electrolyte was degassed by bubbling nitrogen for at least 30 minutes. The number of electrons involved in the ORR reaction mechanism was calculated from the LSVs at different rotating rates using Koutecky-Levich (K-L) equation shown as below:

\[
1/j = 1/j_K + 1/j_L
\]
where \( j_k \) is the kinetic current density and \( j_e \) is the limiting current density. This equation can be written as:

\[
1/j = 1/j_k + 1/B_0 \sqrt{1/2} \\
B = nFD_0^{2/3}B^{-1/6}C_O2
\]

(2)

(3)

\( \omega \) is the rotation speed (200 rpm to 2500 rpm), \( n \) is the number of electrons, \( F \) is the Faraday constant (96485 C mol\(^{-1}\)), \( D_0 \) is the diffusion coefficient of \( O_2 \) (1.4 \( \times \) 10\(^{-5}\) mol cm\(^{-2}\) s\(^{-1}\)), \( \theta \) is the kinetic viscosity (0.010 cm\(^{2}\) s\(^{-1}\)) and \( C_O2 \) is the bulk concentration of \( O_2 \) (1.1 \( \times \) 10\(^{-3}\) mol cm\(^{-3}\)) in the \( H_2SO_4 \) solution.\(^{36} \)

The ionic liquid (dema-TfO) was used as an electrolyte for all intermediate operating temperature electrochemical studies of NG. The experiments were carried out at different temperatures (30°C, 60°C, 90°C and 120°C). The operating temperature was controlled by immersing the cell in a temperature controlled oil bath connected with a PID type temperature controller equipped with a type-k thermocouple. Prior to all electrochemical measurements, the dema-TfO was degassed by nitrogen purging for at least 30 minutes. Linear sweep voltammograms were recorded with changing the electrode rotation speed from 400 rpm to 1600 rpm in oxygen saturated dema-TfO with a scan rate of 5 mV s\(^{-1}\). The durability test was performed based on the protocol of the Fuel Cell Commercialization Conference of Japan (FCCJ).\(^{37} \) 2000 cycles of cyclic voltammetry (CV) were performed in an oxygen saturated dema-TfO at 120°C with a scan rate of 0.5 V s\(^{-1}\) in the potential range of 1.0 to 1.5 V vs. RHE. LSV was taken with an electrode rotation speed of 1600 rpm at a scan rate of 5 mV s\(^{-1}\) in the 1st cycle and 2000th cycle.

The amount of hydrogen peroxide and number of electrons transferred in ORR at 120°C in dema-TfO were measured by a Faraday balance at 120°C in dema-TfO with a scan rate of 0.5 V s\(^{-1}\) which is equal to 0.38,38,39 Considering the fact that the cell resistance at intermediate temperature is negligible, all the provided electrochemical voltammograms are without any IR compensation.

3. Results and Discussion

The preparation process of NG is illustrated in Scheme 1. The morphological features of NG obtained from the SEM (Fig. 1a) and TEM (Fig. 1b) analysis clearly show the typical graphene structure (porous sheet like morphology). The elemental distribution obtained from EDS reveals the homogeneous distribution of N in the graphene sheet (Fig. 1c) at this scale.

In order to determine the structural defects, extent of graphitization and the number of layers of graphene present in NG, Raman spectroscopy was carried out.\(^{40} \) For comparison, the spectra of RGO and GO were also collected. The Raman spectra of each sample (Fig. 2a) showed two distinct bands corresponding to D band (~1350 cm\(^{-1}\)) and G band (~1590 cm\(^{-1}\)) which are characteristic bands associated with carbon structure. The G band arises from the E\(_{2g}\) vibrational mode of the C–C bond stretching and D band from the extent of the defects of the system.\(^{41} \) The heat treated samples namely NG and RGO showed their G bands at lower wavenumbers compared with GO. This can be attributed to the removal of oxides and hydroxides from the surface during the heat treatment.\(^{15} \) The intensity ratio of the D band to the G band, i.e. ID/IG ratio was calculated from fitted spectra (Fig. 2b) which indicates the degree of the disorderedness of the carbon matrix. In other words, the higher ratio means the formation of large amount of defects in the carbon matrix.\(^{42,43} \) Nitrogen incorporation has been again confirmed by the higher ID/IG ratio of NG (1.27) compared with those of GO (0.94) and RGO (1.18). This can be related to the doping of nitrogen atom in the graphene plane by replacing carbon atom or loss of carbon atom through the decomposition of oxygen containing groups.\(^{44} \) The increased ID/IG ratio of RGO can be attributed to the decrease in the average size of sp\(^{2}\) domains and the formation of numerous small graphitic domains during the reduction of GO.\(^{45} \) The most significant feature in the Raman spectra of graphene is the presence of 2D peak (Fig. 2a) as its position and shapes are goodfingerprints to differentiate between single layer, bilayer and few-layer graphenes.\(^{46} \) As seen in the figure, a broad 2D peak appears at around 2700 cm\(^{-1}\) showing the presence of few-layer graphene in the sample.\(^{46} \)

Thermal stability of catalyst is mandatory for the study of electrochemical oxygen reduction at intermediate temperatures (>100°C). Influence of nitrogen on thermal stability of NG was clearly evident from the thermogravimetric curve (Fig. 2c). NG is stable below 600°C and the small weight loss below 100°C corresponded to the loss of residual water containing in the sample. In contrast, RGO showed thermal decomposition at 400°C. The incorporation of nitrogen in the graphene structure improves the thermal stability as well. It is also very interesting to see that both RGO and NG are stable at intermediate temperatures. The influence of nitrogen doping on the effective surface area of catalyst was investigated using nitrogen adsorption-desorption isotherms by the Brunauer-Emmett-Teller (BET) method at 77 K. NG shows type IV isotherm according to the IUPAC classification (Fig. 2d).\(^{37} \) The enhanced surface area of NG (804 m\(^2\) g\(^{-1}\)) with respect to RGO (212 m\(^2\) g\(^{-1}\)) and GO (288 m\(^2\) g\(^{-1}\)) may also be attributed to the nitrogen incorporation in the graphene structure.\(^{38} \) The Barrett-Joyner-Halenda (BJH) analysis represents the nature of porosity in the sample, indicating that NG contained mesopores with an average diameter of 21.32 nm.

The chemical bond structure of nitrogen species in NG were examined using X-ray photoelectron spectroscopy (XPS). The incorporation of nitrogen species (7.30 at.% in the graphene lattice

**Figure 1.** (a) SEM image of NG at a scale bar of 20 µm (b) TEM image of NG at a scale bar of 2 µm (c) EDS images of NG at a scale bar of 2 µm.
have been seen in the survey spectra which is supported by elemental mapping (Fig. 3a). The high resolution C1s spectra (284.6 eV) (Fig. 3b) was deconvoluted to different peaks corresponding to C=C (69.54%), C=N & C–O (19.1%), C–N & C=O (8.62%) and O–C=O (2.74%). It has been already well known that the nature of nitrogen species has a great influence on ORR activity and pyridinic nitrogen itself can act as ORR active center. \textsuperscript{39, 40} Therefore, we deconvoluted N1s spectra (Fig. 3c) to determine the nitrogen configuration existing in the sample. The fitted N1s spectra is indicating the presence of 53.02% pyridinic (398.08 eV), 23.51%...
pyrrolic (399.35 eV), 15.22% graphitic (400.77 eV) and 8.25% N-oxidic (402.10 eV) nitrogen configurations.\textsuperscript{51,52} It is worthy to note that pyridinic nitrogen is the dominant form. It has been reported that pyridinic and pyrrolic nitrogen can donate π electrons to the carbon network and thereby can facilitate electron transfer as well as ORR activity.\textsuperscript{51,53} Graphitic nitrogen can be related to the substitution of carbon atom by nitrogen in the hexagonal graphene matrix. From all these results, it can be concluded that nitrogen from urea has been successfully incorporated into graphene sheet during the pyrolysis of GO and urea at 900°C. The mechanism of nitrogen doping have been understood via chemical reaction of urea with urea has been successfully incorporated into graphene sheet during the pyrolysis of GO and urea at 900°C. The mechanism of nitrogen doping have been understood via chemical reaction of urea with surface functional groups of GO and further thermal transformation during pyrolysis.\textsuperscript{15} Furthermore, the high resolution O1s spectra (Fig. 3d) also fitted in to four distinct peak corresponding to C=O (530.33 eV), C (aliphatic)-OH/C (aliphatic)-O-C (aliphatic) (531.83 eV), C (aromatic)-OH (534.29 eV). And chemisorbed water molecules (536.05 eV).\textsuperscript{54} The XPS analysis of RGO was also carried out. The deconvoluted spectra of C1s and O1s are shown in Fig. 4a and 4b shows a well defined oxygen reduction peak with different electrode rotation speed at a scan rate of 5 mV s\textsuperscript{-1} and corresponding (c) K-L plot of NG (d) number of electrons transferred at different potentials.

Before the high temperature electrochemical tests, we have analysed the ORR activity of NG in dema-TFO at room temperature. The comparison between the LSVs recorded in 0.5 mol dm\textsuperscript{-3} H\textsubscript{2}SO\textsubscript{4} and dema-TFO with an electrode rotation of 1600 rpm (Fig. 5a) indicate that the ORR overpotential in dema-TFO was larger than that in the H\textsubscript{2}SO\textsubscript{4} solution. It has been reported that low operating temperature (\textless30°C) PEFCs, the enhanced kinetics of ORR at elevated temperatures.\textsuperscript{34} Figure 5a again shows the comparison between the LSVs of NG at room temperature PEFCs, the effect of elevated operating temperatures on the ORR activity was examined. LSV was carried out at different operating temperatures (30, 60, 90 \& 120°C) with an electrode rotation of 1600 rpm in oxygen saturated dema-TFO. Figure 5b shows the dependence of ORR activity on the operating temperature. Interestingly, the onset potential of ORR (E\text{onset}) shifted to positive direction and current density increased with increasing the temperature. As increasing the temperature from 30°C to 120°C, E\text{onset} shifted from 0.43 V to 0.55 V which might be due to the weak anion adsorption on the catalytic sites at elevated temperatures. The enhancement of oxygen reduction current density from 0.14 mA cm\textsuperscript{-2} to 1.15 mA cm\textsuperscript{-2} at 0.1 V vs. RHE can be attributed to the higher oxygen diffusion in dema-TFO (5.5 \times 10\textsuperscript{-5} mol cm\textsuperscript{-2} s\textsuperscript{-1} at 120°C) due to lower viscosity of dema-TFO along with the enhanced kinetics of ORR at elevated temperatures.\textsuperscript{34} Figure 5a again shows the comparison between the LSVs of NG at room temperature as well as at 120°C in dema-TFO. This result suggested that low operating temperature (<100°C) was fruitless and the elevated operating temperature was more favourable to get better performance. For the detailed investigation of the catalytic activity
of NG, the effect of electrode rotation on ORR activity was examined at 120°C. It was found that the catalytic current due to the oxygen reduction increased with increasing electrode rotation speed (Fig. 5c). The attainment of convection controlled steady state current depends on several parameters such as the intrinsic properties of the catalyst (mass activity and specific activity), particle size, loading amount of the catalyst as well as the nature of electrolyte.61 More detailed studies are required to find the reason behind the lack of convection controlled study state current region in the powder catalyst-dema-TfO system.

It is well known that nitrogen doping has significant contribution in enhancing ORR in acidic and alkaline media. According to the generally accepted mechanism, in carbon based nano structures, a net positive charge is created on carbon atom adjustment to the nitrogen atom due to the electronegativity difference which facilitates the oxygen adsorption and ORR process.54,62,63 In order to understand the importance of N-doping for the ORR activity in dema-TfO, the catalytic activity of RGO in dema-TfO was also studied in the same condition. By comparing the LSVs of NG and RGO (Fig. 5d) at 120°C, it can be seen that nitrogen doping improves the Eonset which shifted to the positive direction by 0.16 V in NG (Eonset 0.55 V) compared with RGO (Eonset 0.39 V), meaning that nitrogen doping has positive impact on ORR in a protic ionic liquid, dema-TfO. Furthermore, the high surface area and highly porous nature of NG provide more exposed catalytic active sites available for ORR which also can be noted as the reason for the improved ORR activity of NG over RGO.56 Figure 6a shows the comparison between the LSVs of NG (catalyst loading = 0.1 mg cm\(^{-2}\)) with Pt/C (catalyst loading = 25 µg cm\(^{-2}\)) in oxygen saturated dema-TfO at 120°C. Even though the onset potential (Fig. 6b and 6c) of commercially available Pt/C (Eonset = 0.97 V) is higher than NG (Eonset = 0.55 V), Fig. 6a shows that NG has better current density in dema-TfO at 120°C.65

Since the electrochemical stability is a crucial criteria for a catalyst to consider its performance, we have studied the durability of NG as well as Pt/C based on the protocol of Fuel cell Commercialization Conference of Japan (FCCJ)37 in an oxygen saturated dema-TfO at 120°C. We have carried out 2000 cycles of CV in a potential range of 1.5 to 1.0 V vs. RHE with a scan rate of 0.5 V s\(^{-1}\). The LSVs were carried out at 1st and 2000th cycles with an electrode rotation of 1600 rpm (Fig. 7). Surprisingly even after 2000 cycles of CV, NG (Fig. 7a) shows only 14% difference in current density (from 0.88 mA cm\(^{-2}\) to 0.75 mA cm\(^{-2}\) at 0.1 V vs. RHE) without any change in Eonset. However Pt/C (Fig. 7b) has 13% negative shift in Eonset (from 0.97 V to 0.84 V) along with 56% loss of current density (from 1.18 mA cm\(^{-2}\) to 0.52 mA cm\(^{-2}\) at 0.1 V vs. RHE). This indicates that NG possesses excellent stability in dema-TfO at 120°C compared with commercially available noble Pt/C catalyst.

In order to obtain more insight into the high durability of NG at 120°C, TEM and EDS observations were carried out. As shown in Fig. 8a and 8b, NG had no clear structural deformation after the durability test, which agrees with the electrochemical test shown in Fig. 7. The high stability of NG can be attributed to the strong covalent bonds between the active sites and graphitic lattice.15 Figure 8c and 8d shows the morphologies of commercially available Pt/C. Before the durability test, Pt particles with ~2 nm diameter were uniformly distributed on carbon support, which is a typical morphology of Pt/C as reported previously. This Pt/C structure changed greatly after the durability test. One of the main differences is the structure of carbon support. A highly crystalline porous structure was observed, suggesting that the amorphous part of carbon support degraded predominantly. In fact, highly graphitic
carbons are more stable in oxidative conditions than amorphous form. The other clear difference is the loss of uniform Pt distribution after the durability test. The Pt particles observed as black spots in TEM image disappeared after repeated cycling, which was also confirmed by EDS analysis. Usually the reason for the activity loss of Pt/C catalyst is the corrosion of carbon support which results in the aggregation of Pt nano particles and thereby the loss of active surface area and electrochemical activity. However, we could not find neither Pt nanoparticles nor their aggregates in the sample. This results suggest that Pt dissolves into dema-TfO or its segregation proceeded during the durability test.

For the complete realization of the stability of NG, Raman analysis after the durability test was carried out and noted the intensity of D band and G band. Figure 9a and 9b show the comparison of Raman spectra of NG before and after the durability test, implying only small change in the I_D/I_G ratio (from 1.27 to 1.23) after durability test which again upholds the high structural stability of NG at intermediate temperatures in dema-TfO. XPS of NG after the durability test (Fig. 10b) was also analyzed to identify the changes in its active sites and chemical composition. After durability test, N1s spectra of NG shows interesting changes in the composition of pyridinic, pyrrolic and graphitic nitrogen. As seen in the Fig. 10b, pyridinic peak decreased while pyrrolic peak shows an increment after the durability test. Normally pyrrolic nitrogen is more sensitive to the oxidation and less stable than pyridinic and graphitic nitrogen. To identify the reason behind this relative changes of nitrogen contents, we have analyzed C1s and O1s peaks of NG after the durability test and seen that the hydroxyl content increases after durability test. From the O1s spectra of NG after the durability test, it is evident that the intensity of C (aromatic)-OH
increases with respect to the decrease in the intensity of the peak corresponding to the C (aliphatic)–OH/C (aliphatic)–O–C (aliphatic). It can also be seen that C–OH peak adequately strengthens in the C1s spectra after the durability. These results suggest that the –OH attached to the aromatic carbon increases after the durability test. It has been reported that nitrogen binding energy shifts towards the position corresponding to pyrrolic peak when –OH attaches to carbon adjacent to the pyridinic nitrogen in graphene. This suggests that the increased content of pyrrolic nitrogen after the durability test corresponds to the increased content of –OH attached pyridinic nitrogen which has a similar XPS peak position corresponding to the pyrrolic nitrogen. It has also been reported that according to the generally accepted four electron mechanism, the intermediate –OH is attached to the catalytic active sites. Therefore the presence of –OH attached to pyridinic nitrogen indicates that pyridinic nitrogen has a significant role and the adjacent carbon should be the active center for ORR reaction (Scheme 3). The durability test of RGO was also performed in oxygen saturated dema-TfO at 120°C in the same condition (2000 cycles of potential sweep in the range of 1.0 V to 1.5 V vs. RHE). The LSVs (Fig. 11a) with an electrode rotation of 1600 rpm before and after durability test were showing outstanding stability of RGO at 120°C. The XPS results after the durability test (Fig. 11c) were also in line with the electrochemical test. It is interesting to see the increased C–O peak intensity in C1s spectra and heightened C (aromatic)–OH

Figure 8. TEM and EDS images of (a) NG before durability test (b) NG after 2000 cycles at the potential range of 1.0 V to 1.5 V vs. RHE (c) Pt/C before durability test (d) Pt/C after 2000 cycles at the potential range of 1.0 V to 1.5 V vs. RHE.

Figure 9. Comparison of (a) Raman spectra and (b) fitted D and G band of NG before and after durability in dema-TfO at 120°C.
peak in O1s spectra after the durability test, corresponding to the
attachment of –OH on the graphene plane after the durability test.
These results are high lighting the excellent stability of graphitic
materials in dema-TFO at intermediate temperatures.

There are few reports available focusing on the dissolution of Pt
metals from the counter electrode and its re-deposition on working
electrode as Pt nanoparticles, which results in the activation of the
carbon materials during the electrochemical experiments. In order
to confirm that there is no role for the Pt counter electrode in the
activity and stability of NG, we have carried out the durability test
using graphite counter electrode in the same condition. As seen in
the Fig. 12a, LSV recorded with an electrode rotation of 1600 rpm
after 2000 cycles of CV shows only 26% loss of current density
(from 0.57 mA cm$^{-2}$ to 0.42 mA cm$^{-2}$ at 0.1 V vs. RHE) with no
significant $E_{\text{onset}}$ change, which displays better stability of NG over
Pt/C. TEM and EDS images after the durability test (Fig. 12b) using
graphite counter electrode show similar morphological features of
NG as shown in Fig. 8a, which was taken after the durability test
using Pt counter electrode. These results prove that Pt counter
electrode has no significant role in the activity and stability of NG
during electrochemical experiments.

Overall, NG possess better electrochemical stability, larger
surface area along with high nitrogen content, which would be
strongly influencing for the formation of active reaction centre and
thereby improving oxygen reduction reaction. Hence, in order to

Figure 10. Comparison of deconvoluted XPS spectra of NG (a) before durability test (b) after durability test in oxygen saturated dema-TFO
at 120°C.

Scheme 3. A diagram showing the attachment of –OH to the
carbon adjacent to the pyridinic nitrogen during the ORR reaction.
optimize the catalyst loading amount on the working electrode for improving ORR to utmost, we have analyzed LSVs with different catalyst loading (0.05, 0.1, 0.2, 0.3 and 0.6 mg cm\(^{-2}\)) on the working electrode in oxygen saturated dema-TfO at 120°C with an electrode rotation of 1600 rpm. The resulting plots are shown in Fig. 13a. The ORR currents at 0.5 V (at which the current is fully kinetically controlled) were plotted against the catalyst loading amount.\(^{71}\) As shown in Fig. 13b, it was found that ORR activity increased linearly with increasing the catalyst loading from 0.05 mg cm\(^{-2}\) to 0.3 mg cm\(^{-2}\) and reached a saturation with further increase in the loading (0.6 mg cm\(^{-2}\)). This indicates that 0.3 mg cm\(^{-2}\) is the optimum catalyst loading for NG to get the best ORR performance in dema-TfO. Hence the ORR activity of NG with 0.3 mg cm\(^{-2}\) catalyst loading was compared with the activity of Pt/C (Fig. 13c).

Interestingly NG shows comparable \(E_{\text{onset}}\) as well as outstanding current density after using the proper loading of NG catalyst. From this result, it can be concluded that NG is a promising electrocatalyst in dema-TfO at intermediate temperatures.

The number of electrons involved in the ORR mechanism of NG in dema-TfO was investigated by a RRDE at 120°C with an electrode rotation speed of 1600 rpm. The ring potential was fixed at 1.4 V. The collection coefficient of Pt ring is 0.38. It was found that ring current was negligible and the peroxide yield (Fig. 14b) calculated was below 2%. Therefore, the ORR process proceeds (Fig. 14a) with the four electron pathway (\(\sim 3.9\) electrons) which is similar to the number of electrons calculated by K-L plot in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\).
4. Conclusion

The electrochemical behavior of non-precious catalyst (nitrogen-doped graphene) has been studied in a protic ionic liquid (dema-TfO) and investigated the effect of operating temperature on its ORR activity along with its stability at intermediate temperatures. The ORR onset potential shifted to anodic potential and the oxygen reduction current density increased with increasing the operating temperature, which can be related to the factors like lowering of anion adsorption on the surface of electrocatalyst, high oxygen diffusion and fast electrode reaction kinetics in dema-TfO at elevated temperature. NG shows excellent electrochemical stability and comparable electrochemical activity with commercially available Pt/C (37.5%) in dema-TfO at 120°C. Moreover, RRDE results indicate that NG favors four electron pathway in dema-TfO at 120°C. These remarkable electrochemical behaviors of NG in dema-TfO indicate that nitrogen doped graphene can be a potential alternative cathode catalyst in ionic liquids for intermediate temperature PEFCs.

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