Sustainable and clean energy conversion technology is demanded to solve the current energy and environmental problems. Fuel cells have been considered as a promising candidate to meet the growing demand of energy due to its high efficiency of energy conversion and environmentally friendly features [1,2]. Fuel cell works through two reactions, which are composed of fuel (such as hydrogen) oxidation reaction in anode and oxygen reduction reaction (ORR) in cathode [1,2]. In this system, ORR is sluggish and it is necessary to load the large amount of catalysts for ORR. Hence, the performance of the catalysts for ORR is quite important to determine the performance and cost of fuel cell [1,2]. Generally, Pt-based catalysts exhibit the highest catalytic activity for ORR [3,4]. However, it is hard to commercialize Pt-based catalysts due to their expensiveness and rareness. Therefore, it is urgent to develop non-precious metal-based [1,2] or metal-free [5] catalysts with comparable performance to Pt-based catalysts for ORR. It is necessary to perform the rational design of non-precious metal-based catalysts for ORR.

Firstly, we focus on the design of active sites of non-precious metal-based catalysts for ORR. Transition metal-based catalysts have been developed as alternative catalysts [6–16]. In particular, it is reported that Fe (or Co)-based catalysts often show high catalytic activity for ORR. FeOx and CoOx decorated carbons show high catalytic activity for ORR [5,7]. In addition, N species is effective to improve the catalytic activity of transition metal-based catalyst for ORR. Fe/N and Co/N doped carbons exhibit more active for ORR.
[8–11]. Recently, many efforts have been made to verify the effective active sites of Fe/N or Co/N doped carbons. Numerous investigations also identify that highly-dispersed FeN\textsubscript{x} and CoN\textsubscript{y} species such as single atomic FeN\textsubscript{x} and CoN\textsubscript{y} are effective activity active sites for ORR [11–16]. Generally, Fe species is inexpensive compared to Co species. In addition, nanoparticles of Fe or Fe\textsubscript{C\textsubscript{x}} (Fe/Fe\textsubscript{C\textsubscript{x}} NPs) boost catalytic activity of single atomic FeN\textsubscript{x} [17–19]. Thus, effective synthesis of highly-dispersed FeN\textsubscript{x} species and Fe/Fe\textsubscript{C\textsubscript{x}} NPs co-doped catalysts is a good strategy for non-precious metal catalysts with comparable performance to Pt-based catalysts for ORR.

Besides the design of active sites for ORR, the porosity of carbon materials is also crucial to improve catalytic activity of FeN\textsubscript{x} based catalysts [8,20–29]. In particular, pore size of carbons is also important for abundant active sites and diffusion of oxygen molecules. Generally, micropores (smaller than 2 nm) can introduce abundant active sites due to high surface area, but diffusion resistance of oxygen molecules is large in micropores [29–33]. Then, mesopores (2–50 nm) can improve diffusivity of oxygen molecules while minimizing the decrease of the surface area which introduces active sites [29,30]. Actually, Fe/N doped mesoporous carbons show good catalytic activity on ORR [20–24]. In addition, pore structures of carbons are also crucial on ORR. In particular, 3-dimensional (3-D) interconnected pore structures improve catalytic activity on ORR [8,25–29]. Therefore, 3-D interconnected dual pores of micropores and mesopores seem to be an ideal for ORR.

Based on the above findings, highly-dispersed FeN\textsubscript{x} species and Fe/Fe\textsubscript{C\textsubscript{x}} NPs co-doped porous carbons are ideal catalysts for ORR. However, it is still hard and complicated to synthesize highly-dispersed FeN\textsubscript{x} species and Fe/Fe\textsubscript{C\textsubscript{x}} NPs co-doped porous carbons. Fe species can be easily aggregated by heat treatments such as carbonization, and additional acid leaching is often required to remove aggregated Fe species [11,34]. Meanwhile, hard templates such as zeolites, mesoporous silica or silica nanoparticles have been often applied to form micropores or mesopores, but it is necessary to remove the templates by additional base or acid treatments [35,36]. Although soft templating methods using triblock copolymer Pluronic F127 (F127) have been developed, normally it takes long time to prepare the composites of F127 and resin in solvent [37,38], and the waste of toxic solution is not favorable for environment. Herein, we synthesized Fe/N doped porous carbons by a solvent-free method using resorcinol, hexamethylenetetramine (HMT), Pluronic F127 and phthalocyanine iron (II) (FePc) as shown in Scheme 1. In this system, F127 works as a soft template for mesopores [39], and we expect that both highly-dispersed FeN\textsubscript{x} species and Fe/Fe\textsubscript{C\textsubscript{x}} NPs s can be obtained without excess agglomeration after carbonization due to strong π–π interaction between resorcinol resin and FePc. Finally, we performed CO\textsubscript{2} activation to form micropores and 3-D interconnected pore structures. We characterized the prepared samples by XRD, TEM, N\textsubscript{2} adsorption/desorption and XPS. We performed catalytic activity tests over the prepared samples on ORR, and discussed the roles of FeN\textsubscript{x} species, mesopore and micropore for ORR performance.

2. Experimental

To synthesis by a solvent-free method, we used solid raw materials of resorcinol (0.5500 g) as a monomer, FePc (0.1132 g) as a resource of the Fe—N—C structure, HMT (0.3000 g) as a cross-linking agent, and Pluronic F127 (0.5000 g) to introduce mesopore. All of materials were put into a mortar and mixed. The pictures of raw materials and the mixture are shown in Fig. S1. After mixing the raw materials uniformly, the obtained composite was heated under N\textsubscript{2} atmosphere at 900 °C for 3 h with a heating rate of 3.0 °C/min. The carbonized sample was donated as Fe/N doped mesoporous carbon (Fe/N meso C). In addition, to form micropore, we activated Fe/N meso-C under CO\textsubscript{2} atmosphere at 750 °C for x h with a heating rate of 750 °C/h, where x = 1, 4 and 8. In order to obtain the excess activated sample, we also performed CO\textsubscript{2} activation at 800 °C for 1 h. The activated sample was donated as Fe/N meso-C activated (Fe/N meso C-act). Furthermore, for comparison, we also synthesized carbon materials without F127 and FePc, respectively. We also tried to prepare Fe/N meso-C by using a solvent, but FePc was not dissolved in water and phase separation occurred as shown in Fig. S2.

Powder X-ray diffraction (XRD) patterns were recorded on the PANalytical X’Pert PRO X-ray diffractometer with Cu-K\textalpha\textsubscript{r} radiation. Transmission electron microscopy (TEM) images were recorded on Hitachi H800. N\textsubscript{2} adsorption/desorption isotherms at 77 K were measured using BEL-SORPmax (MicrotracBEL). The pore size analysis was performed by Barrett–Joyner–Halenda (BJH) method using adsorption branches. X-ray photo electron spectroscopic (XPS)
analysis was carried out on a JPS-9000MX spectrometer (JEOL) with Mg Kα source radiation (10 kV, 10 mA) as the energy source. The amounts of Fe were determined by Inductively Coupled Plasma (ICP) measurements. As for Fe/N meso C-act, the amount of Fe was calculated using the result of Fe/N meso C and the weight loss after CO₂ activation.

Before catalysts loading on the disk, the rotating ring disk electrode (RRDE) with a disk diameter of 0.4 cm was polished with polishing alumina and washed by distilled water. The catalysts ink was prepared by putting 1.0 mg catalytic powders into 1.0 mL of the solution composed of distilled water, 2-propanol and 5 wt% Naion dispersed solution with the volume ratio of 8:1:1, respectively. Subsequently, the obtained mixture was sonicated for 5 min to disperse the catalytic ink uniformly. 62 µL of catalytic ink was placed on the disk electrode of RRDE. After the catalytic ink was dried, the catalyst with a content of 500 µg/cm² was loaded on the working electrode. For comparison, the catalyst ink was prepared using a commercial Pt/C (20 wt%) with the same method.

The ORR activity of the as-prepared catalysts was tested on Model 2325 Bi-Potentiostat (BAS, Japan) attached with the RRDE apparatus system (BAS, Japan). All of the electrochemical measurements were performed in a normal three-electrode system. Pt wire was used as the counter electrode for the ORR test. Calomel electrode (RHE) referred to the Nernst equation:

\[ \text{ERHE} = \text{E}_{\text{Hg/HgCl}_2} + 1.083 \]

Linear sweep voltammetry (LSV) measurements were applied for the evaluation of catalytic activity on ORR. The LSV measurements were carried out from 1.20 to 0.20 V (vs. RHE) with the rotation speed of 1,600 rpm and scan rate of 1 mV/s. The potential of the ring was kept at 0.60 V (vs. RHE) and the ring current by H₂O₂ oxidation was also measured during the LSV measurement. The onset potential was determined by the current density of 0.1 mA/cm². I-t plot measurements were performed to investigate the stability. Then the potential of the disk was kept at 0.60 V (vs. RHE).

The electron transfer number (n) of ORR on the catalysts modified electrode was determined by the following equation [46],

\[ n = (4I_d) / (I_d + I_r / N) \]

where \( I_d \) is disk current, \( I_r \) is ring current, and \( N \) is the collection efficiency of the ring which is determined to be 0.42 by the sizes of disk and ring.

3. Results and discussion

We measured XRD patterns in order to identify the crystal structure of carbon and iron species in the samples. The XRD patterns of all samples show two broad peaks around 26° and 44° which can be assigned to graphitic carbon as shown in Fig. 1. Fe species would promote graphitization. The diffraction peaks at 43.7° and 44.7° were detected in XRD patterns of Fe/N C, Fe/N meso C and Fe/N meso C-act. The two peaks are corresponding to (102) planes of Fe₃C and (110) planes of cubic Fe, respectively [17,41]. This result exhibits that FeN C (w/o F127), Fe/N meso C and Fe/N meso C-act have the crystalline phase of metallic Fe and Fe₃C. Moreover, the peaks at 29.8°, 35.6°, 57.6° and 63.5° corresponding to Fe₂O₅ [42] were detected in the XRD pattern of Fe/N meso C-act. This could be because carbon layers coating metallic Fe and Fe₃C are removed by CO₂ activation, and then metallic Fe and Fe₃C are exposed to air and oxidized by air. Meanwhile, any peaks derived from FeNx species were not obtained in the XRD patterns of Fe/N C (w/o F127), Fe/N meso C and Fe/N meso C-act, implying that those samples have highly-dispersed FeNx species.

We performed TEM observation to observe pore structure and iron nanoparticle. Firstly, we focused on the pore structure of the samples. Uniform mesopores (ca. 7 nm) were clearly observed in the TEM image of meso C as shown in Fig. 2 (a). However, no mesopores were observed in the TEM image of Fe/N C (w/o F127) as shown in Fig. 2 (b). From these results, F127 is essential to form mesopores in this solvent-free synthesis method, and the mesopores are formed via self-assembly of F127 and resorcinol resin. As for Fe/N meso C, mesopores seems to be slightly disordered compared to meso C as shown in Fig. 2 (c). The possible reason is that FePc inhibits uniform self-assembly. After CO₂ activation, larger mesopores (ca. 20–30 nm) were observed in the TEM image of Fe/N meso C-act as shown in Fig. 2 (d). These mesopores would be formed by connecting small two or three mesopores after CO₂ activation. In addition, 3-D inter-connected pore structure seems to be formed in Fe/N meso C-act. Next, we focus on iron species. The TEM images of Fe/N C (w/o F127), Fe/N meso C and Fe/N meso C-act containing FePc confirmed aggregation of iron species.
The aggregated iron species can be assigned to metallic Fe, Fe₃C and Fe₃O₄ considering the above results of XRD measurements.

N₂ adsorption/desorption measurements were carried out to obtain the more detailed information regarding the porosity of the samples. In the N₂ adsorption/desorption isotherms of meso C, Fe/N meso C and Fe/N meso-C-act collected at 77 K, the hysteresis loops were obtained and indicating the presence of mesopores as shown in Fig. 3(a). Meanwhile, the hysteresis loops were not observed in the N₂ adsorption/desorption isotherms of Fe/N C (w/o F127). Obviously, this result confirms that F127 works as a template for mesopores. The mesopore size was around 7 nm as shown in Fig. 3(b). Moreover, the formation of larger mesopores (20–30 nm) was observed in only Fe/N meso C-act. These mesopores would be formed by connecting small two or three mesopores after CO₂ activation. This result is in accord with the result of TEM reservation. Next, we discuss microporosity before and after CO₂ activation. The adsorption volume in low relative pressure region (around P/P₀ = 0.1) increased after CO₂ activation. The adsorption in this low relative pressure region is contributed by micropores. Therefore, the result suggests that the microporosity was improved after CO₂ activation.

We performed X-ray photo electron spectroscopy (XPS) to examine composition and local chemical state of Fe species in Fe/N C, Fe/N meso C and Fe/N meso C-act. The signals at around 711 eV, 709 eV, 708 eV and 707 eV were observed in XPS spectra of the samples on Fe 2p as shown in Fig. 4(a). These peaks could be assigned to Fe in FeNx [43,44], Fe in FeOx [45], Fe in FeCx [44,45] and metallic Fe [44,45]. All samples have FeNx, FeCx and FeOx species. The XRD measurements (Fig. 1) and TEM observations (Fig. 2) confirmed that FeCx and FeOx species were nanoparticles. Meanwhile, any peaks derived from FeNx species were not obtained in the XRD patterns (Fig. 1) and FeNx nanoparticles were hardly observed in TEM images (Fig. 2). Therefore, the detected FeNx species in XPS spectra must be highly dispersed like single atomic FeNx species. A specific peak derived from metallic Fe species was observed for Fe/N meso C. However, the specific peak derived from metallic Fe disappeared after CO₂ activation as shown in Fig. 4(b). In addition, the intensity of FeCx became weaker and the peak of Fe disappeared after CO₂ activation. In these results, Fe and FeCx were transformed into FeOx by CO₂ activation. The results of XRD measurements (Fig. 1) can also support this as mentioned above. In addition, Fe/N C (w/o F127) has similar Fe species as shown in Fig. 4(c), and the Fe/N C (w/o F127) would be a good comparison to demonstrate the role of mesoporosity on ORR.

Finally, we evaluated catalytic property of the samples on ORR using RRDE. Fe/N meso C showed the highest onset potential as shown in Fig. 5. The value of onset potential was 0.99 V vs. RHE which is comparable to that of Pt/C as listed in Table 1. In addition, the onset potential is higher than those of other Fe/N doped porous carbon electrocatalysts reported in the literatures as listed in Table S2. We explored important factors leading to this high onset potential. Firstly, we tested the catalytic property of meso C (w/o FePc). The meso C showed much lower onset potential (0.83 V vs. RHE) than Fe/N meso C; iron species apparently contributed to high onset potential. To obtain the further insights, we prepared Fe/N meso C with lower and higher amount of FePc than Fe/N meso C. Fe/N meso C with low and high amount of FePc showed lower onset potential than Fe/N meso C as shown in Fig. S3 and Table S1; the amount of FePc was optimized in the case of Fe/N meso C. To obtain the appropriate understanding, we performed LSV measurement over Fe/N meso C with similar Fe content of Fe/N meso C (low). The similar onset potential was obtained as shown in the below Fig. S4, indicating that both samples have similar active sites derived from Fe, but the content of the active sites is different. In other words, Fe/N meso C (low) also have efficient active sites, and the lower catalytic activity of Fe/N meso C contributed by the insufficient amount of active Fe. Meanwhile, Fe/N meso C (high) showed slight low catalytic activity with Fe/N meso C as shown in Fig. S3 despite that the Fe content is higher as listed in Table S1. This result implies
that the formation of active Fe species is saturated and inactive Fe species is formed as for Fe/N meso C (high). To verify the role of highly-dispersed FeNx species and Fe/FeCx NPs, we carbonized FePc and tested its catalytic property on ORR. The carbonized FePc showed no catalytic activity on ORR as shown in Fig. S3. TEM images of the carbonized FePc confirmed that the carbonized FePc has aggregated iron nanoparticles mainly as shown in Fig. S5 because the density of iron species is high and there is no interaction between FePc and resorcinol resin. These results confirm that only aggregated iron nanoparticles do not work as main active sites for ORR, but just boost the catalytic activity of highly-dispersed FeNx species for ORR.

Besides the state of iron species, mesoporosity would have an impact on the catalytic property on ORR. Then, we discuss the role of mesoporosity on onset potential. Interestingly, Fe/N C (w/o F127) showed much lower onset potential (0.85 V vs. RHE) than Fe/N meso C as shown in Fig. 5 and Table 1 although Fe/N C has both highly-dispersed FeNx species and Fe/FeCx NPs. This is a good demonstration that mesoporosity is also essential to high onset potential. The results imply that the combination of highly-dispersed FeNx species, Fe/FeCx NPs and mesoporosity would contribute to the high onset potential of Fe/N meso C.

Next, we discuss the effect of CO2 activation on the catalytic property on ORR. We explored the optimized condition of CO2 activation. Fe/N meso C activated by CO2 at 750 °C for 4 h named as Fe/N meso C-act showed the best catalytic performance on ORR as shown in Fig. S6. The Fe/N meso C-act is a comparable catalyst to Pt/C as shown in Fig. 5. This condition of CO2 activation seems to be best and we discuss the effect of CO2 activation focusing on the Fe/N meso C-act mainly. The high limiting current density was improved after CO2 activation as shown in Fig. 5, which was comparable to Pt/C although the amount of Fe was similar even after CO2 activation. The improvement of the limiting current density is caused by the 3-D interconnected hierarchical pore structure of Fe/N meso C-act. Meanwhile, the Fe/N meso C-act showed slightly lower onset potential (0.96 V vs. RHE) than Fe/N meso C. This is because the amount of Fe and FeCx species boosts the catalytic activity of highly-dispersed FeNx species decreased after CO2 activation as confirmed by the results of XRD and XPS measurements (Figs. 1 and 4). This result also supports that Fe and FeCx species are better than FeOx species to boost the catalytic activity of highly-dispersed FeNx species. The onset potential decreased after severe CO2 activation at 800 °C as listed in Table S3; the graphene structure of the carbon support and highly-dispersed FeNx species on the carbon matrix were decomposed by this severe CO2 activation. From this result, it is found that CO2 activation at 800 °C was too severe. From these results, the limiting current density can be improved without a drastic decline of onset potential by optimized CO2 activation. The value of the onset potential is still high after optimized CO2 activation as listed in Table S2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eonset [V vs. RHE]</th>
<th>n [-]</th>
<th>Fe content [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/N meso C</td>
<td>0.99</td>
<td>3.97</td>
<td>1.02</td>
</tr>
<tr>
<td>Fe/N meso C-act</td>
<td>0.96</td>
<td>3.97</td>
<td>1.08</td>
</tr>
<tr>
<td>meso C</td>
<td>0.83</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe/N C (w/o F127)</td>
<td>0.85</td>
<td>-</td>
<td>0.50</td>
</tr>
<tr>
<td>Pt/C</td>
<td>1.00</td>
<td>3.98</td>
<td>-</td>
</tr>
</tbody>
</table>

Finally, we performed durability and methanol tolerance tests over Fe/N meso C-act and Pt/C. Fe/N meso C-act showed similar relative current density with Pt/C up to 2 h as shown in Fig. 6. Then, we added methanol after 2 h as a methanol tolerance test. The relative current density of Fe/N meso C-act maintained while that of Pt/C changed from negative to positive due to preferentially methanol oxidation reaction; the methanol tolerance of Fe/N meso C-act is high unlike Pt/C. We continued the durability test for Fe/N meso C-act after methanol injection. The catalytic performance of Fe/N meso C-act is very stable. From the results of durability and methanol tolerance tests, Fe/N meso C is a catalyst with high methanol tolerance and durability.

4. Conclusion

We synthesized Fe/N doped mesoporous carbon (Fe/N meso C) by a facile solvent-free method using resorcinol resin, F127 and FePc. The Fe/N meso C has uniform mesopores with a size of 7 nm, highly-dispersed FeNx species and Fe/FeCx NPs. F127 and FePc work as a template for mesopores and sources of highly-dispersed FeNx species and Fe/FeCx NPs, respectively. The Fe/N meso C showed high onset potential (0.99 V vs. RHE) on ORR in alkaline media. The combination of mesoporosity, highly-dispersed FeNx species and Fe/FeCx NPs contributes to the high onset potential. In particular, our investigation revealed (1) mesoporosity provides high accessibility to active sites, (2) highly-dispersed FeNx species works as main active site, and (3) Fe/FeCx NPs boost catalytic activity of highly-dispersed FeNx species. In addition, we performed CO2 activation for Fe/N meso C. After CO2 activation, 3-D interconnected hierarchical pore structure was formed, and the 3-D interconnected hierarchical pore structure improved limiting current density without a drastic decline of onset potential. The activated Fe/N meso C showed a comparable catalytic activity to Pt/C and high durability and methanol tolerance.

Credit author statement

Yuya Toyama First Author, Material synthesis, Electrochemical measurements, Visualization and Writing.
Koji Miyake Corresponding Author, Conceptualization, Methodology, Supervision.
Yasuhiro Shu XPS, XRD and N2 adsorption measurements.
Koki Moroto Electrochemical measurements.
Jiaojiao Ma Electrochemical measurements.
Tao Zheng ICP measurements, Review and Edit.
Shunsuke Tanaka XPS measurements, Review and Edit.
Norikazu Nishiyama TEM measurements, Review and Edit.
Choji Fukuhara Review and Edit.
Chang Yi Kong Supervision, Review and Edit.

Declarations of competing interest

There is no conflict of interest to declare.

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Appendix A. Supplementary data

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References