## **Supporting Information**

## Ionic Liquid-Derived Fe-N/C Catalysts for Highly Efficient Oxygen Reduction Reaction Without Any Supports, Templates, and Multi-Step of Pyrolysis

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**Fig. S1.** CV curves of MIm+Fe-C, IL-1-C and Pt/C in O<sub>2</sub>-saturated (solid line) and N<sub>2</sub>-saturated (dash line) 0.1 M KOH solution. The arrows indicated the peak potential. The scan rate is 10 mV s<sup>-1</sup>.

The cyclic voltammetry (CV) curve of the carbonized IL-1 at 750 °C (IL-1-C) showed a well-defined cathodic peak in O<sub>2</sub>-satrurated 0.1 M KOH with a peak potential 49 mV positive than that of the commercial Pt/C (20 wt.%), suggesting an excellent electrocatalytic ORR activity of the as-obtained IL-1-C. Simultaneously, the cathodic peak of IL-1-C was 83 mV positive than that of MIm+Fe-C, indicating homogeneous distribution of iron ions in precursors at molecular level contributed to increase electrocatalytic activities of the resultant catalysts.



Fig. S2. LSVs of MIm+Fe-C (a), IL-1-C (b) and Pt/C (c) with a sweep rate of 10 mV s<sup>-1</sup> at different rotating speeds.

Typically, the current of MIm+Fe-C and IL-1-C simultaneously increased as the rotating speeds increased, indicating ORR was a diffusion-controlled process. Such current also increased as potential reached -0.3 V. After that, the ORR current of MIm+Fe-C increased slightly. However the ORR current of IL-1-C remained a stable platform when the potential went more negative, up to -0.8 V, similar to that of Pt/C.



Fig. S3. The calculated kinetic limiting current  $(J_k)$  at -0.3 V based on the Koutecky-Levich (K-L) equation.

Depending on the Koutecky-Levich (K-L) equation, the calculated kinetic limiting current ( $J_k$ ) of IL-1-C was 35.1 mA cm<sup>-2</sup>, comparable to that of Pt/C (37.8 mA cm<sup>-2</sup>), indicating IL-1-C possessed the high activity of ORR. Simultaneously,  $J_k$  of IL-1-C as far superior to that of IL-1-C (27.4 mA cm<sup>-2</sup>), confirming that well-isolated iron in the molecule level could increase the catalytic activity of ORR.



Fig. S4. LSVs of IL-1-C and Pt/C in 0.1 M PBS (a) and 0.5 M H<sub>2</sub>SO<sub>4</sub> (b) with a sweep rate of 10 mV s<sup>-1</sup> at 1600 rpm.

As shown, the onset potential of IL-1-C in 0.1 M phosphate buffer solution (pH 7.4, PBS) was only shifted negatively by 23 mV in comparison to 20% Pt/C. Nevertheless, it is worth noting that the half-wave potential for as-prepared IL-1-C (68 mV) was  $\sim$ 10 mV lower than that of 20% Pt/C (78 mV), which was an unprecedented ORR activity for non-noble metal catalysts in PBS. Interestingly, IL-1-C was also active for ORR in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. As shown in Fig. S4b, in acidic media, the ORR polarization curve of IL-1-C exhibited E<sub>onset</sub> (551 mV), close to that of 20% Pt/C (636 mV). The corresponding E<sub>1/2</sub> of IL-1-C was 381 mV, 173 mV lower than that of 20% Pt/C.



Fig. S5. The thermogravimetric analysis (TGA) curves of IL-1, IL-2 and IL-3 in N<sub>2</sub> (10 °C min<sup>-1</sup>).

The thermogravimetric analysis (TGA) curves (Fig. S5) showed that the apparent plateau of constant weight for IL-1 occurred at lower temperature than IL-2 and IL-3 exhibited no apparent plateau, verifying that the less rigidity of substituent group on the imidazolium cation was beneficial to graphitization. This result was consistent well with XRD and Raman results.



Fig. S6. The Raman spectra of IL-1-C, IL-2-C, IL-3-C and IL-3'-C.

The Raman spectra were also used to confirm the different graphitization, and consistent well with the XRD results (Fig. 2b). Notably, the high  $I_G/I_D$  of IL-1-C (1.67), signifying the highest degree of graphitization in this study, had never been reported so far by one-step carbonization at temperatures as low as 750 °C.



**Fig. S7.** The N<sub>2</sub> adsorption and desorption isotherm of MIm+Fe-C, IL-1-C, IL-2-C, IL-3-C and IL-3'-C. Before acid treatment, MIm+Fe-C exhibited the aggregated and larger Fe-containing species, which was confirmed by the newly added SEM and EDAX images (Fig. S13). The BET analysis showed that MIm+Fe-C exhibited a more obvious hysteresis-loop in the pressure (p/p<sub>0</sub>) of ca. 0.48~1.0, revealing the presence of more mesopores compared to that of IL-1-C, which was attributed to agglomeration of iron species resulted from the uneven distribution of Fe in MIm+Fe. Though more mesopores existed in MIm+Fe-C, the uneven dispersion of iron in MIm+Fe resulted in poorer conductivity and loss of the active pyridinic and graphitic N species during pyrolysis (Table 1). Accordingly, MIm+Fe-C showed poorer ORR activity (Fig. 1a).



**Fig. S8.** <sup>1</sup>H NMR (a) and Raman (b) spectra of ionic liquid precursors. \* and # represented the solvent peaks of DMSO and H<sub>2</sub>O, respectively.

To confirm the corresponding structures of ionic liquid precursors, <sup>1</sup>H NMR spectroscopy analysis was first performed. Each characteristic H in ionic liquid precursors went well with the corresponding peak in <sup>1</sup>H NMR (Fig. S8a), indicating that the expected configurations of ionic liquid precursors were obtained successfully. Moreover, the Raman spectra of the synthesized ionic liquid precursors were also measured to obtain information about the anion compositions. As shown in Fig. S8b, four dramatic bands belonging to anion FeBrCl<sub>3</sub><sup>-</sup> were present in Raman spectrum. The strong band at 221, 242 and 266 cm<sup>-1</sup> corresponded very well with literature values for Fe-Br.<sup>1</sup> Additional weak feature at about 328 cm<sup>-1</sup> was assigned to the symmetric Fe-Cl stretch vibration.<sup>1, 2</sup>



**Fig. S9.** RDE voltammograms of IL-1-C pyrolyzed at different temperatures in O<sub>2</sub>-saturated 0.1 M KOH. For all experiments, the rotating speed was 1600 rpm. The scan rate was 10 mV s<sup>-1</sup>.

Previous studies showed that the pyrolysis temperature has an important influence on the catalytic activity of Fe–N/C catalysts. To find an optimized pyrolysis temperature for our catalysts, the precursor IL-1 was heated ranging from 600-800°C. By rotating disk electrode (RDE) measurements, the ORR activity for IL-1 synthesized at different temperatures in 0.1 M KOH electrolyte at a scan rate of 10 mV s<sup>-1</sup> was investigated. As shown in Fig. S9, the IL-1 sample prepared at 750°C (IL-1-C) showed the highest catalytic ORR activity.



**Fig. S10.** RDE voltammograms of IL-1-C (a) and 20% Pt/C (b) with different loading amount in O<sub>2</sub>-saturated 0.1 M KOH. For all experiments, the rotating speed was 1600 rpm. The scan rate was 10 mV s<sup>-1</sup>.

In general, the loading amount of the catalysts influences the ORR catalytic activities (Fig. S10). The detailed mechanism has not been fully understood so far, but factors such as incomplete coverage of the substrate electrode by insufficient loading and interruptive electron-transfer and mass diffusion by excessive loading were expected to be not favor of an effective ORR. In this sense, for a fair comparison, a minimum loading amount of Fe-N/C catalysts but with maximum activities (283  $\mu$ g cm<sup>-2</sup>) and the most common loading amount of Pt/C (20%, 114  $\mu$ g cm<sup>-2</sup>)<sup>3-6</sup> were adopted in this study.



**Fig. S11.** The influence of acid treatment on ORR activity of IL-3-C. For all experiments were performed in O<sub>2</sub>-saturated 0.1 M KOH. The rotating speed was 1600 rpm. The scan rate was 10 mV s<sup>-1</sup>. After acid treatment, IL-3-C showed the enhanced ORR activity (Fig. S11), suggesting that some inactive iron species were leached.



Fig. S12. The specific resistance of catalysts.

The specific resistance of catalysts was obtained by the equation of R=U/I. The relative specific resistance of

catalysts was obtained by normalizing the measured specific resistance with that of the graphite reference.



Fig. S13. The SEM images and EDAX data of MIm+Fe-C (a) and IL-1-C (b) before acid treatment. Before acid

treatment, MIm+Fe-C exhibited the aggregated and larger Fe species compared to that of IL-1-C.



Fig. S14. The RRDE curves (a) and electron transfer number (b) of IL-1-C, IL-2-C and IL-3-C.

	MIm+Fe-C	IL-1-C	IL-2-C	IL-3-C	IL-3-C- without-acid-leaching
Fe wt. % <sup>a</sup>	0.45	0.68	0.23	0.27	8.5

 Table S1.
 Summary of Fe content in catalysts.

<sup>a</sup> The total Fe content of all catalysts was estimated by XPS.

Multi-steps of pyrolysis would make structure of N-doped carbon catalysts more unpredictable, thus we proposed to

prepare the catalysts as simple as possible. Nevertheless, to further optimize the activity, multi-steps of pyrolysis was

feasible, would be studied in the future work.

## **Supporting References**

1. M. Dobbelin, V. Jovanovski, I. Llarena, L. J. C. Marfil, G. Cabanero, J. Rodriguez and D. Mecerreyes, *Polym. Chem.*, 2011, 2, 1275-1278.

- 2. J. Gao, J. Q. Wang, Q. W. Song and L. N. He, Green Chem., 2011, 13, 1182-1186.
- 3. W. H. He, C. H. Jiang, J. B. Wang and L. H. Lu, Angew. Chem. Int. Edit., 2014, 53, 9503-9507.

4. Y. G. Li, W. Zhou, H. L. Wang, L. M. Xie, Y. Y. Liang, F. Wei, J. C. Idrobo, S. J. Pennycook and H. J. Dai, *Nat. Nanotechnol.*, 2012, 7, 394-400.

- 5. L. Lin, Q. Zhu and A. W. Xu, J. Am. Chem. Soc., 2014, 136, 11027-11033.
- 6. M. L. Xiao, J. B. Zhu, L. G. Feng, C. P. Liu and W. Xing, Adv. Mater., 2015, 27, 2521-2527.