Anchoring Co/2-methylimidazole complex on ion exchange resin and its transformation to Co/N-doped carbon as an electrocatalyst for oxygen reduction reaction(ORR)

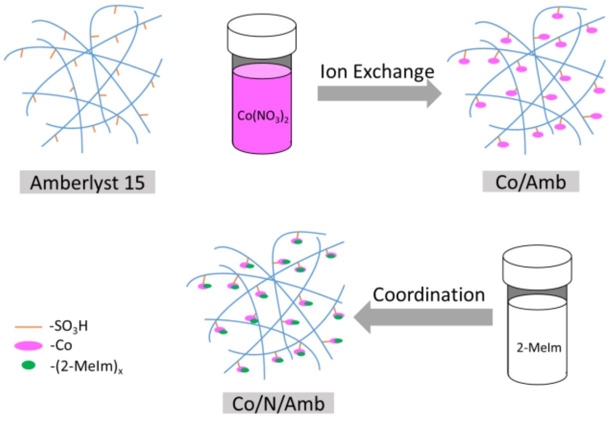
Yexin Zhu,[a] Koji Miyake,[a] Yuichiro Hirota,[a] Yoshiaki Uchida,[a] Norikazu Nishiyama[a]
[a] *Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Japan*
**Corresponding author: +81-06-6850-6255, E-mail address nisiyama@cheng.es.osaka-u.ac.jp*

Abstract: Heteroatoms (N, S, P etc.) doped carbons with metal nanoparticles have been known as excellent materials, especially electrocatalysts. The interfaces of metals, heteroatoms and carbon often work as active sites. Thus, enlarging the interfaces is so important to enhance the performance of carbon materials. In this work, we have developed a novel synthesis method of carbon materials using ion exchange resin anchoring cobalt species coordinated with 2-methylimidazole as a precursor. The resulting N doped carbon with highly dispersed cobalt species showed an excellent catalytic performance on oxygen reduction reaction (ORR).
Keywords: Electrocatalyst, Oxygen reduction reaction, ion exchange method.

1. Introduction

Heteroatoms (for example N, S, P and so on) doped carbons with metal nanoparticles have been known as excellent materials, especially electrocatalysts. Recently, metal organic frameworks (MOFs) including zeolitic imidazolate frameworks (ZIFs) have been a promising candidate as a precursor to synthesize heteroatoms doped carbons with metal NPs[1,2] because the interfaces of metals, heteroatoms and carbon can be successfully formed. However, metal nanoparticles derived from MOFs often aggregate and their particle size grow to a larger size by after the carbonization since the concentration of metals in MOFs is so high. As a result, their catalytic performances are limited. Therefore, a novel method to enlarge the interfaces of metals, heteroatoms and carbon is desired in order to improve their performances.

In this study, we used Amberlyst 15 which is a commercial acidic ion exchange polymer with sulfonic acid group. Cobalt cations were incorporated into Amberlyst 15 by an ion-exchange method. Nitrogen doping was performed by coordination of 2-methylimidazole (2-MeIm) to cobalt ions. Scheme 1 shows the procedure to fabricate the precursor (Co/N/Amb). The precursor (Co/N/Amb) was carbonized to obtain a Co/N/C composite. The Co/N/C composite was used as a catalyst for oxygen reduction reaction (ORR) in alkaline media.



Scheme 1. The preparation method for a Co/N/Amb.

2. Experimental

In a typical synthesis of Co/N/C, the Amberlyst 15 polymer (Amb) was grinded into powder firstly and then added into deionized water. The Co^{2+} solution was added into the Amb solution drop by drop to perform the ion exchange. After filtration and drying, the one fourth of the obtained precursor (Co/Amb) was carbonized under N2 at 800ºC to give Co/C and the rest of the precursor mixed with a 2-MeIm solution by the same operation with ion exchange. The resulting material (Co/N/Amb) was washed by methanol to remove excess 2-MeIm and dried for several hours. After that, the precursor (Co/N/Amb) was heated under the same condition as the Co/C. The resulting black powder referred to Co/N/C was activated under CO_2

atmosphere to increase the surface area of the carbon (Co/N/C-act). As the application, we performed oxygen reduction reaction (ORR) in alkaline media over our prepared carbon materials.

3. Results and discussion

We prepared Co/N/Amb with different content of cobalt. The color of powder with high content of cobalt turned into purple after adding Co/Amb into the 2-MeIm solution, indicating that the coordination of N to Co ions was successfully achieved. We measured X-ray diffraction (XRD) patterns of Co/N/Amb. There are no peaks derived from ZIF even when the content of cobalt was high. These results show that Co species coordinated with 2-MeIm were successfully anchored on ion exchange sites.

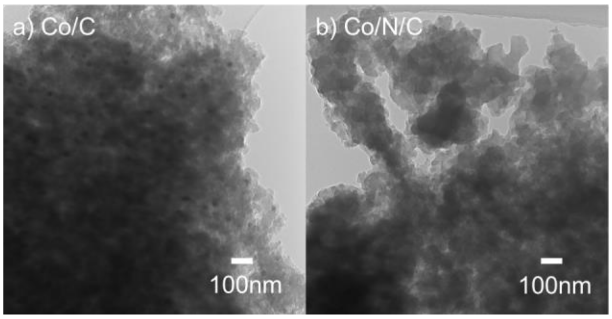


Figure 1 TEM images of a) Co/C and b) Co/N/C.

Cobalt particles can only be observed from TEM images of Co/C. Meanwhile, The XRD pattern of Co/N/C in Figure 2 only showed broad peak comparing with Co/C, which has a peak close to 45 degree corresponding to cobalt species. These results indicated that the aggregation of Co species during carbonization was suppressed by coordination of 2-MeIm.

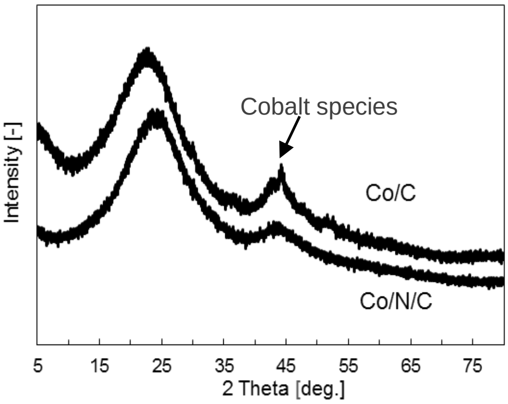


Figure 2 XRD patterns of Co/C and Co/N/C.

The electro-catalytic performance of the prepared materials toward the ORR was evaluated in 0.1 M oxygen saturated 0.1M KOH solution. The further study on electoactivity and physical characterization was performed with samples carbonized at 800°C. For comparison, the carbonized Amberlyst 15 C(Amb) and commercial Pt/C (5 wt% Pt) were also investigated. The onset potential of Co/N/C was higher compared with Co/C which suggested that Co-N species in carbon matrix is an active site for ORR. The current density was significantly increased for Co/N/C-act possibly because the surface area was increased by CO2 activation. The current density of Co/N/C-act at 0.7 V was higher than that of Pt/C although the metal content of Co/N/C-act was lower than that of Pt/C. The Co/N/C composite would be a promising candidate for ORR catalyst.

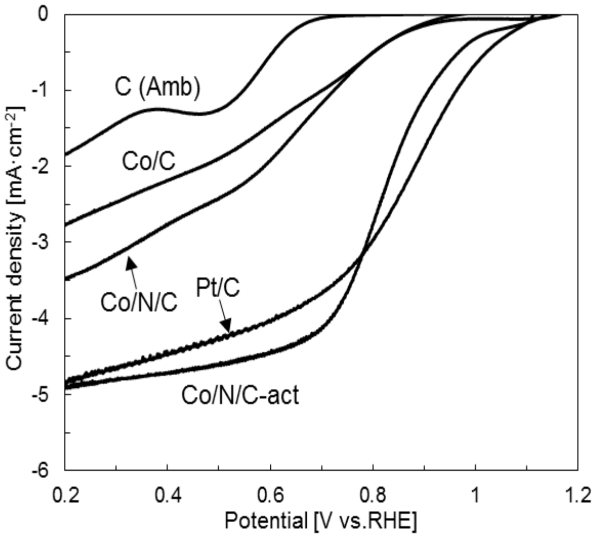


Figure 3 LSV curves.

4. Conclusions

We have developed a simple approach to obtain the Co/N-codoped carbon electrocatalysts. Our prepared Co/N/C-act showed the excellent catalytic performance on ORR. This work provides a new strategy for carbon material design.

References

1. N. L. Torad et al., Chem. Eur. J., 20 (2014) 7895.
2. Y.-N. Hou et al., Chem. Commun., 53 (2017) 7840.