Effects of edge structures on the oxygen reduction reaction activity of nitrogen-doped graphene nanoribbons

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Recently, much attention has been devoted to the oxygen reduction reaction (ORR) on nitrogen (N) -doped graphene [1]. It has been reported that N atoms prefer to be doped at the edge of graphene [2]. The structure of graphene edge can be classified into two types, zigzag and armchair edges. However, the effect of edge structures on ORR activity has not been fully understood.

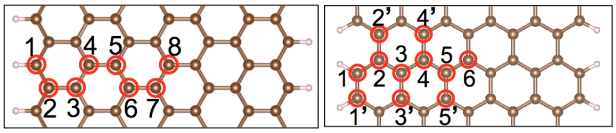

Fig. 1. Calculation models of N-ZGNRs and N-ACGNRs. Doping sites and reaction sites are labeled by numbers.

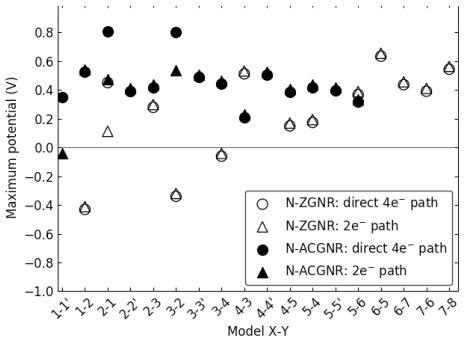

Fig. 2. Maximum potentials for different nitrogen doping

We investigated the ORR activity on N-doped graphene nanoribbons with zigzag (N-ZGNRs) and armchair (N-ACGNRs) edges using first-principles calculations within the density-functional theory. Figure 1 shows the calculation models. The model of "X-Y" indicates a doping site of N (X) and a reaction site (Y). We used the computational hydrogen electrode model [3] to evaluate the maximum electrode potential. ORR mainly proceeds via the direct four-electron ($4e^-$) and the two-electron ($2e^-$) pathways. We also examined the selectivity with respect to these two pathways.

Figure 2 shows the maximum electrode potential of ORR for each doping site. The maximum potential for N-ACGNR becomes positive for each doping and reaction site. On the other hand, the maximum potential for N-ZGNR has a parity dependence with regard to the nitrogen doping site in the vicinity of the zigzag edges. For the even-numbered doping sites from the edge, the maximum potentials are larger than 0 V, while for the odd-numbered ones, the maximum potentials become negative. The reaction selectivity for the $4e^-$ pathway appears only in the vicinity of armchair and zigzag edges.

For the models showing the reaction selectivity, the sp^2 configuration of GNR is maintained, even if reaction intermediates are adsorbed on GNR. One the other hand, reaction intermediates adsorb on GNR with sp^3-like configuration for the other models. The mechanism for appearance of the selectivity will be discussed in the presentation.

[1] K. R. Lee *et al.*, Electrochem. Commun. **12**, 1052 (2010).
[2] S. F. Huang *et al*., Phys. Rev. B **80**, 235410 (2009).
[3] J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Phys. Chem. B **108**, 17886 (2004).

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