Enhance Oxygen Reduction Reaction Using Carbon-Based Nanostructured Electrocatalysts

Bin Liu[1]*, Jiayi Xu[1], Ayyappan Elangovan[2] and Jun Li[2]
[1]*Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506 (US)*
[2]*Department of Chemistry, Kansas State University, Manhattan, KS 66506 (US)*
*binliu@ksu.edu

Introduction

Oxygen reduction reaction (ORR) is a critical performance-determining step for direct methanol fuel cells. Carbon-based electrocatalysts, thanks to their superior durability, electrical conductivity, low material cost, as well as intrinsically high catalytic reactivity, have made steady progress in establishing themselves as potential replacements of platinum group metals (PGMs) for ORR. In this regard, vertically aligned carbon nanofibers (VACNFs), essentially a stack of conical graphitic structures rich in unsaturated carbon edges (red lines in Figure 1(a)), carry dual functions as a ORR promoter and Pt catalyst support, enabling low metal loading. Under alkaline conditions, the current density measured on VACNF-based cathode can be up to two times higher than that over commercial Pt catalysts. In this study, the molecular origin leading to such high ORR activity will be understood by combining density functional theory (DFT), carbon structure characterization, and electrochemical voltammetry. Specifically, the objectives of this study aims to: (1) identify the nature of active sites and influence of nitrogen doping as well as the addition of noble transition metals such as Pt; (2) establish relationship between ORR reactivity and governing reaction pathways corresponding to the responsible active centers.

Materials and Methods

For modeling, periodic spin-polarized DFT calculations were performed using Vienna *Ab initio* Simulation Package (VASP), with the GGA-PBE functional for electron exchange-correlation interactions. Moreover, Grimme's DFT-D3 method was also considered to account for the dispersion interactions. The PAW method was used to represent the ionic cores. The computational parameters were systematically tested in convergence test until good agreement with reported literature values were achieved. In this work, semi-periodic fishbone-like stacked graphene sheets, bare or terminated with H and OH, were employed for mechanistic investigations. The preferred $4e^-$ ORR mechanisms, via dissociative or associative pathways will be investigated on the VACNF models established for this study for the first time. For Pt-free VACNF systems, the $2e^-$ pathway, producing OOH- was also tested.

Experimentally, VACNFs (with a length of ~3.5 μm) were grown on graphite paper using the plasma enhanced chemical vapour deposition method.[1] Pt was deposited using the high-resolution ion beam coater system. The surface morphology of the as-grown VACNF was characterized with a Field-emission SEM. The microstructure of the Pt/VACNF was analyzed using TEM. Elemental analysis and mapping were done using energy-dispersive X-ray spectroscopy (EDS) in the TEM. The electrochemical properties were studied using a CHI 760D electrochemical workstation on a rotating disk electrode (RDE).

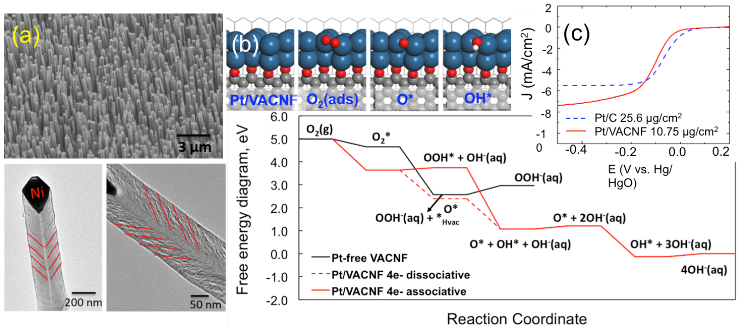

Figure 1. (a) SEM image of as-grown VACNF and magnified image of an individual nanofiber. The Ni catalyst particle used for nanofiber growth can be seen. The edges of carbon cone stack are highlighted in red; (b) Optimized structures for ORR pathways and free energy diagrams comparing the $2e^-$ pathway with the two $4e^-$ pathways considered; (c) Linear sweep voltammetry (LSV) over commercial Pt and Pt/VACNF catalysts.

Results and Discussion

Experimentally, VACNF structures have been demonstrated as a versatile and highly functional 3D support architecture in electrocatalysts.[2] In this case, through LSV, the enhanced ORR activity over Pt/VACNF has been confirmed when compared to the Pt/C catalyst (Figure 1(c)). The ORR pathway is also elucidated to follow a 4e- dissociative reaction mechanism by DFT calculations (red dashed in Figure 1(c)). The improved reactivity can be explained by enhanced molecular O_2 adsorption. The subsequent O-O bond cleavage can also be facilitated. Once the 4e- pathway is completed, active site can be readily freed upon OH desorption. In this study, we also identified that the carbon edge of VACNF (terminated with OH) can also promote ORR (black) via an O shuttling mechanism. However, the 2e- pathway is thermodynamically favored.

Significance

This study provides insights into the ORR process over VACNF, 3D carbon architecture acting as both the Pt catalyst support and a catalytically functional structure. Such a carbon nanostructure can also be further manipulated through heteroatom (N, B) doping to achieve higher catalytic performance.

References

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