

Functionalized Aligned Carbon Nanotubes as Pt-free Electrocatalyst with Novel Nanoarchitecture for PEMFC

Junbing Yang and Di-Jia Liu*

Chemical Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave.
Argonne, ILL 60439, (USA)

*liud@cmt.anl.gov

Introduction

Development of proton exchange membrane fuel cell (PEMFC) as the future high-efficiency, H₂ based power generation device has attracted extensive efforts recently. At present, the most effective electrocatalyst for PEMFC is made of finely divided platinum supported on carbon, Pt/C. The use of expensive Pt adds significant cost to the overall fuel cell system. At Argonne National Laboratory, we are actively exploring low cost alternatives to platinum. One such material is catalytically functionalized aligned carbon nanotubes (ACNT) prepared through a chemical vapor deposition (CVD) reaction. In a preliminary study, we successfully prepared uniform, dense layers of multi-wall carbon nanotubes under carefully controlled experimental conditions. The nanotubes can be controlled to 10 to 100 nm diameter and uniform orientation perpendicular to the growth substrate. An example is shown in Fig. 1a. The preparation of ACNT is based on the floating catalyst method [1], with a CVD mixture generally composed of a transition metal (TM) organometallic and a hydrocarbon. We found that by adding ammonia into the CVD mixture, a significant improvement occurs in the ACNT's electrocatalytic activity for the oxygen reduction reaction (ORR). The ORR is an important cathodic electrochemical reaction requiring the majority of the Pt/C in the PEMFC. In addition to electrocatalytic activity, ACNT offers several potential improvements in future fuel cell design based on new electrode structures and physical properties. First, ACNT has an integrated graphitic structure with higher corrosion resistance and better electron conductivity than that of amorphous carbon. Second, the vertical alignment of the ACNT can be transferred onto the polymer electrolyte membrane to form a spatially oriented electrode assembly [2]. Finally, the ACNT layer can be patterned into various 3-dimensional shapes, mimicking the flow field of PEMFC bipolar plates. Such membrane electrode assemblies will have improved electrical conductivity, better fuel gas/air distribution, and enhanced catalyst utilization. This presentation describes our recent efforts in improving ACNT electrocatalytic activity and characterizing the nature of the catalytic center using synchrotron X-ray absorption spectroscopic methods.

Materials and Methods

ACNTs were prepared in a CVD reactor with the input mixture of ferrocene and xylene (both from Sigma-Aldrich) and a carrier gas containing H₂ and Ar. For the N-doping study, ammonia was also added to the gas mixture. The images of ACNT were taken by a high-resolution scanning electron microscope at Argonne's Electron Microscopy Center. The cyclic voltammograms (CVs) for the ORR over ACNT electrodes were obtained in oxygen-saturated perchloric acid electrolyte using Ag/AgCl as the reference electrode. *In situ* X-ray absorption spectroscopic investigation (by EXAFS and XANES) of the Fe active site under different polarization potentials was conducted at Beamline 12BM of the Advanced Photon Source at Argonne National Laboratory.

Results and Discussion

Our SEM/EDX results indicate that adding ammonia leads to N-doping into the ACNTs, most likely in the form of pyridinic nitrogen. Such functional groups can coordinate with Fe to form -FeN₄- or -FeN₂- moieties, which are known to be catalytically active toward ORR [3]. Figure 1b shows the CV's of an N-doped ACNT sample with an onset ORR potential at 0.7 V (NHE), which represents a significant improvement over that of the N-free catalyst. To investigate the nature of the catalytic site, we conducted *in situ* XAS experiments, in which the ACNT catalyst sample was subjected to a range of polarization potentials simulating those inside a PEMFC cathode. The results indicate that Fe is coordinated by 4 N at the ORR active site. At high polarization potentials, iron is mainly in +3 oxidation state. Below the ORR onset potential, however, iron is reduced to Fe⁺². The first shell coordination number increases counterintuitively at this potential, suggesting the binding of O₂ to Fe⁺² as the activation step. This observation is consistent with the hypothesis that oxygen can only be activated by Fe⁺², as is observed in biological systems.

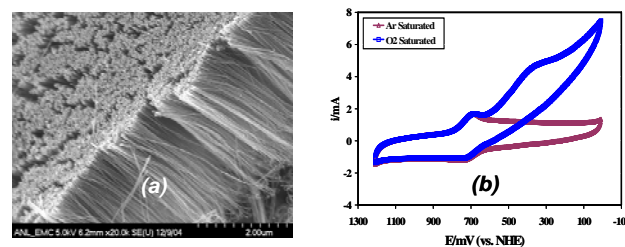


Figure 1. (a) ACNT bundle prepared through CVD process; (b) CV's of ACNT sample in O₂ saturated or Ar purged HClO₄ solution (0.6 M).

Significance

This presentation describes a method of preparing innovative nanostructured electrocatalyst layer for PEMFC, together with a fundamental study on the catalytic active site using advanced imaging and synchrotron X-ray spectroscopic methods.

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References

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