Characterization of Water/Gas Separation and Energy Generation Membrane Materials by Solid-State NMR Spectroscopy

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Introduction

We have investigated graphene/graphene oxide (GO) as potential candidates for membrane materials that can provide superior properties in the permeation of gas or liquid molecules and in the selective separation (rejection) of certain molecules and ions. In order to understand the fundamental properties of GO materials on the molecular level we have utilized solid-state NMR spectroscopy for understanding the structural and dynamic properties of GO membrane materials in the solid-state. One of the key features that is not completely understood yet is the role of water molecules that may exist between molecular chains/fragments of GO sheets. Water molecules and hydrated ions that may exist between GO membrane sheets would connect different GO sheet layers via hydrogen bonding. Thus the presence of water molecules can highly affect GO membrane properties such as mechanical toughness and ion or gas transport. Understanding the state and transport behavior of water molecules in GO membrane sheets will be essential for the utilization of this material as a candidate membrane system for the separation of water, solute molecules, and/or ions.

Experimental

We have employed ^{1}H and ^{1}H-^{13}C cross-polarization NMR spectroscopy in solid-state to investigate the bound nature and dynamics of water molecules in the matrix of graphene oxide (GO). Also employed was ^{1}H T_1 relaxation measurements to examine the dynamics of the water molecules that are bound in GO membranes.

Results and Discussion

Fig. 1 shows the ^{1}H static (A) and ^{13}C CP MAS (B) spectra of a typical GO material. Carbon nuclei in GO material possess sp^{2} hybridization and do not contain any directly bonded protons that provide ^{1}H-^{13}C dipolar interactions. The proton peak shown in Fig. 1A is entirely from water molecules that are bound between GO sheets. In Fig. 1B, the ^{1}H nuclei of tightly bound water molecules provide intermolecular ^{1}H-^{13}C dipolar contacts with the ^{13}C nuclei in the GO skeleton for CP signal transfer. The rf-pulse strengths of ^{1}H and ^{13}C channels during the CP were $\nu_1(^{1}H)$ = 35 kHz, $\nu_1(^{13}C)$ = 50 kHz under the magic-angle spinning rate of ν_r = 7.6 kHz. Thus, the spectra shown in Fig. 1B manifests the tightly bound nature of water molecules around the carbon framework of GO sheets. The ^{1}H T_1 relaxation time measured on the bound water was in the range of 0.13~0.15 s that is an order of magnitude faster than that of bulk water (3.5 s) [1-2], reflecting the ordered status of water molecules in the matrix of GO material. Our next step will be the investigate of the motional time scale of water molecules that are in the GO matrix depending on the treatment or process of GO material.

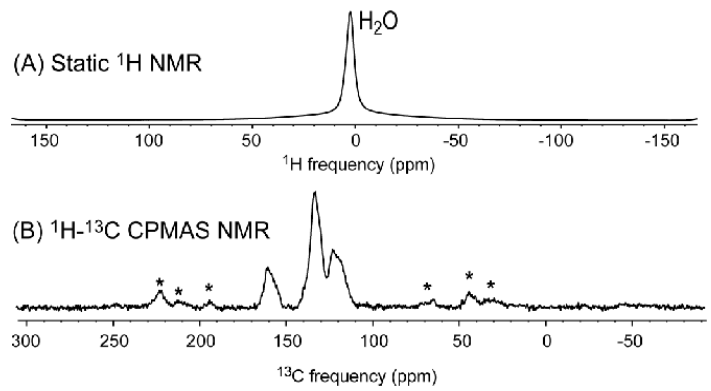

Fig. 1 ^{1}H and ^{1}H-^{13}C CP NMR spectra of GO film. The spinning sideband of each site is indicated by star marks (ν_r = 7.6 kHz).

Conclusions

This work provides a molecular-scale evidence that the ^{13}C framework of GO material can interact with liquid water molecules nearby. Water molecules that are captured in the matrix of GO sheets are in ordered states with an average motional correlation time that is at least an order of magnitude slower that that of bulk water (10^{-12}-10^{-11} s) [2].

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References

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