Communications

Solid-State $^2$H NMR Determination of Poly(aniline) Conformation Within a MoO$_3$ Nanocomposite**

By Gillian R. Goward, Tracy A. Kerr, William P. Power,* and Linda F. Nazar*

The focus of much recent research activity and interest, including our own, has been the synthesis, structure, and properties of conductive polymer/transition metal oxide nanocomposites. These hybrid materials comprise conductive organic polymers, such as poly(aniline) (PANI), interleaved between the layers of an inorganic oxide lattice, and are intriguing candidates for advanced material applications. In particular, the redox-active natures of both the polymer and inorganic components offer promising possibilities in electrochemical applications such as positive electrode materials in lithium batteries. While the materials demonstrate interesting bulk properties, little is understood about the microscopic interplay between the polymer and the oxide. Preliminary NMR studies have begun to provide details about the local structure of polymer and cations within the lattice.[1,2] It is surmised that the conducting polymer can augment the electron transport properties, and enhance lithium diffusion within the oxide host by minimizing steric and electrostatic limitations to lithium transport. Several investigations into the electrochemical performance of these nanocomposites as cathodes in lithium batteries have indicated complex behavior.[3,4] The primary concern addressed here is that of the interaction between the polymer and the oxide. Namely, we are trying to understand the role of the polymer, how it is ordered, and whether the polymer order affects the electrochemical response of the system.

Characterization of these systems at the microscopic level is difficult. Large single crystals of polymer/oxides are almost non-existent, except for (PANI)$_x$FeOCl, prepared by Kanatzidis et al.[2] Although the locations of the polymer, and hence conformation of the PANI chains, could not be determined, their single-crystal X-ray studies showed that the PANI is intercalated in an ordered fashion that forms a superlattice commensurate with the FeOCl lattice. In all other interleaved polymer/oxide nanocomposites, however, information must be gleaned from powder X-ray methods (PXRD). Typically, the PXRD patterns show strong $d_{eq}$ reflections, and only weak mixed reflections. This provides limited information on the order of the oxide host itself, and cannot be used to probe order of the polymer within the oxide. Our current research involves $^2$H NMR to probe polymer conformation and dynamics in nanocomposites containing perdeuterated PANI between the layers of MoO$_3$. Our one-dimensional (1D) and 2D experiments reported here unequivocally show that the PANI is organized within the interlayer region.

Figure 1a shows the solid-state $^2$H NMR lineshape obtained for crushed powder samples of deuterated (PANI)$_{0.24}$MoO$_3$ nanocomposites at 298 K. The $^2$H quadrupolar interaction dominates the two overlapping transitions in the NMR spectrum of this spin-1 nucleus. The polymer is rigid on the NMR time scale; the static value of the $^2$H quadrupolar coupling constant is 178 kHz with an asymmetry parameter of 0.05, values which are characteristic of poly(aniline).[5] The high-temperature (370 K) $^2$H NMR spectrum of (PANI)$_{0.24}$MoO$_3$ (Fig. 1b) displays a set of inner doublets at $\pm$17 kHz, indicative of phenyl deuterons undergoing two-site exchange due to 180° phenyl ring-flipping about the polymer chain axis. The degree of motion at this temperature is slightly greater than that of the corresponding bulk poly(aniline) in its emeraldine salt form, and less than that of the emeraldine base.[6] In the latter, there is only physical constraint to phenyl ring flipping; in both the salt and polymer/oxide nanocomposite, the dynamics are influenced by the electrostatic interaction between the delocalized positively charged polaron on the PANI chain, and the negatively charged lattice or counteranion, albeit to different degrees. The relative chain rigidity allows us to examine polymer conformation within the oxide host. Solid-state $^2$H NMR is an ideal probe for investigating preferential orientation distributions; however, both the polymer and the host oxide lattice must first be macroscopically and microscopically ordered. FeOCl/PANI bronze, although highly crystalline, contains a relatively large fraction of paramagnetic sites, whose interaction with the polymer obscures the information being sought.[7] In V$_2$O$_5$ itself, as well as in the corresponding PANI bronze,[8] the inherent lack of structural order within the sheets (as is evident from the XRD patterns of these materials) inhibits study of the polymer order and makes it difficult to ascertain the degree of macroscopic order of the sheets.

In contrast, the relatively high degree of both macroscopic and microscopic order attainable in MoO$_3$ and its PANI bronze is apparent from the degree of order in oriented film XRD patterns obtained on suspensions of...
(PANI)$_{0.24}$MoO$_3$ that were cast onto glass slides and allowed to dry.\cite{3} This results in preferred orientation of the layered crystallites. SEM photographs of the films confirm that a very high fraction of microcrystallites are preferentially aligned, the oxide layers lying parallel to the plane of the slide due to their highly anisotropic nature. In this macroscopic orientation, the effects of any preferred orientation of the polymer can be probed by $^2$H NMR of the deuterated poly(aniline) lying between the layers. Thus MoO$_3$ provides an ideal system for study by comparison to other host lattice systems.

Our studies rely on the orientation dependence of the Pake pattern. The distribution of spectral intensity across the NMR lineshape can be directly correlated to the orientation distribution of the corresponding C–D bonds.\cite{9} For example, a randomly oriented powder sample gives rise to the characteristic powder lineshape with a spherical distribution, seen in Figure 1. A single crystal, however, would give rise to narrow doublets corresponding to the angle between a given C–D bond and the magnetic field director, $B_0$. Since the molecular orientation, $\Theta_M$, is fixed within the magnetic field by the crystal lattice, the unique molecular orientation leads to a unique value of the quadrupolar splitting, and all the spectral intensity will be concentrated at frequencies corresponding to this orientation. Such single-crystal $^2$H NMR spectra have been used to determine the orientation of perdeuterated cobaltocenium cations within SnSe$_2$\cite{10} and MnPS$_3$\cite{11} layers. A preferential distribution of C–D vectors, as in the case of poly(aniline) intercalated within MoO$_3$ will give neither a random powder distribution nor a single-crystal pattern, but rather amplification or attenuation of corresponding portions of the deuterium lineshape according to the distribution. The limited range of quadrupolar splittings is centered about a preferred director of the distribution, $Z_D$. By acquiring the $^2$H NMR spectrum of the sample in two orthogonal orientations, and simulating the resulting effect on the lineshape, we are able to approximate the preferred orientation distribution using the appropriate Gaussian.

The response of the $^2$H NMR lineshape to changes in the orientation of the thin film samples is shown in Figure 2. For (PANI)$_{0.24}$MoO$_3$, striking differences were evident.
when the glass slides were oriented perpendicular (Fig. 2a) and parallel (Fig. 2b) to the magnetic field axis. When the slides were placed perpendicular to the magnetic field axis, the shoulders (where \( \theta = 0^\circ \)) of the \(^2\)H NMR lineshape were amplified relative to the peaks (where \( \theta = 90^\circ \)). Rotation of the slides without any other adjustment to the experimental conditions resulted in an attenuation of these shoulders and concomitant amplification of the peaks. Both spectra are also substantially different from the polycrystalline sample (Fig. 1a). Using MoO\(_3\) as a reference frame, in which the basal oxide layers form the \(xy\) plane, the \(^2\)H NMR spectra in Figure 2a were modeled using a distribution \( R(\Theta_{ma}) \) of C–D vectors. These spectra were simulated using 100 % order parameters. Two axes are used to describe the two types of deuterons on the aniline rings; these C–D vectors are aligned at 60°, and at 0° to the normal to the MoO\(_3\) layers. All of the C–D vectors are allowed to “wobble” such that they circumscribe a cone of angular width 25° (equivalent to a distribution breadth \( \sigma_{\Theta_{ma}} \)). This best fit to the data effectively allows for canting of the phenyl rings to either side of a plane perpendicular to the oxide layer normal, and/or tipping of the 0° and 60° C–D vectors within the plane (see Fig. 4). The key features of the lineshape are accurately represented, albeit with some intensity variance in the center-band region. Attempts to improve the quality of the simulations by decreasing the degree of polymer order (i.e., below 100 %), or increasing the angular width of the distribution led to poorer spectral simulation. The slight intensity discrepancies between experimental and simulated spectra may be due to numerous factors, for example, the insensitivity of the technique to interchain order.

We were also able to confirm the presence of a preferential distribution of poly(aniline) within MoO\(_3\) using 2D synchronized magic angle spinning experiments (2D sync MAS).\(^{[12,13]}\) In this method, the NMR pulse is synchronized with the position of the MAS rotor using a fiber optic detector. For an isotropic sample, the NMR signal is independent of the phase of the rotor at the time of the NMR pulse, whereas if the sample is preferentially ordered the rotor phase will modulate the amplitude of the NMR signal. This experiment, developed recently by Spiess et al. to elucidate structural details in processed bulk polymers, is therefore a highly sensitive probe of the microscopic orientation within a sample. To our knowledge, it has not been used to examine ordering in polymer/oxide composites of any type.

Figure 3 shows the 2D sync MAS data (in 1D slices) for the isotropic powder (PANI)\(_{0.24}\)MoO\(_3\) sample, and the corresponding results for the oriented films. The latter displays signal modulation in the sideband manifold \((m = \pm 1)\), whereas no evidence of signal modulation is evident in the powder sample, in spite of the significantly superior signal-to-noise ratio. Signal/noise remains an issue for the thin film samples due to the comparatively minute amount of sample that can be accommodated within the rotor. These data, however, do unequivocally confirm the polymer ordering suggested by the 1D experiments, and lead us to the model proposed in Figure 4. The polymer chains are oriented along an axis that lies parallel with the “grooves” be-

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![Fig. 3. Sync-MAS \(^2\)H NMR spectra of (PANI)\(_{0.24}\)MoO\(_3\) at 298 K showing different slices corresponding to the various rotor periods in the frequency domain: a) randomly oriented powder sample; b) oriented films.](image-url)
between the aligned MoO₆ octahedra, forming a sinusoidal pattern in a plane perpendicular to the oxide sheets; the phenyl rings, however, are tipped away from this plane about a dihedral angle of about ±13°. This model was used in fitting the 1D data shown in Figure 2, and will also be used in our further studies to simulate the 2D Sync MAS data. Significantly, the polymer structure within the layers is similar to that of the oligoaniline “pentamer” (five phenyl-ring molecule) determined by crystallographic studies. The structure of PANI itself is not known, owing to its insolubility and lack of crystallinity.

The ²H NMR results provide substantial detail concerning the polymer in (PANI)$_{0.24}$MoO₃, as these show that order is not determined solely by the oxide layers, but is manifested by the polymer between the layers as well. The oxide host acts as a highly anisotropic 2D “cage” that can be readily aligned on glass slides, which in turn can be oriented in the magnetic field. This allows the structure of the PANI chains to be probed as a function of orientation of the oxide host. Such a study is only possible in the nanocomposite, as bulk PANI cannot be oriented in a similar fashion. The combination of 1D and 2D Sync MAS ²H NMR provides unique and irrefutable evidence as to the preferential orientation of polyaniline within the molybdenum trioxide host lattice. We add that the heterogeneity of the local carbon site environments along the polymer chain made characterization of order using high-resolution $^{13}$C cross polarization (CP) MAS NMR fruitless. In contrast, solid-state ²H NMR is uniquely suited to providing this information, by virtue of the large quadrupolar field that dominates the spectra. Thus, ²H NMR studies of polymers intercalated within transition metal oxide hosts can provide important and unique information about the structure of the polymer that cannot be obtained by other methods. Further investigations of these materials, including two-dimensional NMR experiments to better characterize the distribution and electrochemical and NMR studies of lithium insertion in these materials, are ongoing.

[5] Solid-state NMR spectra of perdeuterated polyaniline nanocomposites were performed at 11.7 T, for which the $^{1}H$ Larmor frequency was 76.77 MHz. The quadrupole echo pulse sequence was used, with 90° pulse widths of 2.0–2.2 µs when radio-frequency pulses of approximately 450 W were applied. As well, a much shorter pulse (0.5–1.0 µs) was used for the initial excitation of the spins, with no difference due to finite pulse width effects evident in the spectra when compared to those obtained with the traditional 90°–90° sequence. Acquisition was initiated before the peak of the quadrupole echo with subsequent left-shifting of the free-induction decay to ensure the peak of the echo was correctly obtained. Spectral widths of 1 MHz were used, corresponding to dwell times of 1 µs between each of the 8192 complex time-domain points collected.


Chemical Contrast on a Microphase-Separated Block Copolymer Surface Observed by Scanning Force Microscopy**

By Michel P. L. Werts, Eric W. van der Vegte, Valérie Grayer, Eddy Esselink, Constantinos Tsitilias, and Georges Hadziioannou*

Since the introduction of chemical specificity in scanning force microscopy (SFM), the use of this technique to distinguish between chemically different functional groups down to the molecular level has become a challenge for many re-

** This work was financially supported by the Netherlands Foundation for Chemical Research (SON) and the Foundation for Fundamental Research of Matter (FOM).