A New Redox Host for Intercalative Polymerization: Insertion of Polyanieline into α-RuCl₃

Lei Wang,¹ Paul Brazis,¹ Melissa Rocci,¹ Carl R. Kannewurf,¹ and Mercouri G. Kanatzidis*¹

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, Michigan 48824, and Department of Electrical and Computer Engineering, Northwestern University, Evanston, Illinois 60208

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Lamellar nanocomposites with conductive polymers can display novel properties which can result from the molecular level interaction of the two dissimilar chemical components which comprise them. These nanocomposites have been synthesized by various intercalative methods, such as in situ redox intercalative polymerization,¹² monomer intercalation followed by polymerization,³ encapsulative precipitation from solutions of exfoliated lamellar solids,⁴ in situ oxidative polymerization coupled with encapsulative precipitation from solutions of exfoliated lamellar solids,⁵ and other methods.⁶ Among these, the in situ redox intercalative polymerization reaction is the most direct, and its topotactic character least disturbs the crystalline structure of the host.¹³ This type of reaction requires a strongly oxidizing host to provide the driving force to pull the monomers into the galleries and oxidize them into polymers. Because of the scarcity of such highly oxidizing hosts, the reaction has been limited to FeOCl₁₀,⁷ V₂O₅,¹⁰ and VOPO₄.² Here we demonstrate that α-RuCl₃ is also a suitable such host and can form an intercalative nanocomposite with polyanieline.

The lamellar structure of α-RuCl₃ is related to that of FeCl₃, which crystallizes in the defect CdCl₂ structure type.⁷ Each RuCl₃ layer is composed of a hexagonal sheet of Ru atoms sandwiched between two hexagonal sheets of Cl atoms with ABC stacking. In the Ru sheet, one-third of the positions are left unoccupied, which leads to a honeycomb pattern and to the RuCl₃ stoichiometry.

Ruthenium chlorides show interesting catalytic and photochemical properties. α-RuCl₃ shows intralayer ferromagnetism, interlayer antiferromagnetism,⁵ andphotoconductivity.¹⁰ Although there were only a few reports on the properties of α-RuCl₃ before the 1990s,¹¹ this material has attracted increasing attention in recent years.¹²,¹³ The intercalative properties of α-RuCl₃, however, have not been extensively studied except for some simple cations (e.g. Li⁺ and Cu⁺) and neutral Lewis bases such as pyridine.¹⁴ The intercalation of a polymer in α-RuCl₃, reported here, is a large step forward in exploiting the potential of this material as a host and opens up new possibilities for new conductive nanocomposites.

The reaction of a solution of aniline in CH₃CN with α-RuCl₃, in air, results in intercalative redox polymerization to polyanieline (PANI) within the gallery space of RuCl₃.¹⁵ The powder X-ray diffraction (XRD) patterns of the product show a 6.2 Å increase in the separation of the RuCl₃ layers (see Figure 1A). This expansion is reasonable for insertion of a monolayer of PANI molecules and is comparable to the 5.94 Å observed in (PANI)_xFeOCl₁₀ and 5.2 Å in (PANI)_{0.6}V₂O₅.¹⁶ The for-
mation of polyaniline between the RuCl₃ layers is supported by infrared (IR) spectroscopy (see curve c of Figure 1, right). Almost all peaks in the IR spectra of the (PANI)ₓRuCl₃ (0.50 < x < 0.60) are associated with polyaniline (emeraldine salt) except for a few weak peaks associated with anilinium or small oligomers (see curves a and b of Figure 1, right).

Scanning electron microscopy (SEM) images show that the size and morphology of the plates of (PANI)ₓRuCl₃ particles are very similar to that of α-RuCl₃ (see Figure 2), suggesting that the in situ redox intercalative polymerization reaction is topotactic and does not disrupt the structure of the host. The surfaces of the (PANI)ₓRuCl₃ plates are rougher than those of α-RuCl₃, with many microcracks. Due to the much larger basal spacing of (PANI)ₓRuCl₃, some delamination around the edges is visible.

Thermal gravimetric analysis (TGA) measurements for (PANI)ₓRuCl₃ done under both oxygen flow and nitrogen flow¹⁶ show little weight loss in the temperature range 100–200 °C. Differential scanning calorimetry (DSC) measurements, under a nitrogen atmosphere up to 210 °C, detected no obvious thermal event until decomposition at >190 °C.

In the process of intercalation, a fraction of Ru³⁺ atoms is reduced to Ru²⁺, resulting in a mixed valence compound. The formation of Ru²⁺ results in very stable, low-spin diamagnetic d⁵ c² centers. By virtue of the maximized ligand field stabilization energy (LFSE), this probably acts as a powerful driving force for the oxidation of aniline. Similar to the intercalative polymerization of aniline into FeOCl¹c and V₂O₅,¹d the presence of oxygen is key to a successful outcome of the reaction. This was verified by control experiments, where in the absence of air or oxygen no reaction occurred for 23 days.

(¹⁶) Under oxygen flow, (PANI)ₓRuCl₃ decomposes to RuO₂ when heated to 800 °C. Under nitrogen flow, both (PANI)ₓRuCl₃ and RuCl₃ continue to loss weight up to 710 °C. The total weight losses were 57.9% and 42.1%, respectively, for RuCl₃-PANI and RuCl₃, forming perhaps a high metal content phase.

The electrical conductivity of (PANI)ₓRuCl₃ at room temperature is ~2 S/cm, 3 orders of magnitude higher than that of α-RuCl₃, 5 × 10⁻⁴ S/cm.¹¹c Since LiₓRuCl₃

Figure 1. (left) Powder XRD diagrams of α-RuCl₃ and (PANI)ₓRuCl₃. (right) IR spectra of (a) aniline, (b) polyaniline, and (c) (PANI)ₓRuCl₃.

Figure 2. SEM images of (a) α-RuCl₃ and (b) (PANI)ₓRuCl₃. The pictures cover an area of 200 × 150 μm.
has only a conductivity of 0.3 S/cm, the conductivity of (PANI)\textsubscript{x}RuCl\textsubscript{3} seems to originate from both components, i.e., by charge transport through polyaniline as well as [RuCl\textsubscript{3}]\textsuperscript{x}-. By comparison, doped polyaniline (i.e. emeraldine salt) has a room-temperature conductivity of 5–8 S/cm. Variable temperature measurements reveal that the conductivity of pressed pellets of (PANI)\textsubscript{x}RuCl\textsubscript{3} is thermally activated (see Figure 3a), which is due to the grain boundaries in the sample. The thermopower measurements (which are less sensitive to grain boundary effects) indicate that the material is a hole conductor with a room-temperature Seebeck coefficient of $-12.2 \mu$V/K (see Figure 3b). This is consistent with the fact that both the reduced RuCl\textsubscript{3} layers as well as polyaniline (emeraldine salt) are p-type conductors.

In contrast to α-RuCl\textsubscript{3}, which shows antiferromagnetic (AF) ordering below 15.6 K,\textsuperscript{7,12a} (PANI)\textsubscript{x}RuCl\textsubscript{3} does not exhibit this transition. The disappearance of the AF transition is explained by the introduction of diamagnetic Ru\textsuperscript{2+} centers in the Ru sublattice and the increased separation of the RuCl\textsubscript{3} layers. The (PANI)\textsubscript{x}RuCl\textsubscript{3} follows Curie–Weiss law down to 10 K.\textsuperscript{17} The derived Weiss constant is $\theta = -19.5$ K, in contrast to the positive value of RuCl\textsubscript{3}, 11.0 K,\textsuperscript{18} indicating an AF exchange interaction on the average. The magnetic moment ($\mu_{\text{eff}}$) for (PANI)\textsubscript{x}RuCl\textsubscript{3} is 1.63 $\mu_B$, versus 2.32 $\mu_B$ for α-RuCl\textsubscript{3}. The drop of the magnetic moment is due to the decrease in the number of unpaired electrons in the RuCl\textsubscript{3} layer as the population of low spin Ru\textsuperscript{2+} centers increases.

In conclusion, α-RuCl\textsubscript{3} is a new host for conjugated polymer insertion via an in situ redox intercalative polymerization process. In the general class of polymer/RuCl\textsubscript{3} nanocomposites, the combination of the high conductivity of polyaniline and the wide-ranging catalytic properties of RuCl\textsubscript{3}\textsuperscript{8,9} could provide new materials with valuable electrocatalytic properties.

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Figure 3. (a) Variable temperature conductivity of pressed pellet (PANI)\textsubscript{x}RuCl\textsubscript{3}. (b) Thermopower for pressed pellet (PANI)\textsubscript{x}RuCl\textsubscript{3}.

(17) (a) An overall diamagnetic correction of $-133 \times 10^{-6}$ emu/mol was calculated from that of RuCl\textsubscript{3}, $-101 \times 10^{-6}$ emu/mol,\textsuperscript{17b} and polyaniline, $-53 \times 10^{-6}$ emu/mol-ring.\textsuperscript{17c} For the best fitting of the experimental data to the Curie–Weiss Law, $\lambda = -19.5$ K, and the $\theta$ was 15.8 K. The literature value was $2.25 \mu_B$ and 23 K. (b) Selwood, P. W. Magnetochemistry, 2nd ed.; Interscience Publishers: New York, 1956; p 78. (c) Epstein, A. J.; Ginder, J. M.; Richter, A. F.; MacDiarmid, A. G. In Conducting Polymers; Alcacer, L., Ed.; D. Reidel Publishing Company: Dordrecht, 1986; p 121–139.

(18) When no diamagnetic adjustment was given, the derived $\mu_{\text{eff}}$ was 2.25 $\mu_B$, and the $\theta$ was 15.8 K. The literature value was 2.25 $\mu_B$ and 23 K.