Stabilization of Anilinium in Vanadium(v) Oxide Xerogel and its Post-intercalative Polymerization to Poly(aniline) in Air

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We report the oxygen-induced polymerization of anilinium to poly(aniline) in the layered compound $(C_6H_5NH_3)_{0.4}V_2O_5\cdot0.40H_2O$ forming $\{1/n(-C_6H_4NH-)_n\}_{0.4}V_2O_5\cdot0.40H_2O$.

During the last few years we have investigated in detail the redox intercalative polymerization of several organic molecules such as aniline, pyrrole and 2,2'-bithiophene in $V_2O_5\cdot nH_2O$ xerogel.[1] The products contain the corresponding conjugated polymers [poly(aniline) (PANI), poly(pyrrole) and poly(thiophene)] within an electronically conductive, mixed-valence $V^{4+/5+}$ lamellar host. Redox intercalation[2,3] alters the band structure of $V_2O_5\cdot nH_2O$ forming bronze-like electrically conductive materials.[4] The formation of PANI from anilinium and $V_2O_5\cdot nH_2O$ is relatively fast, and study of

this heterogeneous reaction is difficult. It is presumed that the first step in the insertion of PANI is intercalation of the monomer in V_2O_5.

One way to follow the oxidation of aniline by the vanadium oxide would be to trap anilinium between the layers of the host and then observe its conversion to PANI upon oxidation. The challenge is to prevent AnH^+ from being oxidized by $V_2O_5 \cdot nH_2O$ before controlled polymerization can be initiated. We accomplished this by satisfying the oxidative power
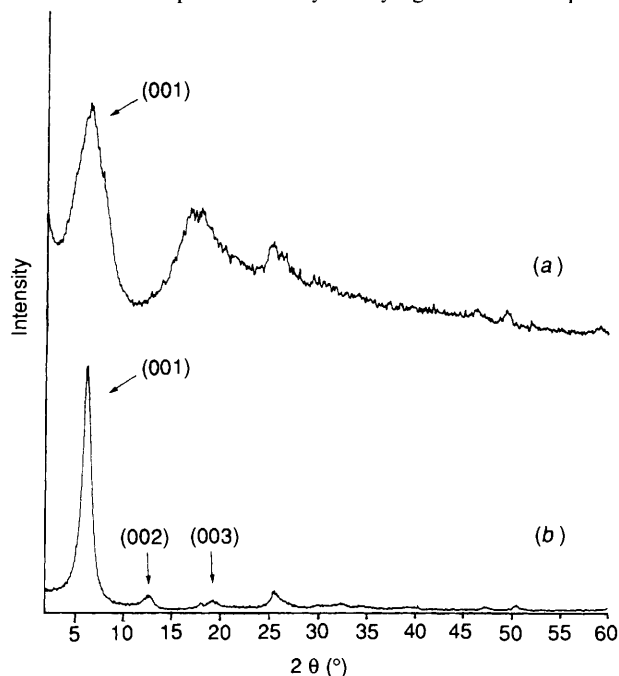
of $V_2O_5 \cdot nH_2O$ with electrons from a different source such as iodide. Here, we report the successful insertion of anilinium molecules in $V_2O_5 \cdot nH_2O$ and the surprising result of its intralamellar conversion to PANI upon exposure to ambient oxygen.

The synthesis of anilinium/$V_2O_5 \cdot nH_2O$ was accomplished by simply mixing CH_2Cl_2 solutions of anilinium iodide with the xerogel in a 4:1 molar ratio. The dark-blue product has the stoichiometry $(C_6H_5NH_3)_{0.4}V_2O_5 \cdot 0.40H_2O$ **1** and it is formed according to eqn. (1). The formation of iodine, which

$$x\, C_6H_5NH_3{}^+\, I^- + V_2O_5 nH_2O \rightarrow$$
$$(C_6H_5NH_3)_x V_2O_5 nH_2O + (x/2)I_2 \quad (1)$$

is removed by washing with acetone, is observed spectrophotometrically. The intercalation is confirmed by the net increase of *ca.* 5.1 Å in the interlayer distance, see Fig. 1(*a*). The very broad (001) diffraction peak corresponds to a very short coherence length, perpendicular to the stacking *c*-axis, which is estimated to be 25 Å.[5] This is considerably smaller than the 100 Å found in $V_2O_5 \cdot nH_2O$ itself and indicates considerable disruption of the stacking order of the vanadium oxide layers upon intercalation. The presence of AnH^+ is unambiguously established by FTIR (Fourier transform infrared) spectroscopy, see Fig. 2(*a*). By reducing the V_2O_5 framework with iodide, which is a better reducing agent than anilinium, the oxidizing ability of the host is diminished and

Fig. 1 X-Ray diffraction pattern from (*a*) $(C_6H_5NH_3)_{0.4}$-$V_2O_5 \cdot 0.40H_2O$ and (*b*) $\{1/n(-C_6H_4NH-)_n\}_{0.4}V_2O_5 \cdot 0.40H_2O$ and $V_2O_5 \cdot nH_2O$
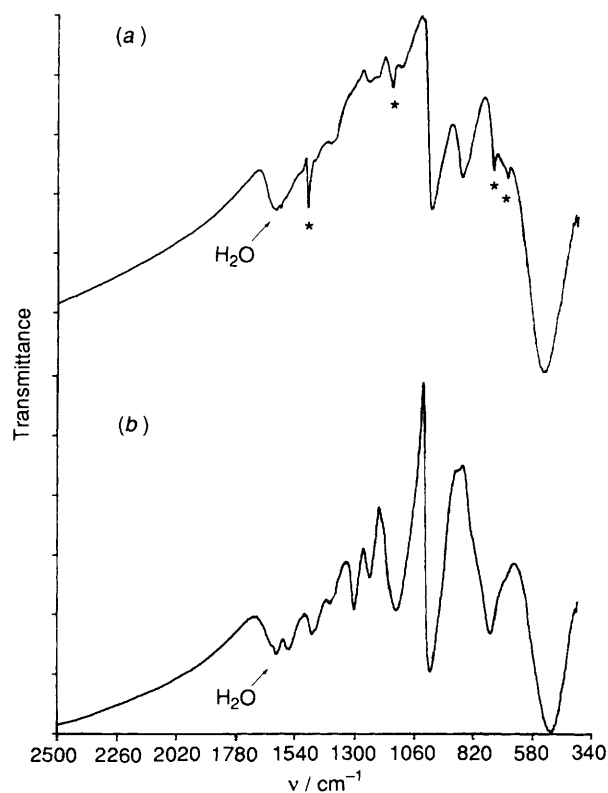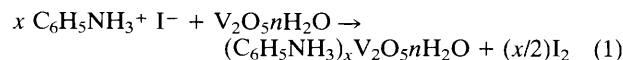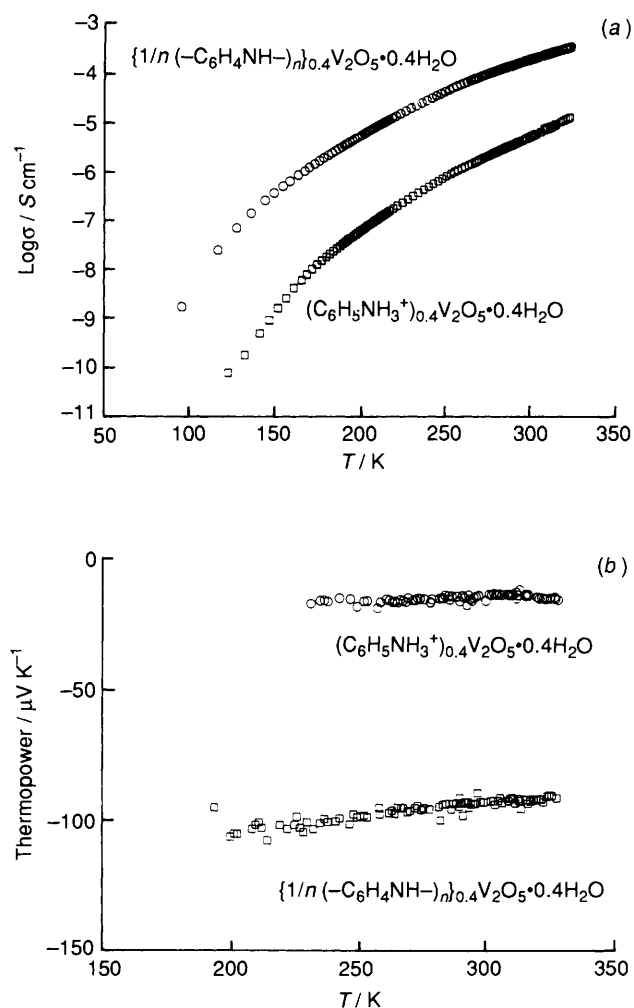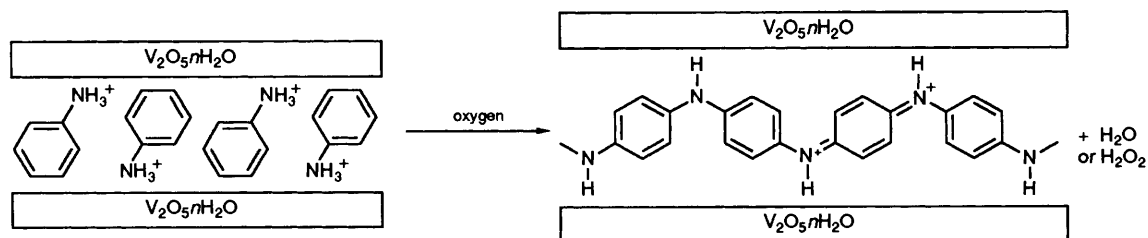

Fig. 2 (*a*) FTIR spectrum (KBr pellet) of $(C_6H_5NH_3)_{0.4}$-$V_2O_5 \cdot 0.40H_2O$, * peaks are from anilinium ion and (*b*) $\{1/n(-C_6H_4-$NH$-)_n\}_{0.4}V_2O_5 \cdot 0.40H_2O$

Fig. 3 (*a*) Four-probe pressed-pellet variable temperature electrical conductivity data of $(C_6H_5NH_3)_{0.4}V_2O_5 \cdot 0.40H_2O$ and $\{1/n-(-C_6H_4NH-)_n\}_{0.4}V_2O_5 \cdot 0.4H_2O$ and (*b*) variable-temperature thermoelectric power data of $(C_6H_5NH_3)_{0.4}V_2O_5 \cdot 0.40H_2O$ and $\{1/n(-C_6H_4-$NH$-)_n\}_xV_2O_5 nH_2O$

Scheme 1

thus further electron transfer from the anilinium is not favourable. This stabilizes the molecule in the inorganic framework. The electrical conductivity of pressed pellets of **1** at room temperature is 10^{-5} S cm^{-1}.

Exposure to air induced profound changes in the IR spectrum of the material, shown in Fig. 2, in which the anilinium peak pattern slowly disappears and the strong characteristic pattern of the emeraldine salt form of poly-aniline becomes evident.[6] We also observe significant changes in the position and shape of the stretching vibration peaks of the vanadium oxide framework (at v/cm^{-1} 990, 852 and 530 in **1** vs. 1000, 750, 496 in **2** respectively). This spectroscopic difference is due to the greater degree of reduction in the V$_2$O$_5$ in **1** than in **2** (see below). The peak in the X-ray diffraction pattern, shown in Fig. 1(b), of the oxidized product {1/n-(–C$_6$H$_4$NH–)$_n$}$_x$V$_2$O$_5$nH$_2$O **2** narrows dramatically compared with that of **1** and reveals a small 0.5 Å interlayer expansion. This indicates that the polymerization reaction is intra-lamellar, forming polyaniline chains inside the framework. This conversion is complete in three to four weeks. The estimated coherence length along the stacking axis increases threefold to ca. 90 Å, suggesting a significantly improved lattice organization. The overall reaction is represented in Scheme 1. To the best of our knowledge, this is the first time ambient oxygen is reported to react with an intercalated guest resulting in a coupling product.

The mechanism of this unprecedented post-intercalative oxidative polymerization is complicated but it must be related to the ability of vanadium centres to activate oxygen.[7] Simple anilinium salts are not oxidized to polyaniline under the experimental conditions employed here.† Therefore, the vanadium oxide framework must be implicated. One role for it could be as an electron relay between the reducing guest and oxygen. This is supported by the magnetic susceptibility data of **1** and **2**, which show that the number of spins in **2** is smaller, consistent with partial removal of electrons from the material. Both compounds are paramagnetic exhibiting Curie–Weiss behaviour with a contribution of temperature-independent van Vleck paramagnetism (TIP).‡ The μ_{eff} for **1** and **2** is 1.30 and 0.87 μ_B, respectively ($\mu_B \simeq 9.2740 \times 10^{-24}$ J T^{-1}) indicating fewer V^{4+} (d^1) centres in **2**. These data suggest that oxygen removes electrons from (V$_2$O$_5$)$^{x-}$, which in turn removes electrons from AnH$^+$.

2 shows slightly enhanced electrical conductivity consistent with the presence of PANI. Variable-temperature conductiv-ity plots of pressed pellets of (C$_6$H$_5$NH$_3$)$_x$V$_2$O$_5$nH$_2$O and {1/n(–C$_6$H$_4$NH–)$_n$}$_x$V$_2$O$_5$nH$_2$O are shown in Fig. 3(a). Over-all, the electrical conductivity of **2** is approximately two orders of magnitude smaller than that of PANI/V$_2$O$_5$nH$_2$O **3**, the product formed directly from aniline and V$_2$O$_5$·nH$_2$O.[1a] This

may be due to the smaller chain length of PANI in **2** compared with **3** (see below). The different electrical properties of **1** and **2** are emphasized in the thermoelectric power measurements. At 300 K **1** shows a small negative thermopower of –15 to –20 μV K^{-1}, while **2** exhibits a large negative thermopower of –90 to –110 μV K^{-1}, see Fig. 3(b). The more negative Seebeck coefficient of **2** is consistent with the fewer charge carriers (electrons) in the vanadium oxide framework compared with those in **1**, as suggested by the magnetic measurements. However, this is inconsistent with the higher conductivity of **2**. The thermally activated temperature dependence of conduc-tivity and the negative thermoelectric power suggests n-type semiconducting character for both materials. For comparison, PANI generally shows a very small positive metal-like thermopower.§[8] From these results we conclude that in **2**, despite the presence of PANI, the charge-transport properties are dominated by the vanadium oxide framework. The role of PANI in assisting charge transport is probably significant since the material shows higher conductivity than **1**, but it contains fewer carriers in its V$_2$O$_5$ framework.

The PANI isolated from **2** is soluble in N-methylpyrrolli-done (NMP) and molecular mass studies using gel permeation chromatography (GPC) were carried out in comparison with similar studies on bulk chemically prepared PANI.¶[9] The GPC results show a broad monomodal molecular mass distribution with a peak maximum corresponding to ca. 14 000, compared with a peak maximum of ca. 32 000 found for bulk PANI. By comparison, a molecular mass of 27 000 is obtained from PANI extracted from **3**. The considerably smaller molecular mass of the polymer in **2** is rationalized by the fact that its formation occurred in a structurally con-strained environment, in the solid state, in which the polymerization kinetics are slow.

In summary, the topotactic oxidative polymerization of intercalated anilinium in V$_2$O$_5$·nH$_2$O xerogel is unpreceden-ted and it is remotely reminiscent of the solid-state topotactic radiative polymerization of diacetylene monomers to poly-diacetylene in other layered hosts.[10] The reaction itself carries important implications for studying potentially regioselective intralamellar coupling reactions and for the future inclusion synthesis of conjugated polymers in a broad class of layered materials by solid-state polymerization of their corresponding monomer intercalated precursors.

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† In our experience, small amounts of polymer appear in anilinium salts after exposure for several months.

‡ $\chi_{(TIP)}$ for **1** 3.40×10^{-4} emu mol^{-1}. $\chi_{(TIP)}$ for **2** 6.50×10^{-5} emu mol^{-1}. The last number is more correctly due to, not only van Vleck TIP, but also Pauli TIP originating from the emeraldine salt.

§ The thermopower of PANI changes with doping level from slightly negative (high doping levels) to positive (low doping levels). The temperature dependence of the negative thermopower is very different from that of **2** as it tends to zero with falling temperature.[8]

¶ The molecular mass measurements were done using a Shimadzu LC-10A HPLC system coupled to a GPC column PLgel 5 μ mix which was held at 75 °C. The eluent NMP contained 0.5% wt LiCl. The elution rate was 0.2 ml min^{-1}. $M_n = 12\,300$, $M_w = 19\,800$. $M_w/M_n = 1.6$.

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