Experiments Illustrating Metal–Insulator Transitions in Solids

Steven W. Keller and Thomas E. Mallouk[1]
Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712

In most introductory chemistry courses, significant emphasis is placed on theories of bonding in molecules. Students are exposed to concepts ranging from Lewis dot structures to molecular orbital descriptions of transition metal complexes. Simple inorganic crystal structures are presented (ZnS, CaF_2, $NaCl$), but the discussion often ends at the radius ratio rule. The electronic properties of extended crystalline solids usually receive little attention. Although an *ab initio* derivation of band structures for solids is beyond the scope of most introductory chemistry classes, an elementary introduction to band theory, and to solid-state chemistry in general, can be included easily. The aim of the experiments and demonstration described in this article is to expose undergraduate students in a fun and painless way to concepts relating to the electronic properties of solids, and to interesting new materials, such as conducting polymers, which are the subject of significant current research.

Molecular Orbitals and Energy Bands

The idea of overlapping atomic orbitals that form orbital energy bands in a crystalline solid follows naturally from the development of molecular orbitals in simple molecules such as hydrogen (*1*). Quantum mechanically, electrons are allowed only to exist in certain ranges of energy (bands) in solids, much in the same way as they can exist only at discrete energies (orbitals) in molecules. The molecular orbital picture for the hydrogen molecule is extended easily to that of an infinite one-dimensional chain of hydrogen atoms. The bonding in the H_2 molecule is described by a filled bonding orbital lying below an empty antibonding orbital (Fig. 1). In the chain case, instead of two atomic orbitals combining to form two molecular orbitals, there are $\sim 10^{23}$ atomic orbitals combining to form as many delocalized molecular orbitals, which together make essentially continuous bonding and antibonding bands of allowed energies. Similarly, albeit with slightly more complexity, the band structures of three-dimensional crystalline solids can be derived by combining atomic basis orbitals. The four sp^3 orbital hybrids of a silicon atom, for example, combine to produce two bonding and two antibonding combinations per atom, which merge into valence and conduction bands, respectively, in solid silicon. The four electrons per atom exactly fill the available two orbitals per atom in the valence band, and silicon is, therefore, a semiconductor.

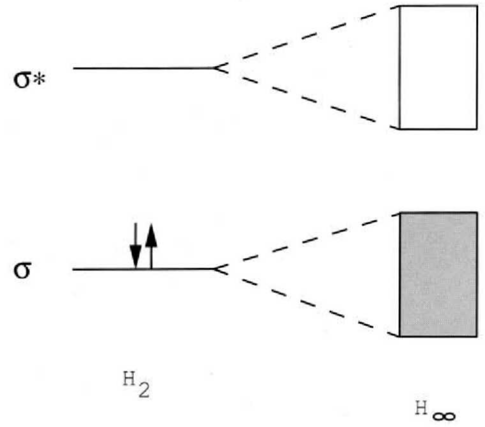


Figure 1. Left: molecular orbital diagram for H_2. Right: block band diagram for an infinite chain of hydrogen atoms.

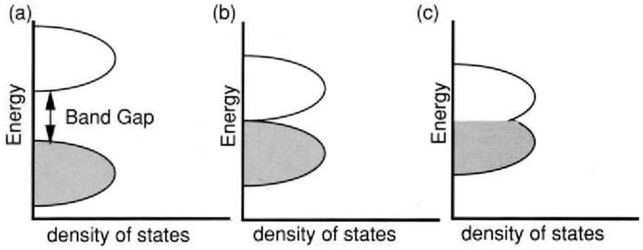


Figure 2. Schematic band diagrams for; (a) an insulator/semiconductor, (b) a semimetal, and (c) a metal. The larger the density of states, the more levels exist at that energy; i. e., there are fewer levels at the upper and lower parts of the band compared to the middle. Shaded areas indicate electron occupation.

Crystalline solids often are separated into categories based upon their electronic properties. Materials with completely filled bands are insulators/semiconductors[2] or semimetals, while those having partially filled bands are metals, as shown in Figure 2. Oxidation or reduction of insulators, semiconductors, and semimetals can create partially filled bands; therefore, their conductivity can be increased, often by many orders of magnitude, via a chemical reaction (*2*). Sometimes, these reactions can be done in such a way as to retain the bonding connectivity between atoms in the reactant solid, and in this case they are called *topochemical* reactions. Topochemical reactions offer the pedagogical advantage that they conserve, to a first approximation, both the physical and electronic structure of the solid; therefore, the same band picture applies to both reactant and product. In addition, they often can be reversed chemically or electrochemically. The experiments described in this paper take advantage of this property for a class of topochemical reactions called *intercalation* or *insertion* reactions. These reactions involve the introduction of an electron donor or acceptor (guest species) into a relatively rigid (host) structure, altering the occupation of its electronic energy bands (*3*).

Reduction (adding electrons) to an insulator, semiconductor, or semimetal populates the lowest energy orbitals of an unfilled band (called the *conduction band*). Because it is electrons that carry current in these materials, the conduction is said to be *n-type* (*n* stands for *n*egatively charged carriers). Oxidation (loss of electrons) creates electron vacancies, or *holes*, in the highest energy orbitals of the occupied (or *valence*) band. Both processes are presented schematically in Figure 3.

While it always is the electrons that move, we can think of the hole as a positively charged carrier, and the conduc-

---

[1] Present address: Department of Chemistry, Pennsylvania State University, University Park, PA 16802.

[2] The distinction between semiconductors and insulators is rather arbitrary. Conventionally, those materials with band gaps in excess of 3eV are considered insulators, and those less than 3eV are semiconductors.

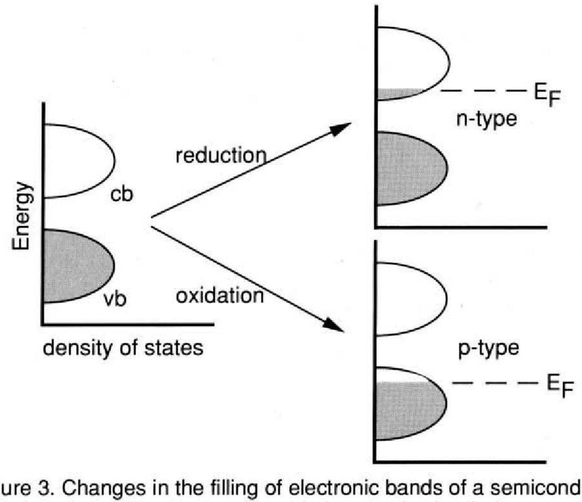


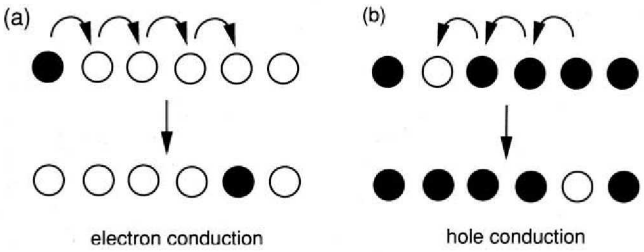
Figure 3. Changes in the filling of electronic bands of a semiconductor resulting from reduction or oxidation. Reduction induces partial filling of the conduction band, and oxidation causes partial emptying of the valence band. Both processes make the material an electronic conductor. E_F denotes the Fermi level.

tion in materials where holes are the dominant carrier is, therefore ,said to be p-type. An analogy that helps to understand electron and hole conductivity in solids is a large lecture hall that fills up at the beginning of a class period. Initially, all the seats are empty (empty seats are analogous to holes), and gradually they are filled with students (electrons). While the room still is relatively empty, it is the electrons that are moving to fill the seats, (Fig. 4a). As the room (now a partially filled band) fills up, the seats on the aisles are taken before those in the middle of the rows. A row with empty seats in the middle can be filled by everybody moving over one seat. Even though it is people (electrons) who are actually shifting seats, it appears as though the empty seat (hole) moves toward the aisle, (Fig. 4b).

We can think of the electrons in a filled band as being delocalized, but with equal numbers moving in opposite directions. Applying an electric field changes the energies of electrons moving with and against the field, but because there are no unfilled orbitals close enough in energy into which electrons can go, the number moving in any direction cannot change. Hence there is no current flow, and the filled band does not contribute to electronic conduction. In a partially filled band, there are available orbitals of only slightly higher energy than the highest occupied level, and in the presence of an electric field, electrons that were moving against the field can switch directions by entering an unfilled orbital.

Lecture Demonstration: Oxidative Intercalation of Graphite, a Semimetal

Graphite, a semimetal with little overlap between valence and conduction bands, can be made into a metallic conductor by oxidation with bromine.[3] The bromine intercalates between the layers of the solid, with partial charge transfer to produce positively charged carbon sheets, as shown in Figure 5.



electron conduction

hole conduction

Figure 4. The analogy between electron (a), and hole (b) conduction. The black circles represent electrons and the curved arrows indicate the direction of electron motion.

Materials

2 glassy carbon electrodes
Teflon tubing
1–2 g crystalline graphite powder, 200 mesh
1–2 mL bromine, or 10% (v/v) Br_2 in MeOH
6-V battery
1–2 Ω light bulb
Wires and alligator clips to connect the parts in series

Procedure

The intercalation reaction is carried out in a section of Teflon tubing containing the graphite powder. The apparatus is constructed by sandwiching about 5 mm of polycrystalline graphite powder ("Ultra Carbon F" works well) between two glassy carbon rods as shown in Figure 6. Apply enough pressure to the graphite so that the resistance between the two rods is 10–30 W. This apparatus is then held in a glass tube horizontally with a hole in the top and is connected in series via alligator clips to a 6-V battery and a light bulb with a resistance of 1–2 W. The light bulb should glow faintly or be dark, showing that the graphite powder is resistive. With a razor blade, cut a notch in the tubing to expose a small area of the graphite powder. Several drops of bromine (or 10% v/v Br_2 in methanol) are introduced directly onto the notch, and after a few seconds the light bulb will begin to glow brightly.

- ***Caution*: Elemental bromine is volatile, corrosive, and highly toxic. If liquid bromine is used, this demonstration should be carried out in a fume hood, and the demonstrator should wear gloves.** The experiment also

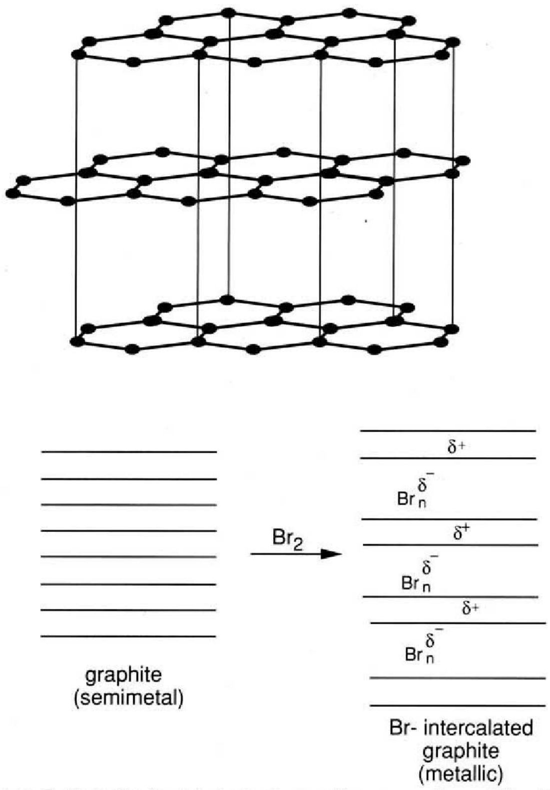


Figure 5. Top: the layered structure of hexagonal graphite. Bottom: the oxidative intercalation of graphite imparts partial positive charge to the carbon sheets while simultaneously propping them further apart.

---

[3] To the best of our knowledge, this demonstration was first performed by A. R. Ubbelohde in the 1960's.

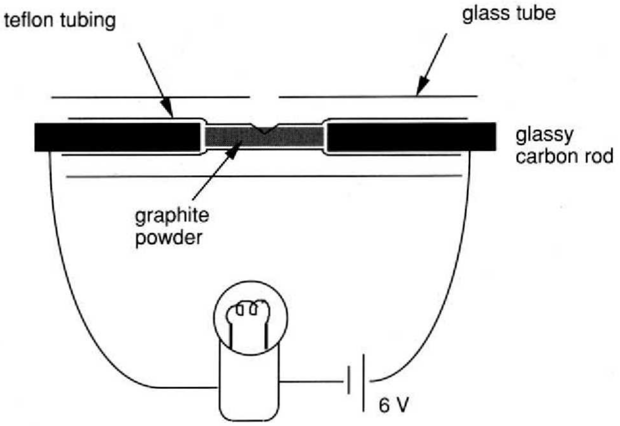


Figure 6. Conductivity apparatus for demonstrating Br-intercalation into graphite.

> can be done safely in a classroom with a methanol/bromine solution, although in this case the response is slightly less impressive. The change in conductivity is sufficient in either case to light the bulb.

Discussion

Graphite intercalation first was observed over 150 years ago by Schauffaütl, who prepared acid sulfate intercalation compounds (*4*). Intercalation by either electron donors, such as alkali metals, or by electron acceptors such as bromine or fluorine, is possible. In both cases the electronic conductivity in increased relative to pure graphite.

The bromineintercalation reaction increases the conductivity of the graphite by taking electrons out of the valence band (Fig. 3) and the conductivity is therefore p-type. The Fermi level, which is the energy at which the probability of electron occupancy is 50%, equivalent to the highest occupied molecular orbital (HOMO) in an individual molecule, also is shown in Figure 3. To a first approximation, the number of electrons (density of states) at the Fermi level is proportional to the conductivity. Bromine intercalation lowers the Fermi level, increasing the number of hole carriers and transforming graphite from a semimetal to a metal. Additionally, the intercalation process swells the individual graphite particles, increasing the pressure inside the Teflon tubing and thereby improving electrical contact between particles, further lowering the resistance.

Although not explicitly demonstrated here, this experiment can lead easily into a discussion of the anisotropy of layered solids. Ask students how they think the anisotropy affects the electrical and mechanical properties of graphite. What differences in conductivity might be expected using single crystal graphite?

Experiment One:
n-Type Conduction in Vanadium Pentoxide

In this experiment students carry out a reductive intercalation of V_2O_5. The reaction causes a change of 1–2 orders of magnitude in electronic conductivity and a characteristic color change. Re-oxidation of the intercalated solid with commercial bleach returns the original color and low conductivity. A redox titration allows the student to determine the stoichiometry of the intercalation reaction, and demonstrates that solids can have nonstoichiometric elemental compositions.

Vanadium pentoxide is a layered semiconductor that can be reductively intercalated according to the half-reaction shown below:

$$V_2O_5 + xLi^+ + xe^- \rightarrow Li_xV_2O_5\ (x \leq 1) \qquad (1)$$

The electrons are supplied by the concurrent oxidation of I^- to I_3^-. In undoped V_2O_5, the valence band (derived primarily from O 2p orbitals) is full and the conduction band (V $3d_{xz}$,$3d_{yz}$) is empty. In the presence of lithium ions and a suitable reducing agent, intercalation of Li^+ occurs, and electrons enter the empty conduction band. Since this band is doubly degenerate, it could in principle be occupied by four electrons per V atom. In practice, intercalation occurs to the extent of about 0.5 electron per V atom, and hence the conduction band is filled only partially.

Experimental Procedure (one 3-h lab period)

Materials

Caution: V_2O_5 is toxic. Gloves should be worn and waste should be disposed of properly. Since V_2O_5 is a polymorphic solid, not all commercial samples may give the same results. Our experiments were performed with V_2O_5 from Aldrich Chemical Co.

Bandgap Energy

Students are asked to note the color of the V_2O_5 powder, and to tell what colors of light are *absorbed* by it, recalling that the color of the powder indicates the light that is *reflected*. A typical semiconductor would have a UV-visible absorption spectrum like that shown in Figure 7. They can estimate the approximate bandgap energy of V_2O_5 from the color, using the relation that photon energy (in eV) = $1240/\lambda$, where λ is given in nanometers. (To help in their calculation, blue light has a wavelength of about 420–470 nm; green light, about 510–540 nm; red light, about 600–630 nm.)

Conductivity of V_2O_5

Some V_2O_5 powder is placed into a pellet press (these are normally used to make KBr pellets for infrared spectroscopy), and compressed to form a thin, translucent pellet. The pellet is placed on a microscope slide, and the electrical resistance across its diameter is measured using an ohmmeter (adjust the meter to read in the 10–100 kΩ range). Ask the student how the resistivity of this semiconductor compares with that of metals like aluminum, or semimetals like graphite.

Reduction / Intercalation

A suspension of ~0.7 g V_2O_5 in 10 mL distilled water is prepared. The solid is allowed to settle for a minute or two. A known excess of ~3.0 g LiI is added carefully to the V_2O_5

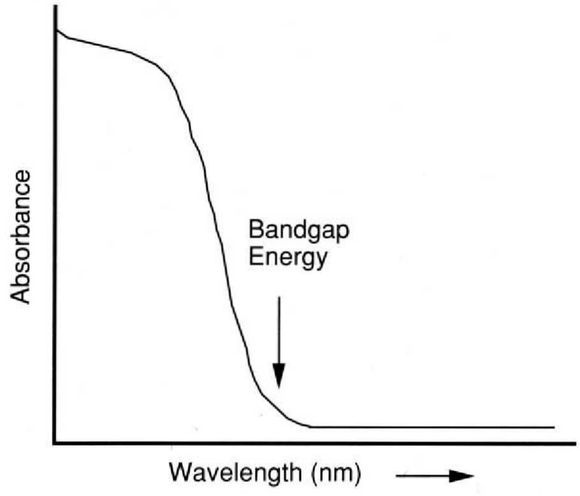


Figure 7.Typical absorption spectrum of a semiconductor in the UV-visible region. The onset of absorption coincides with the band-gap energy (i.e., the lowest energy required to promote an electron from the valence band to the conduction band).

suspension *without stirring*. Ask students to note any color changes that occur in the bottom of the beaker. After about 10 min, the solution is stirred briefly and allowed to stand for another 10 min. The solution is suction-filtered through a Büchner funnel, and the filtrate is collected. Dilute this solution to the mark in a 100-mL volumetric flask and set aside. The solid is then washed thoroughly with water and allowed to air-dry completely. The color of the solid, and of the solution that passed through the filter should be noted. Students can be asked to identify the source of these colors (darkening of the V_2O_5 because of partial filling of the conduction band, darkening of the solution because of formation of triiodide ion), and to write out a balanced equation for the reaction of LiI and V_2O_5. They should also try the reaction with NaI. The fact that the latter reaction does not work shows that it is necessary but not sufficient to have a reducing agent (I^-) in the reaction; the intercalation reaction also requires the small Li^+ cation, which can fit between layers, and which diffuses in the solid fast enough to permit intercalation on the timescale of the experiment.

To analyze the amount of lithium that intercalated into the V_2O_5, an iodometric titration is performed. This requires a $Na_2S_2O_3$ solution, approximately 0.05 M, and a KIO_3 solution of accurately known concentration, also ~ 0.05 M. The thiosulfate solution can be standardized with KIO_3, which is a primary standard. The endpoint of this titration is easier to see if a back-titration is done. For this, all of the I_2 formed in the filtrate solution 1 (which is mostly present as I_3^-) is reduced to I^- by the addition of a known amount of thiosulfate ion. The iodide is then titrated with potassium iodate using a starch indicator, until a faint blue color remains. The number of equivalents of I_2 originally produced from the oxidation of I^- (and associated intercalation of Li^+ into V_2O_5) is then the difference between the equivalents of thiosulfate added and the equivalents of iodate needed to reach the endpoint, using the appropriate balanced reactions constructed from the following half-reactions:

$$I_2 + 2e^- \rightleftharpoons 2I^- \qquad (2)$$

$$2S_2O_3^{2-} \rightleftharpoons S_4O_6^{2-} + 2e^- \qquad (3)$$

$$IO_3^- + 6H^+ + 6e^- \rightleftharpoons 2I^- + 3H_2O \qquad (4)$$

Students can use the result of their titration to calculate the value of x in $Li_xV_2O_5$. They are asked to think about why we sometimes find that inorganic solids have nonstoichiometric compositions; whereas, gaseous and liquid compounds, as well as *molecular* solids, are almost invariably stoichiometric. Pooling the class results for the value of x, and computing the mean and standard deviation, willillustrate the nonstoichiometry of the reaction product.

Conductivity and Reoxidation of $Li_xV_2O_5$

A pellet is made from the Li-intercalated solid the same way as was done with V_2O_5. Measuring the conductivity as before shows the increase, relative to the semiconductor before intercalation. Next, a solution consisting of 20 mL bleach (grocery store bleach is approximately 5% NaOCl) and 80 mL water is made, and the pellet and the remaining $Li_xV_2O_5$ powder are added to it. The suspension is stirred, stopping occasionally to let the solid settle so that any color changes can be observed. After about 10–15 min the reaction should be complete. The solid is suction-filtered and washed with water as before, allowed to air-dry. A pellet is then made and its conductivity measured. Students are asked to tell what has happened to the $Li_xV_2O_5$ and to write a balanced equation for its reaction with hypochlorite.

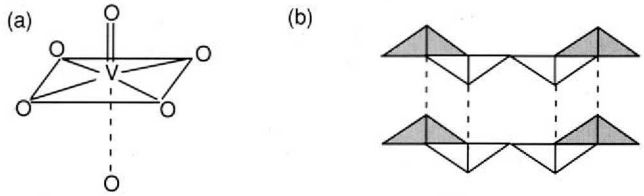


Figure 8.(a) The distorted octahedral coordination of vanadium in V_2O_5. (b) A schematic representation of the layered structure of V_2O_5. The solid lines (pyramids) outline the polyhedra formed by the vanadium atom and its five short oxygen bonds. The dashed lines are the indicate the one long V–O bond.

Discussion

In V_2O_5, the coordination around the vanadium atom is a distorted octahedron of oxygen atoms. One of the V–O bonds is short (i.e., formally a double bond), and the bond *trans* to it is long, so that there are chains of V=O—V units as in Figure 8a (*5*). In addition, each V is coordinated to four O atoms that lie in a plane perpendicular to the V=O—V chains, and these oxygen atoms are shared with other V atoms to make planar sheets (Fig. 8b). Upon intercalation, the sheets are spread apart, further elongating the long O–V bond and Li^+ ions then are located between the sheets, coordinated to both chain and sheet oxygen atoms. As more lithium is introduced, the sheets buckle to accommodate them; however, no V–O bonds are broken.

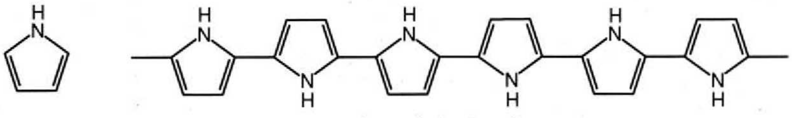
It should be noted that although the reduction of V(V) to V(IV) can be thought of as a population of the conduction band, the electrons introduced are not "nearly free electrons" as would be found in the silver or copper, or even in the more poorly conducting metallic elements or alloys. The electrons are somewhat localized at specific V(IV) sites, and the increased conductivity comes from a very small activation energy for hopping of these electrons to an adjacent site (~0.02 eV), as compared with the much larger band gap of undoped V_2O_5 (*6*). Good questions one might ask at this point are:

- What are the major sources of electrical resistance in normal metals?
- What sort of function of temperature would you expect for the conductivity of normal metals? For semiconductors? For intercalated solids?

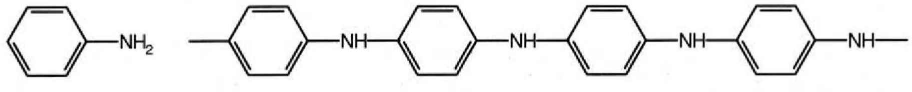
In the reaction with hypochlorite, the lithium ions are removed by re-oxidizing the solid, and the original structure and color are restored. Since no bonds in the V_2O_5 framework need to be broken and re-formed, the solid is stable over many cycles of reduction/oxidation. Other layered vanadium oxides (such as V_6O_{13}) undergo these reactions with even less structural distortion and are considered to be promising materials as reversible electrodes for high-energy-density secondary batteries (*7*).

Experiment Two: Bipolaron Conduction in Polypyrrole and Polyaniline

Polypyrrole and polyaniline are two of a wide and ever-growing class of electronically conducting organic polymers. They are formed by oxidation of pyrrole or aniline monomer to form a linear polymer. Using appropriate concentrations of graphic monomer and an oxidizing agent, these polymers can be made to grow in their conducting forms on substrates such as paper or cloth. The undoped form of either polymer is an insulator, but each can be made conducting by oxidants such as persulfate. Positive charges on the polypyrrole chain, at sufficiently high concentration, tend to localize in pairs over approximately four pyrrole units. This localized pair of holes, with the

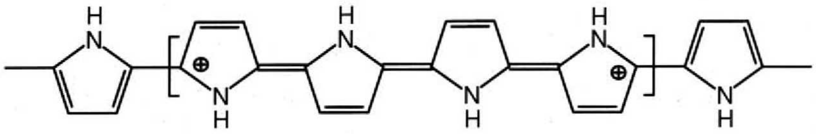


polypyrrole (undoped)



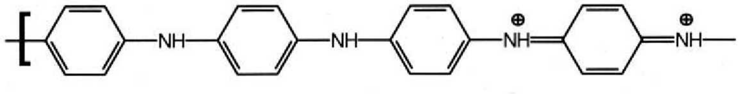
polyaniline (undoped)

bond length distortions it introduces, is called a *bipolaron*. Bipolarons can move along a chain as a traveling lattice distortion and spinless pair of positive charge carriers. The situation is a little different from the band picture we used above. The bipolaron energy levels are intermediate in energy between the valence and conduction bands (distortion of the polymer chain makes for new quantum mechanically allowed orbitals *within* the bandgap) .

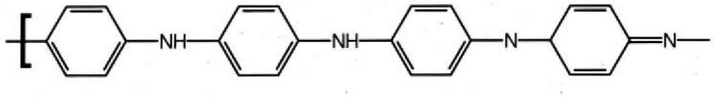


bipolaron in polypyrrole (spread over four monomer units)

With polyaniline the situation is a little more complicated. A bipolaron is formed by two-electron oxidation of small segment of the polymer, as with polypyrrole. However, this bipolaron can easily lose protons from the NH groups where the positive charge is localized, as shown below.



emeraldine salt (conducting)



emeraldine base (insulating)

The resulting quinoid form (called the "emeraldine base" form) is again insulating. When the emeraldine base is protonated by acid, each nitrogen again has a proton attached, and the bipolaron can move along the chain without the need for protons to hop as well. This form is a good electronic conductor. The polymer can be switched back and forth between conducting and insulating forms by simply changing the pH.

Experimental Procedure (One 3-h lab period)

Filter paper is cut into roughly 1 × 2 in. strips (each student will need about four of these strips). Pyrrole and aniline are polymerized onto these strips in the following way:

Polypyrrole

A solution is made of 1 mL pyrrole in 350 mL water.

- ***Caution*: Pyrrole and aniline are toxic. Avoid skin contact.**

The solution is swirled until it is homogeneous. A separate solution is made containing 1.1 g $FeCl_3 \bullet 6H_2O$ in 50 mL water. Fifty milliliters of each solution is added to a 200-mL beaker, and two strips of filter paper are put in (if possible, these strips should be suspended or made to stand up so that both sides are contacted by the solution). Gradually the solution will begin to change color. The reaction is allowed to proceed for about 1 h. (This is a good time to begin the polyaniline experiment; see below.) Then the paper strips are removed with a spatula and rinsed with deionized water. The polymer-containing strips are dried on a stack of 2–3 pieces of clean filter paper. The resistance from one end of the strip to the other is then measured. An alligator clip at each end works well for this purpose. Students can compare the conductivity of these samples to filter paper containing no polypyrrole and can write a balanced reaction for the formation of conducting polypyrrole from $FeCl_3$ and pyrrole monomer.

Polyaniline

Each student should prepare 500 mL of a 1.0 M aqueous HCl solution, and then a solution of 1 mL aniline in 250 mL of the HCl solution, and another solution of 0.5 g ammonium persulfate in 50 mL of the HCl solution. Fifty milliliters of the polyaniline solution and 50 mL of the persulfate solution are combined in a beaker, a couple of strips of filter paper are added, and the polymerization reaction is allowed to proceed for about 1 h. The paper strips are then removed from the solution, washed with deionized water, dried, and their resistance measured. At this point the paper strips are conducting. Now a solution of 2.0 g $NaHCO_3$ in 100 mL water is made, and one of the strips swirled in it for about 5 min. Students are asked to note any color changes. The other strip is put in 100 mL of 1.0 M HCl. Both strips are then washed with water, dried, and their resistances measured. There will be a significant difference in both color and resistance. Now the strip that was in the basic solution is put into the acidic solution, and the strip that was in the acidic solution is put into the basic solution. After swirling for 5 min, color changes are noted, and the strips are washed, dried, and their resistances measured as before. This experiment illustrates clearly why the conducting form of polyaniline is called "emeraldine," and the reversible switching between conductive and nonconductive forms via protonation/deprotonation. Students can be asked to write a balanced equation for the formation of the conducting emeraldine salt from aniline and ammonium persulfate, and to offer an explanation of why electronic conductivity is unusual for linear chain polymers.

Discussion

Conducting polymers were first made over 100 years ago. They have been studied intensely over the last 15 years because of potential applications as rechargeable battery electrodes, as electrodes for electrochromic displays, as lightweight "plastic wires", as active components of "molecular electronic" devices such as diodes and transistors, and as gas separation membranes (*8*). The fact that conducting polymers may be rapidly switched, chemically or electrochemically, between insulating and conducting forms, and the fact that they may be grown as fibers or thin films makes them attractive alternatives to conventional metals and semiconductors in these applications.

Acknowledgment

The authors thank Margret Geselbracht and Art Ellis for testing the graphite–bromine demonstration and the V_2O_5 intercalation experiment, the members of the Solid State Instructional Materials Ad Hoc Committee for helpful suggestions, and the National Science Foundation (grant USE-9150484) for financial support. T. E. M. also thanks the Camille and Henry Dreyfus Foundation for support in the form of a Teacher–Scholar Award.

Literature Cited

1. For an introduction to some of the simple mathematics of band theory see: (a) Weller, P. F. *J. Chem. Educ.* **1970**, *47*, 501–507. (b) Weller, P. F. *J. Chem. Educ.* **1967**, *44*, 391–393, provides an illustrative analogy between energy bands and a water bottle. For more in-depth discussion of bonding in the solid–state see: (c) Burdett, J. K. *Progr. Solid State Chem.* **1984**, *15*, 173–255; *Chem. Rev.* **1988**, *88*, 3–30; (d) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures;* VCH Publishers: New York, 1988.
2. Edwards, P. P.; Sienko, M. J. *Acc. Chem. Res.* **1982**, *15*, 87–93.
3. For a more thorough discussion and examples of intercalation reactions see: (a) Schöllhorn, R. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1392–1400; (b) Rouxel, J. *Chem. Scripta* **1988**, *28*, 33–40; (c) Murphy, D. W. In *Advances in the Synthesis and Reactivity of Solids,* Vol. 1., Mallouk, T. E., Ed.; JAI Press: London, 1991, pp 237–272, and references therein.
4. Schauffaütl, P. *J. Prakt. Chem.* **1841**, *21*, 155.
5. Goodenough, J. B. *Progr. Solid State Chem.* **1975**, *5*, 367–375.
6. Wells, A. F. *Structural Inorganic Chemistry*; 5th ed.; Clarendon Press: Oxford, 1984, pp 567–569.
7. Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651–656.
8. (a) Greene, R. L.; Street, G. B. *Science* **1984**, *226*, 651–656; (b) Kanatzidis, M. G. *Chem. Eng. News,* Dec. 3, **1990**, 36–54.