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Electronic composite of sulfonated tetrafluorethylene copolymer with potassium ferricyanide exhibiting room-temperature negative differential resistance

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A two-phase composite material was prepared by mixing the polymer Nafion with an electroactive molecule, potassium ferricyanide. The current-voltage characteristic of the material shows a finite conductance about zero bias, indicating a metal-like electrical conduction. The conductance is found to be proportional to the concentration of the potassium ferricyanide molecule and temperature. A conductance peak is present at a low bias voltage, providing a region of negative differential resistance. A peak-to-valley current ratio of 1.8 was obtained with a current density of 30 $\mu A/cm^2$. A conduction mechanism based electron tunneling between the active sites of the molecule is proposed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402903]

It is known that when a small amount of foreign material is introduced into an insulating host material, the electrical properties of the host material may change dramatically. The classic example of this phenomenon is the doping of an intrinsic semiconductor with an "impurity" substance, which dramatically alters the electrical conduction in the semiconductor due to an increase of electrons in the conduction band.[1] The electrical conduction of granular metals, which are two-phase mixtures of an insulator and metal particles, can be tuned between a metallic state and a dielectric state due to percolation effect by varying the concentration of the metal particles.[2–4] Certain organic materials can also be doped by undergoing chemical treatment such as protonation so that a transition from the insulating state to the metallic state exists. When polyaniline is protonated, its conductivity varies spatially forming three-dimensional granular metallic regions.[5,6] The granular metallicity has been visualized using scanning tunneling microscopy/spectroscopy.[7] In addition to providing metallic electrical conduction, the present interests in organic electronics also require that organic electronic materials perform specific functions such as switching and rectification. Melanin was shown to process a high conductivity state and negative differential resistance (NDR).[8] Synthesized one-dimensional organic molecules have demonstrated NDR using a molecular-sized junction at low temperature and room temperature.[9,10] Logic operations have been demonstrated using NDR devices made with organic materials.[11,12] Recently, a nonvolatile memory device made with a polymer film containing gold nanoparticles and 8-hydroxyquinoline has been demonstrated.[13]

In this letter, we present a study on the electrical properties of a functional composite material, which can be used in electronic applications. The material is prepared by mixing a polymer with an electroactive molecule. Using a diode whose active medium is a thick film of the composite material, we show that the electrical conduction in the material can be controlled by adjusting the concentration of the electroactive molecule. The diode's zero-bias conductance shows a temperature dependence, indicating that the electrical conduction mechanism in the material is thermally assisted electron tunneling between neighboring molecules. At room temperature, the diode shows a NDR at low bias voltages (~ 0.5 V). The stability of the NDR has been characterized. We present a possible mechanism, which depends on the electronic characteristics of the electroactive molecule, for the observed NDR.

The composite material was prepared using potassium ferricyanide $[K_3Fe(CN)_6]$ and Nafion $(C_7HF_{13}O_5S \cdot C_2F_4)$,[14] which is a sulfonated tetrafluorethylene copolymer with the chemical name of tetrafluoroethylene-perfluoro-3, 6-dioxa-4-methyl-7-octenesulfonic acid copolymer. Nafion was dissolved in de-ionized water, and then potassium ferricyanide was added to the solution to form a composite material. Two-terminal devices in the form of a diode were fabricated with the composite material as the active material. The diode was fabricated by first sputtering gold on a glass substrate as the bottom electrode having an area of 10×10 mm^2. A drop of the composite material was deposited on the bottom electrode. After evaporation, the material became a thick film cast on the bottom electrode. For a 10 μl drop, the film had a thickness of $10-15$ μm after evaporation of water. A second gold electrode of 1×1 mm^2 was sputtered on the film as the top electrode. Electrical characterization of the diode was carried out by measuring the diode's current-voltage (I-V) characteristic using a Keithley 6430 source meter. I-V measurements were made at room temperature and low temperatures in a home made Dewer. No detectable hysteresis associated with sweeping the voltage was observed. For a given concentration of potassium ferricyanide in a volume of Nafion, several diodes were made and tested in order to eliminate the uncertainty in the film thickness. The reproducibility of this kind of device is 90% out of more than 100 devices.

Potassium ferricyanide (PFC) is commonly used in electrochemistry as a mediator shuttling electrons between elec-

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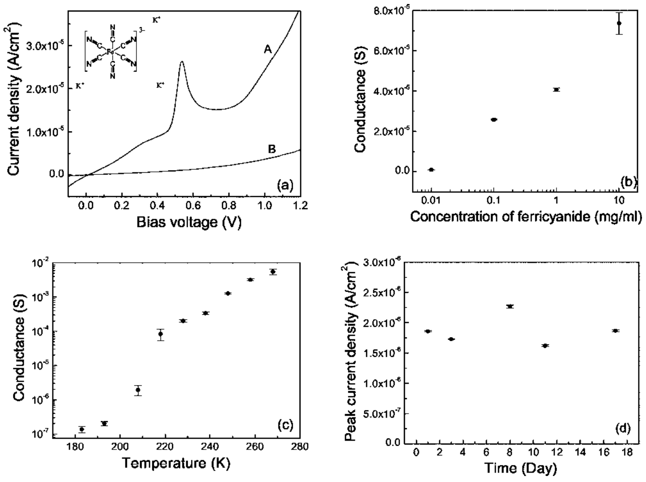

FIG. 1. (a) Curve A is the *I-V* characteristics of a diode using the composite as the active material. The concentration of PFC is 1 mg/ml (see below for explanation). Curve B is the *I-V* characteristic of a diode using Nafion as the active material. The inset shows the structure of the PFC molecule. (b) The relation between the zero-bias conductance of a diode and the concentration of PFC in the composite material. The concentration is expressed in milligrams of PFC in milliliters of Nafion. (c) The dependence of the zero-bias conductance of a diode on temperature. (d) The stability of the current peak of a diode.

troactive species dissolved in a solution and an electrode. The inset of Fig. 1 shows the structure of the PFC molecule. In the present experiment, the polymer Nafion was used to stabilize PFC in a nonsolution environment. The charge transport properties of this composite material were characterized by measuring the *I-V* characteristics of the material used as the active material for a diode under different conditions. The room-temperature *I-V* characteristic of a diode is shown in Fig. 1(a). Curve A shows a finite conductance near zero bias. In general, the diode current increases with increasing bias voltage. Another feature of the characteristic is a current peak located at 0.55 V. Curve B is the *I-V* characteristic of a diode made using only Nafion as the active material. Curve B is featureless with an extremely small conductance throughout the entire bias range. Note that the sputtering process may cause defects or embedding of gold particles below the composite surface. It was observed that if only Nafion is used to make the diode, the diode's *I-V* characteristic appears to be featureless. However, with the same sputtering conditions, when the composite material is used, a current peak appears in the *I-V* characteristic. This observation indicates that the current peak is not caused by possible defects or embedded particles but is caused by the presence of PFC.

Cyclic voltammetry of PFC dissolved in a solution and the composite material was performed. Curve A of Fig. 2 shows the cyclic voltammogram (CV) of PFC dissolved in a buffer solution. The active center, Fe^{3+}, of PFC gives rise to the two redox peaks in curve A. The redox peaks indicate a formal potential of 0.18 V versus Ag/AgCl, which is the textbook value for the redox process of PCF.[15] Curve B is the CV of the composite material deposited on an electrode. The redox peaks also indicate a formal potential of 0.18 V versus Ag/AgCl. The cyclic voltammetry results show the presence of PFC in the composite material.

The zero-bias conductance was measured with diodes having different concentrations of PFC in the composite material, as shown in Fig. 1(b). The conductance increases as a result of increasing the concentration of PFC. This observation indicates that the presence of PFC is responsible for the observed electrical conduction in the composite material. The diode's zero-bias conductance also shows a temperature dependence. Fig. 1(c) shows the measurement of the conductance within a temperature range covering 100 K starting from 180 K. The conductance shows an increase of four orders of magnitude within the temperature range. This observation implies a thermally activated electron conduction process.

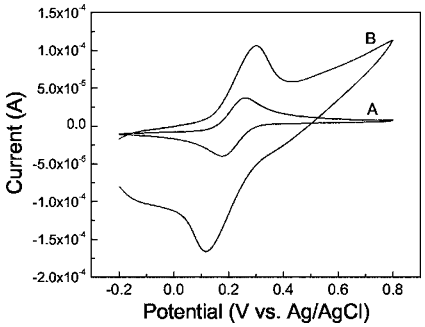

FIG. 2. Cyclic voltammograms of PFC dissolved in a buffer solution measured using a gold electrode (curve A) and of the composite material deposited on a gold electrode (curve B).

Based on the observations described above, a possible scenario for the electron conduction in the composite material is schematically depicted in Fig. 3(a), which shows that adjacent PFC molecules form relaying paths allowing electrons to travel through the material. It is likely that the conduction is due to electrons' tunneling between the Fe^{3+} centers of PFC. Redox molecules such as PFC are characterized with a redox potential E_{redox}, which is equivalent to the

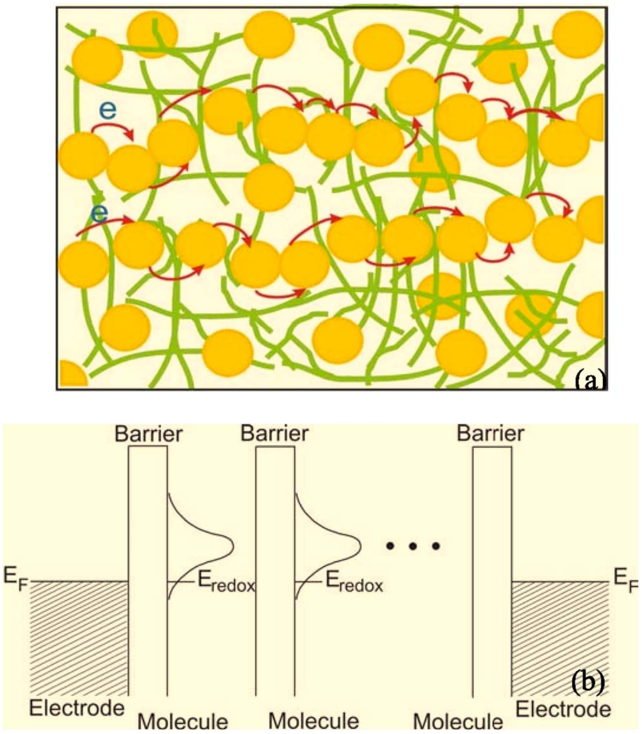

FIG. 3. (Color online) (a) Schematic description of electron conduction within the composite material. The circles and the ribbons present PFC molecules and the polymer Nafion, respectively. (b) A schematic energy band diagram of the diode. See text for explanation of the symbols.

Fermi energy of a solid. The oxidized state of the molecules has a Gaussian density of states (DOS) that peaks at E_{ox}, while the corresponding energy for the reduced state is E_{red}.[16] Figure 3(b) shows a relaying path formed by a series of PFC molecules between two metal electrodes. Each molecule is denoted by a Gaussian DOS centered about E_{ox} with E_{redox} aligned with the Fermi energies E_F, of the electrodes.

Figure 3(b) shows that a tunnel barrier exists between adjacent molecules. The tunnel barrier may be composed of a small amount of the Nafion polymer or part of the PFC molecule excluding the Fe^{3+} center. The average distance between an Fe^{3+} center and the outer part of the molecule is about 3 Å, based on the bond lengths Fe^{3+}–C 1.9928 Å and C–N 1.1933 Å.[17] Assuming that two PFC molecules are connected, the thickness of the tunnel barrier between the active centers is 6 Å, which is thin enough to allow electron tunneling. In general, thermally excited electrons experience a lower tunnel barrier height. Also, for the present system at low bias voltages, the molecules provide empty states for electrons emitted from an electrode, and thermal excitation brings the electrons to a higher energy, where a larger DOS is available due to the Gaussian distribution. Nafion is a proton exchange polymer. Electron transport in Nafion is not a facile process.

The current peak located at 0.55 V in the *I-V* curve provides a region of NDR between 0.55 and 0.6 V. The NDR region is characterized with a peak-to-valley current ratio (PVCR) of about 1.8. The average PVCR for the 100 devices is 1.77 ± 0.34 and the average peak current density is $2.14 \times 10^{-6} \pm 0.43 \times 10^{-7}$ A/cm^2. Figure 3(b) shows the system of PFC molecules and the two electrodes at equilibrium. When a small bias voltage is applied, the system shifts away from equilibrium and the DOS peaks shift slightly away from alignment with respect to each other. The convolution of the shifted DOS peaks serves as a transmission channel, allowing electrons emitted from an electrode to reach the other electrode. However, at higher bias voltages, the DOS peaks become completely misaligned with each other and the long distance between the electrodes prohibits electron transport. These effects cause a decrease in the diode current and result in the observed current peak in the *I-V* characteristic. It was observed that generally the peak current increases as the PFC concentration in the material is increased. The stability of the peak has been characterized, as shown in Fig. 1(d). The peak current density remained reasonably stable over a period of 18 days. The conduction beyond the current peak could be due to high field effects.

In conclusion, the electrical properties of a polymer-based electronic composite material were characterized using *I-V* measurement. The zero-bias conductance shows dependences on the concentration of the electroactive molecule in the material and on temperature. A current peak appears at about 0.55 V in the *I-V* characteristic of the material. The peak remained stable within an observation period of 18 days. A mechanism that involves electron tunneling between adjacent electroactive molecules is proposed for the electron transport in the composite material.

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