PERSPECTIVES: MATERIALS SCIENCE

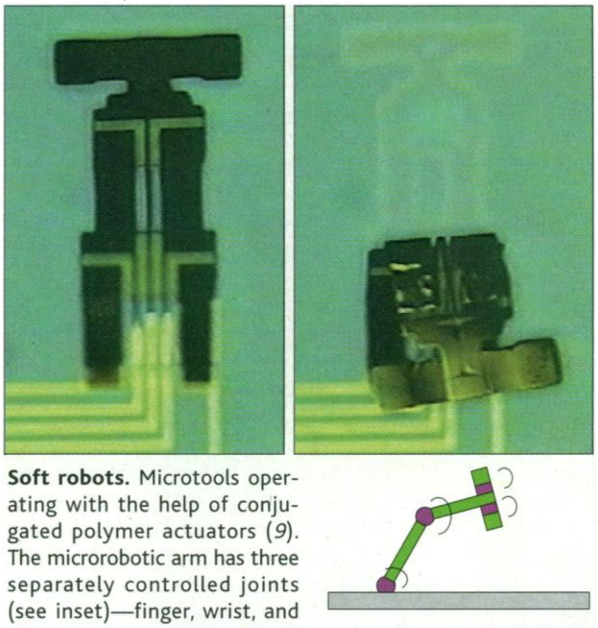
Carbon Nanotube Muscles

Olle Inganäs and Ingemar Lundström

The conversion of mechanical work into electrical energy is one of the legacies of Michael Faraday. We have also inherited the unit "farad" to measure capacitance and the term "faradaic" to mean electron transfer from electrode to electroactive species in electrochemistry. These terms are part of the intellectual background of the report from Baughman *et al.* (*1*) on page 1340 of this issue on the use of nanotubes for electromechanical actuators. The authors report that mats of nanotubes assembled into electrodes will expand and contract when operated as electrodes in an electrochemical cell. They have directly measured the linear strain under electrochemical operation of the material and have found that expansion of the tube along its own length must be approximately 1%. Charging of the electrodes occurs when applying a potential; this entails both a linear change of the covalently bonded carbon nanotube length owing to the introduction of electronic charge on the tube and a restructuring of the double layer of charge in the double layer outside the tube.

A recent meeting (*2*) addressed the larger arena of electroactive polymer actuators, which also includes a number of other mechanisms. The crowded conference halls suggested that, finally, electrochemical actuators are generating some real-world interest. The replacement of biological muscles with these materials is closer to the dream factory than it is to reality, but demonstration of novel microtools based on such materials (*3*) might be coming to laboratories in the near future (see figure).

The prediction of actuator action in another class of materials, conjugated polymers, was made by Baughman and coworkers a decade ago (*4*). The actuation here also included aspects of the charging-induced change of geometry occurring under doping of these materials, as well as the dilation of the polymer materials when counterions are inserted or removed during oxidation or reduction operations. Such devices, from macro to micro dimensions, have been demonstrated (*5*). They mostly include dopant diffusion in the polymer phase, which might or might not be swollen by the solvent; in addition, the dopant is most probably solvent coordinated. Slow diffusion has been suggested as a limiting factor in the operation of these actuators. However, several examples have been studied where the volume change cannot be understood simply from the point of view of ion transport and dilation, indicating that the dopant dilation is only one of several mechanisms operating. The stiffening of polymer chains under doping is caused by the charge driving a geometrical change of the polymer segment, which is a quantum chemical mechanism similar to the length change indicated in the nanotubes. Also, the conformation of the polymer chains is expected to be changed, as has been argued from the point of view of electrochemistry (*6*); likewise, the interaction between solvent, ions, and polymers will be changed during the transition. It is therefore a very complex pattern of mechanisms contributing to the volume change in these materials; recent reviews are available (*7*).



Soft robots. Microtools operating with the help of conjugated polymer actuators (*9*). The microrobotic arm has three separately controlled joints (see inset)—finger, wrist, and elbow—where a gold and polypyrrole microactuator is built. Stiffer polymer films of benzocyclobutene (BCB) carry these joints. When separately addressing the joint microactuator, the microrobotic arm is moved out from the plane and bent to access some object to be gripped by actuating the fingers. The potentials are switched between –1 and 0 V versus Ag/AgCl when operating the micromuscles, which are immersed in an aqueous electrolyte. Films of titanium and chromium are patterned to give adhesion to the surface for the gold film, which is used to prepare the polypyrrole on the joints. Film thicknesses are in the range of 0.1 to 3 μm, and dimensions of the objects are 500 μm long, 250 μm wide, and 180 μm wide at the hand (*9*).

The nanostructure of the carbon nanotube actuator electrodes is of single-walled tubes packed together in bundles, where at least the outer periphery of the bundle is in contact with the electrolyte. The very rapid response of these actuators suggests that the volume change is mainly an electronic effect; Baughman *et al.* call it a quantum chemical effect and have done (almost) first-principles calculations of the system. When estimating the upper limit to actuator performance of the nanotube electrodes, it is suggested that the single-nanotube data can be used where it is implicitly assumed that all nanotubes are in total contact with the electrolyte.

The discussion of double-layer charging in parallel with charge transfer to an electroactive solid entails more issues than that of volume change and comes close to one of the old riddles of polymer electrochemistry: Is there a distinction between doping of a chain and charging of a double layer close to a polymer chain?

If the chain is solvated, then probably there is an electrolyte double layer that carries the extra charge necessary to compensate for the charge of the polymer chain. If the chain is part and parcel of a polymer solid—and many would argue that it cannot be soluble in the doped state—then diffusion of ions must be possible through the solid. This leads to low rates of charging but also suggests that in electroactive solids of high ion conductivity, the distinction would have little relevance.

In recent work (*8*), nanoassembled conducting polymer hydrogels have been analyzed from the point of view of charge and power storage. These materials, which are very much like three-dimensional electrodes and assembled from a water dispersion of doped polymers, include large amounts of electrolyte (up to 95%) and do not show volume change of easily detected size; inclusion of classical actuator materials such as polypyrrole in finely dispersed form eventually turn on the actuation properties. How the coupling between the microscopic and the macroscopic volume change is enabled is important. Here stiff nanotubes are very different from soft polymer chains.

Baughman *et al.* suggest that the mechanism could be reversed to make a mecha-

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noelectrochemical transducer—an electrochemical generator. Thus, the name of Faraday once more returns. As he was pondering his invention of the dynamo and comparing that to the steam engine in the next coal mine, he said: "Of what use is a newborn baby?" Perhaps he would look with the same feeling on the novel but unproven electrical generator operating through electrochemistry and suggest that breaking carbon fibers in batteries might not offer much attraction compared with the turning of wires in magnetic fields in a classical generator. Possibly, but even as actuators made of soft materials, these new devices offer much to keep us interested.

References and Notes

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PERSPECTIVES: CONDENSED MATTER PHYSICS

The Cuprate Pairing Mechanism

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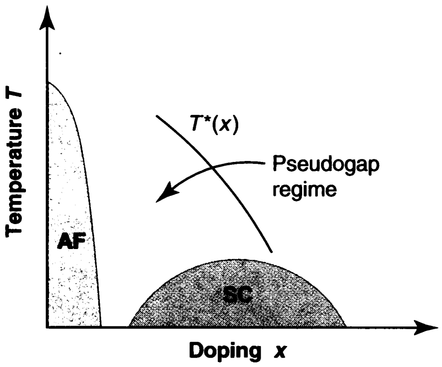
What is the basic interaction responsible for the pairing of electrons in the high–transition temperature (T_c) superconducting cuprates? More than a dozen years after Bednorz and Müller's discovery of this class of materials (*1*), the nature of the pairing mechanism remains unsettled. In part, this is due to the rich phase diagram of these materials (*2*), schematically illustrated in the figure. Depending on the temperature and the doping, one finds vastly different properties: an insulating antiferromagnetic phase, a pseudogap metallic phase (*3*), and a superconducting phase with $d_{x^2-y^2}$ symmetry.



Superconducting jigsaw puzzle. Schematic phase diagram for the cuprates showing temperature T versus hole doping x. The antiferromagnetic (AF) and $d_{x^2-y^2}$ superconducting (SC) regimes are shaded. Below the curve $T^*(x)$, a pseudogap opens in the quasi-particle spectrum.

The $d_{x^2-y^2}$ symmetry of the superconducting gap was, in fact, predicted by various theoretical calculations (*4*) for models in which a short-range Coulomb interaction led to an exchange coupling $J\mathbf{S}_i\cdot\mathbf{S}_j$ between near-neighbor copper spins and strong magnetic spin fluctuations. These same models at zero doping ($x = 0$) lead to the insulating antiferromagnetic phase. Nevertheless, as Dai *et al.* (*5*) note in their report on page 1344 of this issue, "the role of such [spin] fluctuations in the pairing mechanism and superconductivity is still a subject of controversy." The point is that if spin fluctuations provide the basic pairing mechanism, then the spin fluctuations should also be related to the occurrence of the pseudogap regime and to the thermodynamics of the superconducting transition; that is, one model should explain the entire phase diagram.

In their report (*5*), Dai *et al.* present inelastic neutron-scattering data for $YBa_2Cu_3O_{6+x}$ that shows that the onset temperature $T^*(x)$ of the pseudogap regime coincides with the formation of enhanced spin fluctuations at a finite frequency ω_0 and wave vector $q = (\pi/a, \pi/b, \pi/c)$, the so-called π resonance. In addition, the temperature derivative of the exchange energy $J\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle_{\mathrm{res}}$ associated with this part of the spectrum has a temperature, doping, and magnitude that are consistent with the observed anomaly in the electronic-specific heat near the superconducting transition.

For conventional low-T_c superconductors, Chester (*6*) showed that the temperature dependence of the lattice ion kinetic energy was related to the change in the electronic-specific heat associated with the superconducting transition providing a link between the electron-phonon interaction and the pairing mechanism. Recently, Scalapino and White (*7*) suggested that if the exchange coupling $J\mathbf{S}_i\cdot\mathbf{S}_j$ played a similar role in the high-T_c cuprates to that of the ions in the traditional low-T_c superconductors, one would expect that the temperature dependence of the exchange energy would reflect the change in internal electronic energy near the superconducting transition. They noted that because $J\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle$ could be obtained from the q- and ω-dependent magnetic structure factor $S(q,\omega)$ measured in neutron scattering, such experiments could, in principle, provide evidence for an exchange-interaction–based pairing mechanism.

Following this approach, Demler and Zhang (*8*) noted that in the magnetic scattering from $YBa_2Cu_3O_7$, the dominant temperature dependence in $S(q,\omega)$ was associated with the resonance in the spin fluctuation scattering for momentum (π/a, π/b, π/c), the so-called π resonance. In their work, they go on to argue that, in fact, it is the appearance of a spin fluctuation resonance in the superconducting state that enables the antiferromagnetic exchange energy in this state to be lowered relative to the normal state.

In the study of Dai *et al.*, detailed measurements of the spin fluctuations in $YBa_2Cu_3O_{6+x}$ at various temperatures and dopings x are reported. They find that the dominant observed changes in the scattering are associated with this resonance. Furthermore, they find that the onset temperature for these changes is set by the temperature $T^*(x)$ shown in the figure, which is determined from nuclear magnetic resonance and transport measurements to correspond to the onset of the pseudogap regime. After calculating the contribution of the exchange energy associated with the π resonance, Dai *et al.* show that the resonance can provide enough temperature-dependent exchange energy to yield the superconducting-specific heat anomaly as measured by Loram *et al.* (*9*).

As Dai *et al.* note, further neutron-scattering data are needed to provide tighter bounds on the nonresonant part of the spin fluctuation spectrum. In addition, optical data can give tighter bounds on possible models.

To conclude, the results of Dai *et al.* provide support for models in which the exchange interaction $J\mathbf{S}_i\cdot\mathbf{S}_j$ plays a central role. However, the basic pairing interaction remains elusive. That is, even granted that

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