Extreme Response Field-structured Chemiresistors for Chemical Switch Arrays

by D.H. Read and J.E. Martin

Motivation—A chemiresistor is a composite whose electrical conductivity changes in the presence of chemical vapors. These sensor composites traditionally consist of carbon-black particles randomly distributed within a polymer. Chemiresistors have several advantages as chemical sensors. They are small (microdot printable), simple and inexpensive to manufacture, require minimal transduction equipment, and need little power to operate (<10mW). Despite these positive attributes, traditional chemiresistors fail to satisfy numerous criteria essential to a viable chemical sensor technology. Problems include: poor baseline stability (drift); poor sensor-to-sensor consistency; poor response reproducibility; and irreversible response. These problems are due to the chemical affinity of carbon black to organics, the random, uncontrolled structure of the particle network, and the fact that the polymer phase is often non-crosslinked.

Our goal is to determine whether magnetic field-structured composites will yield improved chemiresistors that eliminate all of the current problems. If successful, there are numerous arenas where field-structured chemiresistors (FSCRs) can have impact, including environmental and chemical process monitoring, homeland security, and military applications.

Accomplishment—We have demonstrated that FSCRs successfully address all of the difficulties with carbon black chemiresistors, while achieving much greater sensitivity (Figure 1), and controllability. These FSCRs are composed of electrically conductive magnetic particles encapsulated in an elastomeric matrix. The particles are organized into conducting pathways by magnetic fields during cure. The type of field used determines the structure of the particle network (Figure 2), which in turn determines the chemiresistor sensitivity. When exposed to chemical vapors, the polymer swells only slightly, yet this is amplified into a large resistance change, as much as 100,000,000,000%, at a swelling of only 1.5%. Because FSCRs transition from electrically conducting to insulating over a narrow range of analyte concentration, they function as chemical switches. We have developed methods of shifting the sensor response to lower or higher analyte concentrations and can now vary the switching point over a two-decade concentration range. We can also control the range of analyte concentrations over which the sensor has a measurable response. This tailorability enables us to create chemical switch arrays that cover broad ranges of analyte concentrations.

Finally, we have isolated the fundamental transduction mechanism of FSCR response, and have demonstrated an analyte-independent master transduction curve for a particular sensor. This latter discovery shows that once any individual sensor is calibrated with a single analyte, its response to any other analyte can be reliably predicted. This is an essential characteristic for a practical chemical sensor.

Significance—This patented technology is currently in the process of being licensed for environmental monitoring of underground fuel tanks. Other commercialization opportunities are also being pursued.

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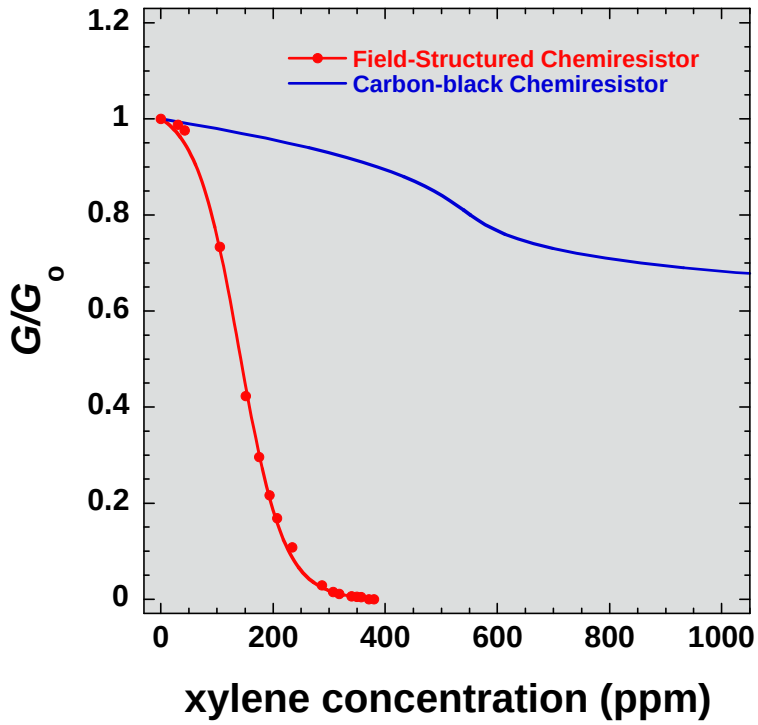

Figure 1. Response data for an FSCR and a carbon-black chemiresistor exposed to xylene. *G* is the conductivity of the sensors at a particular analyte concentration and G_o is the conductivity with no analyte present. The FSCR is a 15vol.% gold-plated nickel particle composite using PDMS as the polymer phase. The carbon-black sensor data represent the fit to the data presented in fig.48, p.63 of SAND2003-3410 for a PEVA polymer sensor.

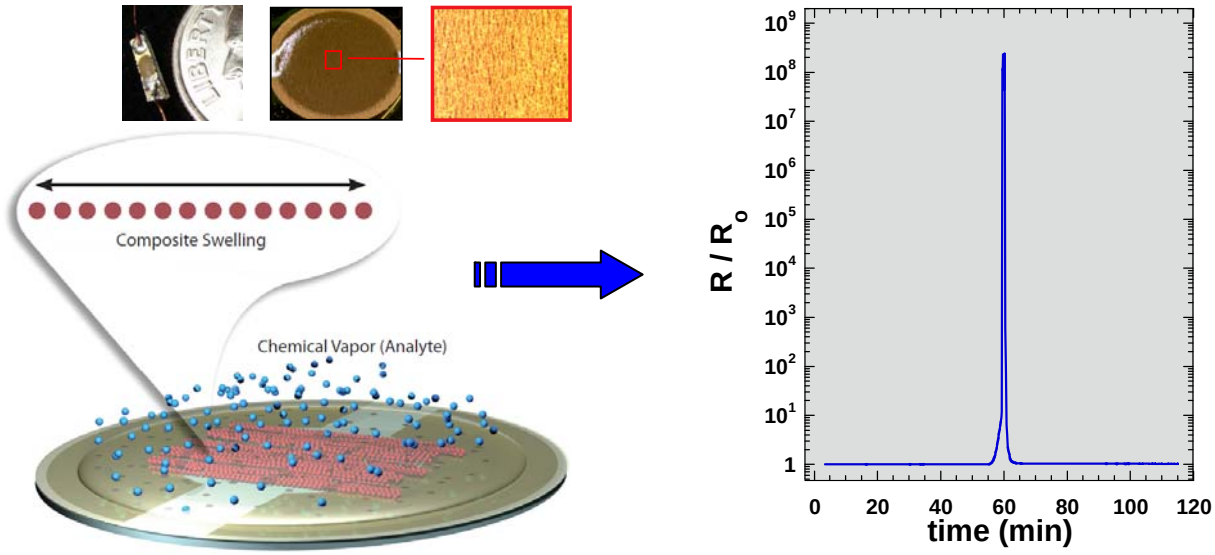

Figure 2. Photos of FSCRs (left: FSCR next to a U.S. dime) with a 60x magnified view of the chain-like particle structure. FSCR operation schematic showing analyte absorption and composite swelling. The composite swelling results in an extreme response of the FSCR to 17µg/mL *p*-xylene. The sensor resistance, *R*, increases by 300,000,000 times over its initial value, R_o.