Electrostatically and electrochemically induced superconducting state realized in electrochemical cells

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Abstract.
We here report the result of in situ magnetization measurements of electrochemical cells at low temperatures. Upon applying voltages between the electrodes of the electrochemical cells, we observed shielding diamagnetic signals from several materials, indicating superconducting transitions. The superconducting states can be induced both electrochemically and electrostatically with appropriate combination of counter electrode materials and electrolytes. The present technique may become a powerful method for searching novel superconductors.

Discovery of a superconductor is one of the events that have a very strong impact in the field of materials physics. Recently, interfacial superconductivity was observed at solid/solid [1, 2, 3] and liquid/solid interfaces [4, 5]. Among them, electric-double-layer transistors (EDLTs), in which an electrochemical cell (or electrochemical capacitor) structure is incorporated into the FET gate [6, 7, 8, 9, 10], has attracted particular interests since superconductivity induced by the application of the strong electric fields to the materials has been demonstrated. Two-dimensional carriers with densities \( n_{2D} \) up to \( 8 \times 10^{14} \text{ cm}^{-2} \), which is much larger than the densities of conventional solid/solid interfaces \( (n_{2D} \sim 1 \times 10^{13} \text{ cm}^{-2}) \), can be accumulated onto the material surfaces [11]. However, this approach has certain bottlenecks such as low throughput of experiments; in addition, atomically smooth samples with excellent electrical contacts are necessary for performing transport measurements on EDLTs at low temperatures.

To overcome the above difficulties, we introduced the electrochemical cell configuration, instead of the EDLT, and in situ magnetization measurements of the electrochemical cell based on several kinds of materials were performed upon applying voltages at low temperatures [12]. We observed the diamagnetic signal in electrochemical cells based on layered nitrides ZrNCl and HfNCl, and that based on C\(_{60}\) and picene, demonstrating electrostatically and electrochemically induced superconducting state.

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Figure 1. Schematic figure of (a) the experimental setup for in situ magnetization measurements and (b) electrochemical cell.

Figure 1(a) illustrates a part of the present experimental setup, in which the electrochemical cell is placed in a vacuum chamber with coils for AC magnetization measurements. The working electrode and counter electrode were inserted into a quartz tube with an electrolyte. The top of the quartz tube was sealed with adhesives by a Teflon cap. The cell was inserted into a He refrigerator with hand-made coils for the AC magnetization measurement by means of a two-coil mutual-inductance technique. The electrodes were connected to electrical leads outside the electrochemical cell, allowing us to measure the magnetization by applying a voltage between the electrodes without taking the electrochemical cell out of the chamber. Figure 1(b) is a schematic figure of the electrochemical cells, in which ionic conductors such as electrolytes and ionic liquids are used as gate dielectrics. When the voltage is applied between the electrodes, mobile cations and anions move toward oppositely charged electrodes. When chemical reaction does not take place, the electric double layer, formed at the interface where ionic and electric charges accumulate, can be considered as a capacitor with a nanometer gap. Therefore, an extremely large capacitance and resultant extremely high electric field at the interface of $\sim 10 \text{ MVcm}^{-1}$ can be achieved. On the other hand, with an appropriate pair of electrode materials and ionic conductors, the accumulated ions can intercalate and transfer charge into the materials (electrochemical doping) as demonstrated in lithium-ion batteries.

For electrostatic charge accumulation, we chose Pt counter electrode and the ionic liquid $N,N$-diethyl-$N$-(2-methoxyethyl)-$N$-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) as an electrolyte [4] since large molecular size of ionic liquid may avoid electrochemical intercalation into the materials. However, for electrochemical doping, K counter electrode and KClO$_4$/PEO electrolyte were used. The working electrode was prepared by mixing sample powders, acetylene black (5 wt%), and polyvinylidene difluoride binder polymer in an $N$-methylpyrrolidone (NMP) solution, and pasting resulting slurry on aluminum foil.

Electrostatic charge accumulation was carried out on layered nitrides ZrNCl and HfNCl using ionic liquid as the dielectric. The magnetization measurements were performed as follows. First, the voltage was applied at low temperatures (10-20 K). Second, the temperature was increased to 220-240 K, slightly higher than the glass transition temperature of DEME-TFSI, and it was maintained for approximately 30 minutes. This procedure is significantly important for
obtaining high-density electrostatic charge accumulation. According to Ref. [11], carrier density is enhanced by more than a factor of two compared with that obtained by the application of voltage at 300 K. Finally, the electrochemical cell was cooled to low temperatures while maintaining the voltage application, and then the magnetization was measured.

Figures 2(a) and 2(b) show the temperature dependence of the magnetization $M(T)$, for ZrNCl and HfNCl electrochemical cells based on ZrNCl. The background magnetization taken before the voltage application was already subtracted. In the beginning, the voltage was applied from 0 to 4.5 V [Fig. 2(a)]. While increasing the voltage, $M(T)$ was close to zero below 3 V. However, at 4.5 V, $M(T)$ suddenly showed a negative value below $\sim 12$ K, which is a signature of the shielding diamagnetic signal due to superconducting (SC) transition. The SC volume fraction estimated from the lowest temperature value was found to be very small, $\sim 0.15 \%$.

To investigate the stability of the observed SC state, we changed the voltage from 4.5 V to 0 V and then returned it to 4.5 V. Figure 2(b) displays $M(T)$ for the corresponding voltage scan. The diamagnetic signal almost disappeared at 0 V, indicating that the sudden release of the voltage kills the superconductivity. However, when 4.5 V was again applied to the electrodes, the SC state recovered completely with an identical volume fraction and $T_c$.

Figure 2(c) shows $M(T)$ for HfNCl cell. The voltage was applied to 6 V, changed from 6 V to 0 V, and then returned it to 6 V as in ZrNCl cell. The superconducting state suddenly appears at 6 V, and switching from non-superconducting to superconducting state was demonstrated also in HfNCl cell. The volume fraction of 0.2 % was slightly larger but was in same order of magnitude as that observed in ZrNCl.

We considered the observed volume fraction of $\sim 0.1-2 \%$. The typical thickness of the platelet flakes in the powder specimen was found to be on the order of 1 $\mu$m by means of electron microscopy [16]. If we assume a charge accumulation on the entire surface of the flakes and a thickness of the electric-double-layer of 1 nm, the fraction of the electron accumulation layer to the whole bulk can be estimated as 0.1 %, which is in good agreement with the SC volume fraction obtained in the present experiment.

Electrochemical doping was carried out on fullerene $C_{60}$ and picene, in which superconductivity induced by alkaline metal intercalation has been observed [17, 18]. However, in picene, there is no report for reproduction of superconducting materials other than Okayama University group. It may be due to the high-temperature synthesis above 150 °C which may
decompose molecules. Therefore, we performed electrochemical doping, in which reaction can take place even at room temperature. Here, K counter electrode and KClO$_4$/PEO electrolyte was used. First, the constant current was applied at room temperature in order to intercalate K ions into the materials. The intercalated K content was counted by integrating current flowing during the reaction. When the K content reached $x = 3$ in $K_xC_60$ and $K_x$picene, the application of current was stopped and the cell was cooled to low temperatures to measure the magnetization.

With decreasing temperature, the diamagnetic signal was observed below 19 K and 18 K in $K_3C_60$ and $K_3$picene, respectively (not shown). The shielding volume fraction is estimated to be $\sim 20\%$, indicating bulk superconductivity; the superconducting transition for $C_60$ is well reproduced, while the study on reproducibility of superconducting transition for picene is now in progress.

In summary, by means of in situ magnetization measurements on electrochemical cells, we observed electric-field-induced superconducting state in band insulators ZrNCl and HfNCl and electrochemically induced superconducting state in $C_60$ and picene, which are demonstrated by the observation of a superconducting shielding diamagnetic signal at low temperatures. The magnetic detection of superconductivity is a powerful probe because of the simple device configurations and contact-free method. The present technique has the ability to search chemically and physically unstable superconducting states, opening a route for unprecedented nonequilibrium superconducting states and possible high-$T_c$ superconductivity.

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