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Final Technical Report
for
Electrochemically Modulated Superconductivity

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Goal

The goal of the project is to test the feasibility of electrochemically modulated superconductivity in the cuprate superconductors. Such a test is possible because the new high temperature superconductors are ionic solids that are extremely sensitive to oxygen potential. Passive optimization of the latter is impossible, not only because of materials processing limitations but also due to thermodynamic and structural instabilities. Our approach is active intervention by electrochemical means, in other words, electrochemical polarization while the material is actually or potentially in the superconducting state. This is possible only by the use of electrolytes that are functional at cryogenic temperatures. Several years ago we discovered cryogenic electrolysis and demonstrated the existence of such electrolytes. Success in this effort would make possible a new class of electronic and photonic devices that exploit the capability to control actively the transition into and out of the superconducting state while the material is in service.

Approach

A cuprate-based superconductor is polarized electrochemically in a cryogenic electrolyte while the electrical resistivity is measured simultaneously.

Tasks

1. Selection of candidate electrolyte. Such an electrolyte should be liquid and conduct electricity at temperatures below 95 K, and should not interact otherwise with the cuprate superconductors (e.g., hydrolysis, as would occur at room temperatures in aqueous electrolytes, is not acceptable). Initial choices for evaluation were:

- * ozone/oxygen
- * carbon monoxide
- * trifluoronitrosomethane/Freon 14
- * trifluoramine oxide/trifluoramine
- * chlorotetroxyfluoride/Freon 14
- * nitropropane/propane
- * sulfur dioxide/propane
- * nitryl chloride/Freon 14
- * carbonyl sulfide/propane
- * allyl alcohol/dimethyl ether

These candidates consisted of an oxidizable species and a solvent. Some of the oxidizable compounds are liquid at 95 K, but most have to be dissolved in a low melting solvent such as Freon 14 or propane.

2. Construction of a test cell. Problems include the fact that condensed ozone is a high explosive.

3. Screening experiments for candidate electrolytes, including electrical conductivity, emf measurements, cyclic voltammetry and ultimately laser Raman spectroscopy.

4. Electrochemical polarization of cuprate superconductors, based on the preceding steps.

Accomplishments

Cryoelectrochemical Cells

Cell design #1: The initial designs were constructed with a "seed money" grant from another sponsor. The apparatus is designed to permit simultaneous electrochemical polarization and 4-point resistive measurement of the electrical resistance of the specimen to determine whether it is superconducting. Such an experiment has never been done before. A schematic drawing of the cell arrangement is included in Figure 1. The cell is machined from solid aluminum; the head flange assembly is designed to absorb the anticipated explosive energy of the candidate electrolytes, directing all forces upward and away from the experimenter. The actual cell geometry is represented in Figure 2. The gross circuit schematic for the cell is shown in Figure 3. This cell has been used for cyclic voltammetry on superconductors using noncryogenic, nonaqueous electrolytes (e.g., propylene carbonate-lithium perchlorate mixtures), and with nonaqueous oxygen-bearing electrolytes such as oxygen/ozone mixtures.

Cell design #2: Because of difficulties with ohmic connections to the superconductor (simultaneous 4-point probe resistance measurement and electrochemical polarization requires five leads which are stable in the electrolyte, reducing the odds considerably for success in any given run) we have designed methods to detect superconductivity in a specimen while it is being actively polarized in the electrochemical cell. The coil (sketch, Figure 4) sits outside the working electrode but within the inner wall of the cryostat. The design, an inverted pancake geometry, has excellent sensitivity at audio frequencies and has been successfully tested with superconducting samples in the cell geometry but without electrochemical modulation. The electrical schematic for this modification is shown in Figure 5. The cryostat is in essence a copper can with appropriate plumbing for introduction of gases and liquids and electrical feedthroughs for thermometry, susceptometry and electrochemical experiments.

Cell design #3: The "weak cell" -- here the considerations are as above, but quartz is used for the cell walls to permit optical access to the cell. This cell can be used with nonexplosive electrolytes, and was used mainly for room-temperature experiments in, e.g., propylene carbonate-based electrolytes.

Screening Experiments

Two systems have been investigated for electrochemical measurements:

- 1) Oxygen-ozone mixtures. The liquid range for oxygen is 54.75-90.19 K, Statement A per Dr. Yoon Soo Park
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while ozone is liquid from 80.45 to 161.25 K. Using an electrical discharge apparatus constructed for this purpose, we have produced solutions of approximately 2% ozone in oxygen. We have performed surface tension measurements to confirm that this solution wets barium yttracuprate. No visible chemical reactions of this solution with the barium yttracuprate have been observed, although subtler interactions may have occurred. We have made preliminary measurements which indicate no measurable ionic conductivity in this solution, that is to say, it does not appear to be an electrolyte, at least in the conventional sense of the word. However, as large scale electron transfer is not required to meet the stated goals of this project, this solution is still a candidate owing to anticipated electron sharing with the double layer along with the associated band bending in the solid.

2) Tetrabutyl ammonium perchlorate (TBAP) in propylene carbonate (PC). PC is an organic liquid, has a liquid range from 224 to 515 K. It is considered to be an excellent solvent for both organic and inorganic solutes, with the distinct possibility of lowering the melting temperatures by the use of eutectic mixtures. It is an ionically conducting material and has been used extensively in lithium battery research. Materials tests indicate that a PC/TBAP electrolyte does not react with barium yttracuprate. Water is miscible with PC and is a persistent impurity (for instance, we have duplicated some of the previously published room temperature results with barium yttracuprate, but only if water contamination is present) but we have found we can reduce the water content to less than 100 parts per million by weight. PC/TBAP mixtures also afford a reasonable operating window for electrochemical measurements, as indicated below.

Electrochemical Experiments

The PC/TBAP electrolyte system has been used to examine the plausibility of electrochemical polarization while monitoring the properties of BYCO with a point probe. [Refer to diagram of 3 electrode electrochemical cell.] Oxygen bubbled over platinized platinum in a PC/TBAP has been determined to be a suitable reference electrode (RE). A potential sweep was applied between the RE and a BYCO specimen acting as the working electrode (WE) while current was delivered to the WE from a platinized platinum counter electrode (CE) -- standard cyclic voltammetry. At the same time the BYCO specimen was subjected to electrochemical influence by the voltammetric sweep, the specimen was simultaneously tested by a 4-point probe affixed to the surface of the BYCO. The voltage drop of the 4-point probe was monitored as a function of time [see Figure 6] during the potential sweep at three discrete 4-point probe currents. As noted in the figure, the voltage of the 4-point probe is affected by the sweep. BYCO in its normal state is relatively resistive when compared to a metal like copper so the assumption that it acts as an equipotential surface during polarization does not hold as demonstrated by the figure. However, should the BYCO enter the superconducting state, it would be equipotential, so testing with a 4-point probe would reveal such a change of state.

The fact that measurements made with a 4-point probe are affected by the electrochemical techniques was a concern, so noncontact measurements using an adaptation of standard susceptibility measurements have been pursued to as to

allow a pancake coil as previously described to monitor the BYCO surface through an electrolyte [see Figure 7]. Preliminary results indicate that it is possible to detect superconductivity with the sample at a distance of at least several mm from the pancake coil when the gap is filled with helium.

Conclusions

The proposed experiments are definitely feasible. Basic physicochemical factors such as wettability of the superconductors by the electrolytes are all in our favor, and all of the more mundane experimental problems, e.g., cell construction and resistive measurements, appear to have been solved. Whether or not the effects of electrochemical modulation will be significant has yet to be discovered. The experiments have not been completed. Further work is necessary.

Recommendations for Future Work

1. Continue the search for and evaluation of candidate electrolytes, including eutectics and slushy materials (i.e., mixtures that are incompletely solidified near 90 K.)
2. Electrochemical measurements to evaluate and characterize the electrode processes, including electromotive force, cyclic voltammetry, electrochemical impedance spectroscopy, and (with cell #3) laser Raman spectroscopy.
3. Electrochemical modulation experiments, using the new susceptometer cell.

Figure 1. The basic layout for cryoelectrochemical cell:

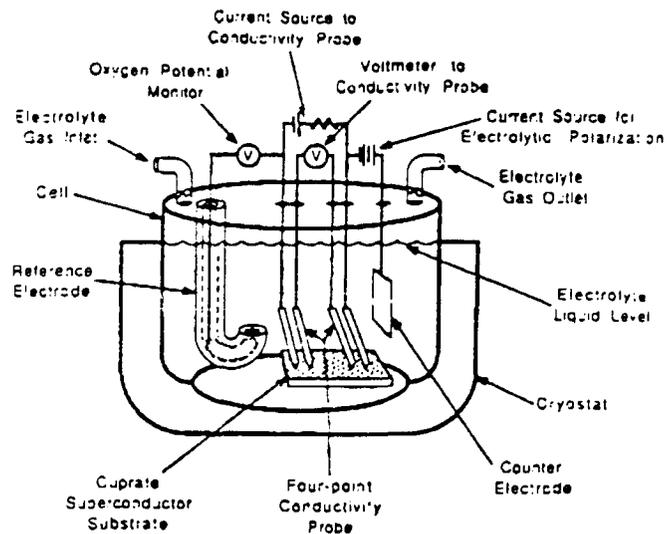


Figure 2. "Strong" cryoelectrochemical cell:

TWO ELECTRODE ELECTROCHEMICAL CELL

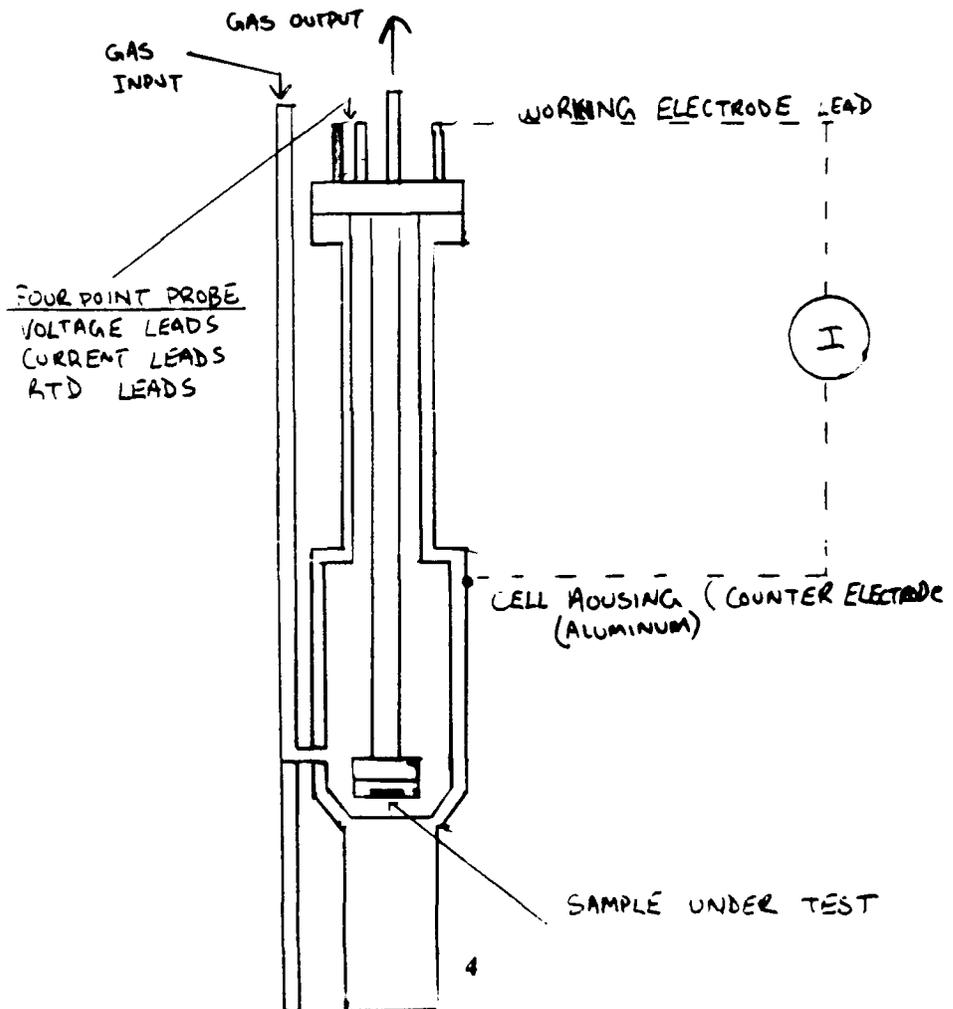
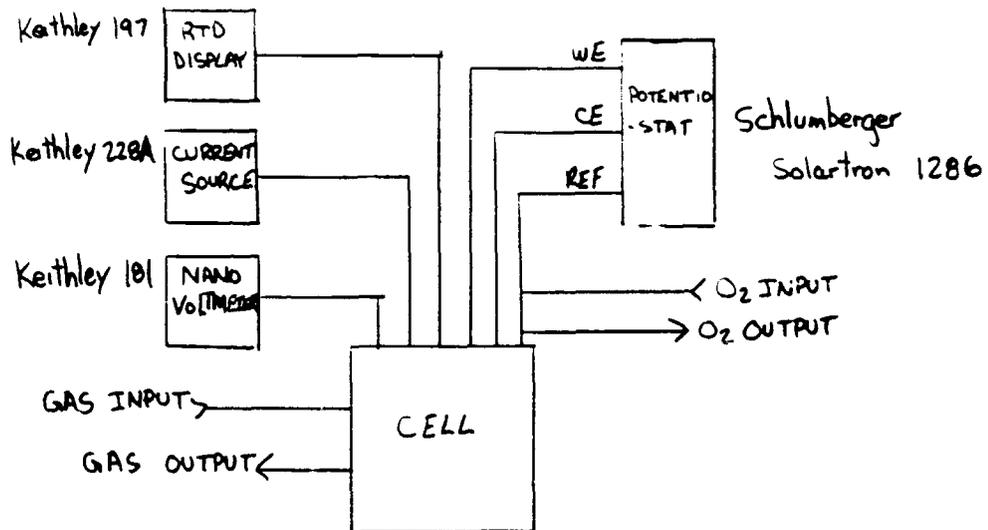


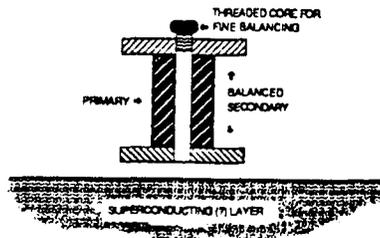
Figure 3. Block circuit diagram for cell:

**ELECTROCHEMICAL CELL WITH FOUR POINT
PROBE APPARATUS BLOCK DIAGRAM**



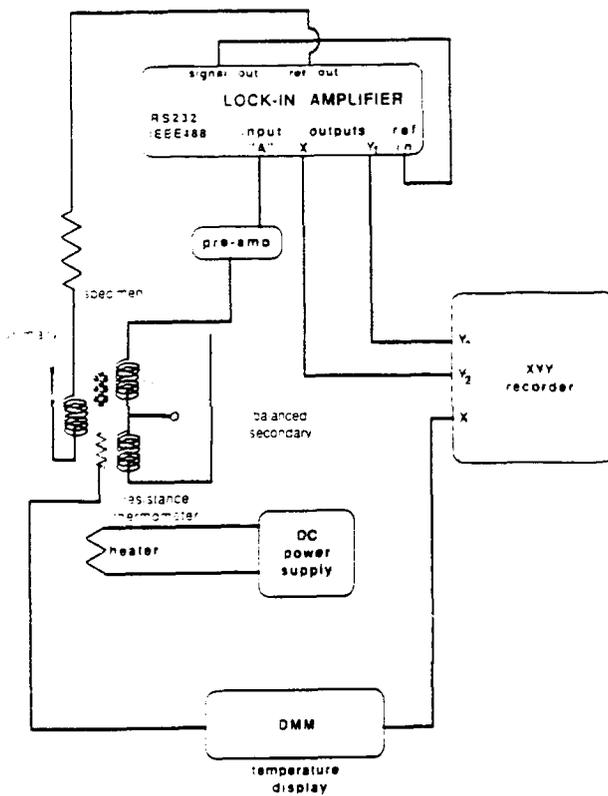
**Figure 4. Coil geometry for susceptometry in
cryoelectrochemical cell:**

Diagram of Polarization Cell for Electrochemically
Modulated Superconductivity



Sketch of coil installed in
wall of cryoelectrochemical
cell.

Figure 5. Electrical schematic for susceptometry circuit:



SUSCEPTOMETER CIRCUIT SCHEMATIC

FIGURE 6. Voltage across BYC vs. time while performing sweep voltammetry.

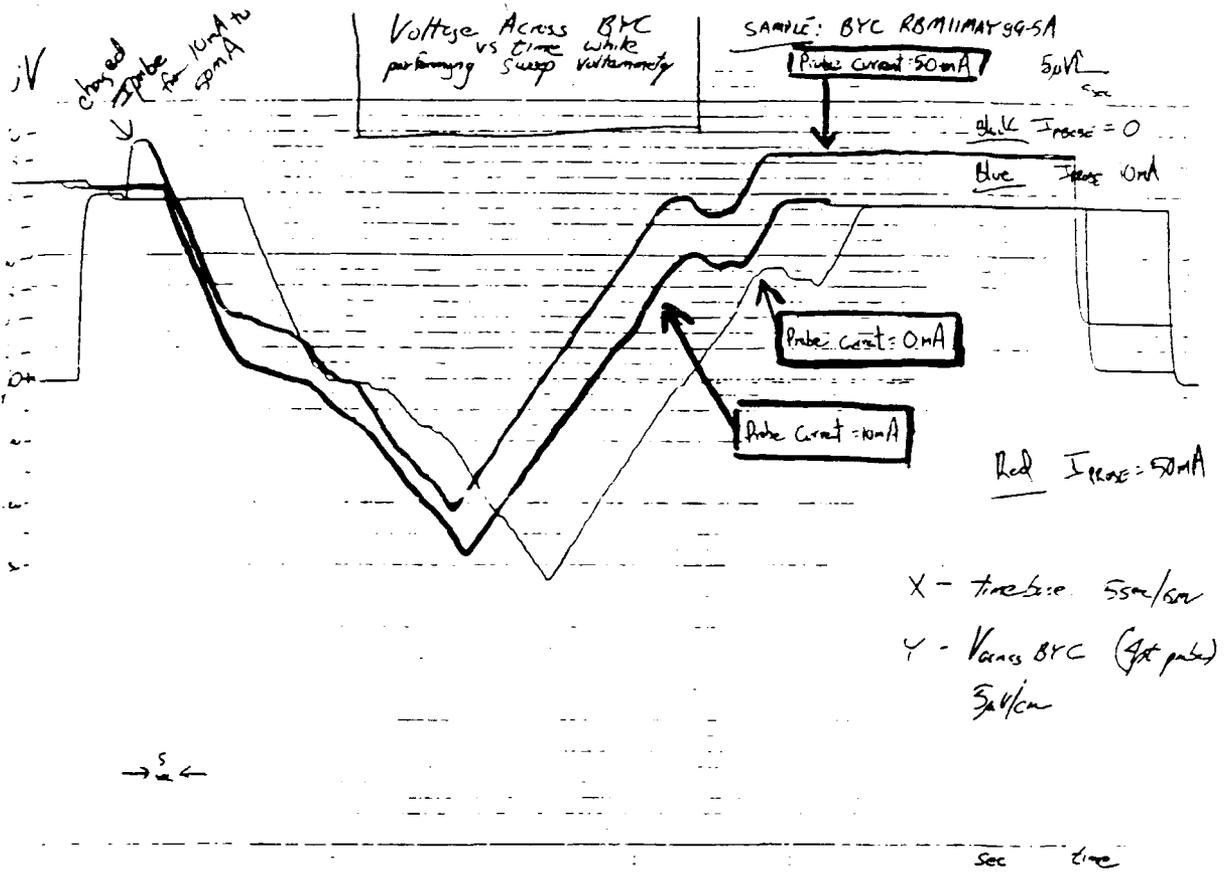


Figure 7. Trial run pancake susceptometer, superconducting to normal transition is at left. Temperature increases left to right.

