

Electrochemical Investigations of Various High-Temperature Superconductor Phases

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The electrochemical responses recorded at nine copper oxide ceramics, including six high-temperature superconductor phases, are described in this paper. The cyclic voltammetric behavior exhibited by these materials is found to depend greatly on the method of surface treatment, the sample preparation technique, the amount of impurities in the high- T_c phase, and the properties of the electrolytic fluid. The voltammetry acquired at these electrodes is used as a diagnostic tool to assess the surface quality of the electrodes and to measure the degree of reversibility of electron flow at the electrode/solution interface. It is shown that the preferred method of surface preparation for the copper oxide materials is a diamond-scribed technique in that well-resolved voltammetry is obtained using this treatment for the majority of copper oxide superconductors.

Introduction

The copper oxide superconductors have intergrowth structures in which the superconducting electron pairs are thought to reside in active CuO_2^{2-} sheets alternating with other inactive layers along the c axis. Oxidation or reduction of the CuO_2^{2-} sheets above or below the Cu formal valence of +2 is one of the conditions necessary to suppress long-range antiferromagnetic order and induce superconductivity. A large number of p-type copper oxide superconductors¹ such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+y}$, $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4-y}$, and $\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3-y}$ exhibit copper formal valences $>+2$. However, there are only two known n-type superconductors, $\text{Ln}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{Ln} = \text{Nd}$ or Eu , $\text{M} = \text{Ce}$ or Th)^{2,3} and $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_2$ ($\text{Ln} = \text{lanthanide}$).⁴ These materials display copper formal valences $<+2$. For the most part, the p-type superconductors have shorter Cu-O bond lengths ($a_0 \leq 3.87 \text{ \AA}$) with 5-fold or 6-fold coordinated copper ions, whereas the n-type superconductors have longer Cu-O bond lengths ($a_0 \geq 3.90 \text{ \AA}$) with 4-fold coordinated copper ions.

Within the copper oxide materials, the copper valence is probably the most important variable responsible for the conductive and superconductive properties of these materials. Copper formal valences for the ceramic materials are often controlled via substitutional chemistry or by adjusting the oxygen content within the lattice. Recently, electrochemical methods have been exploited to alter the copper valence as well as to synthesize high- T_c samples.⁵⁻⁷ In addition, electrochemical techniques can be utilized to provide a wealth of information concerning the surface reactivity of high- T_c phases.⁸⁻¹⁵ This topic is particularly important given that the copper oxide materials are known to react with water, CO_2 , CO, and acids. This reactivity often leads to degradation of the surface of these materials, thereby affecting their long term stability. Many applications for high- T_c materials, such as passive microwave devices, require pristine superconductor surfaces free from the adverse effects of corrosion. Moreover, a large number of important physical measurements which probe the surface properties of high- T_c materials require pristine surfaces. Thus, a better understanding of the surface chemistry of oxide superconductors must be obtained in order to foster further de-

velopments in these important areas.

There are a large number of analytical methods that can be exploited to study the surface chemistry of oxide superconductors. Many studies involving the use of classical surface science methods have been completed such as X-ray photoelectron spectroscopy, Auger electron spectroscopy, ultraviolet photoemission spectroscopy, and scanning electron microscopy. Despite the large amount of effort directed toward this area, much disagreement remains concerning the intrinsic surface properties of the oxide superconductors. High surface reactivity and loss of oxygen from the superconductor lattice complicate the analysis of these materials. Oxygen loss from the ceramic surfaces is particularly problematic given that many of the copper-based superconductors are known to be oxygen ion conductors.¹⁶⁻¹⁸ Thus, oxygen may be lost from the materials under the ultrahigh-vacuum conditions that are normally employed for these methods. Since oxygen

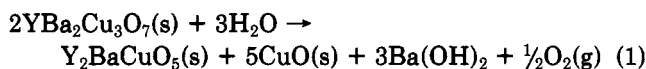
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content affects the electrical and superconductive properties of these materials, it is imperative that new methods be developed to study the surface properties of the oxide superconductors.

Electrochemistry is an ambient-pressure, surface-sensitive technique that can be exploited to study the interfacial properties of conductive surfaces. Previously, we reported the use of cyclic voltammetry as a method to determine the surface quality of oxide superconductor electrodes.⁹⁻¹⁰ According to the method, electrodes are prepared from high- T_c ceramic pellets and cyclic voltammetry for solution dissolved redox couples is recorded. The splitting between the cathodic and anodic peak potentials (ΔE_p) is utilized to acquire diagnostic information related to the surface quality of high- T_c electrodes. In the absence of corrosive reagents, voltammetry similar in appearance to that acquired at noble metal electrodes such as Pt or Au is obtained with ΔE_p close to 59 mV (for one-electron redox events). However, the addition of small amounts of water or acids to the electrolytic fluid leads to a dramatic increase in ΔE_p , the magnitude of which increases with increasing exposure time. Thus, as the high- T_c phase corrodes, the metallic surface of the ceramic material is converted, at least in part, to insulating products which impede the electron transfer. For example, the prototypical superconductor, $\text{YBa}_2\text{Cu}_3\text{O}_7$, undertakes the following reactions when exposed to water:¹⁹



To study many of the properties of high-temperature superconductors, it is necessary to obtain relatively clean, corrosion-free surfaces. Therefore, the method of surface treatment of the superconductor electrode surfaces is vitally important. In this paper, we examine three surface preparation techniques in the evaluation of nine copper oxide materials. The materials were chosen so that a variety of important differences could be addressed with respect to surface properties of the copper oxides. Of the nine materials, six are high- T_c phases ($\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Ca}_{0.4}\text{Y}_{0.6}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.95}$, $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.75}\text{Y}_{0.25}\text{Cu}_2\text{O}_{8.24}$, $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.22}$, $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$), two are semiconductors ($\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$, $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.25}\text{Y}_{0.75}\text{Cu}_2\text{O}_{8.37}$), and one is metallic but not superconducting ($\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.37}$). Eight p-type copper oxides with a formal Cu valence $>+2$ are compared with one n-type superconductor with a formal Cu valence $<+2$.

Experimental Section

Chemicals and Equipment. Acetonitrile (Burdick and Jackson) was dried by passing it over freshly activated alumina and then was stored over 3-Å molecular sieves. 7,7,8,8-Tetracyanoquinodimethane (TCNQ, Sigma) was recrystallized twice from acetone/water, and tetraethylammoniumtetrafluoroborate (Et_4NBF_4 , Alfa) was used as received. A PAR 273 potentiostat, interfaced to an IBM PS/2 model 55SX computer, was utilized to acquire the cyclic voltammetry data.

Experiments were performed in the normal three-electrode mode. Potentials were measured with respect to a silver wire pseudoreference electrode and adjusted to SCE values using internal redox standards. All electrochemical experiments were completed in an Innovative Technology MB 150 M (Newburyport, MA) inert-atmosphere glovebox, and the data were recorded digitally on an IBM computer. Two electroactive solutions were used: (1) 0.1 M Et_4NBF_4 in CH_3CN for measurement of the

capacitive background response of each sample and (2) 0.1 M Et_4NBF_4 in CH_3CN with 2.5 mM TCNQ for examination of the faradaic response of the various electrodes.

Sample Preparation and Characterization. Samples of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ were obtained by firing an intimate mixture of the component oxides/carbonates first at 905 °C for 15 h and then at 1050 °C for 24 h. The samples were reground, pelletized, and refired at 1050 °C for another 24 h and then furnace-cooled. $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ was annealed in an atmosphere of N_2 at 890 °C for 20 h and then quenched to room temperature in the same atmosphere. Samples of $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Ca}_{0.4}\text{Y}_{0.6}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.95}$, and $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$ were obtained by firing the component oxides/carbonates at 930 °C for 15 h. The products were ground, pelletized, and refired at 930 °C for 36 h with one intermediate grinding. The superconductor samples were annealed in 1 atm of O_2 at 450 °C for 24 h and furnace-cooled under O_2 . The $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.25}\text{Y}_{0.75}\text{Cu}_2\text{O}_{8.37}$ and $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.75}\text{Y}_{0.25}\text{Cu}_2\text{O}_{8.24}$ samples were obtained by firing the component oxides/carbonates first at 790 °C for 4 h and then at 860 °C for 20 h. The products were ground, pelletized, and refired at 860 °C for an additional 24 h and furnace-cooled to 100 °C. To prepare the $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{6.3}$ samples, stoichiometric amounts of well-mixed Tl_2O_3 , BaO_2 , and CuO salts, which were pelletized and wrapped in gold foil, were introduced into a muffle furnace maintained at 900 °C. The mixture was fired at 900 °C for 10 min with one intermediate grinding and then quenched into liquid nitrogen. One-half of the $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{6.3}$ mixture was then annealed in 1 atm of O_2 at 350 °C for 6 h and furnace-cooled. Both the liquid nitrogen quenched and O_2 -annealed samples were analyzed and found to have Tl contents equal to 1.5.

All ceramic samples were characterized by X-ray powder diffraction using a Phillips diffractometer. The oxygen contents were determined by an iodometric procedure.²⁰ The thallium and oxygen contents in the thallium cuprates were determined as reported elsewhere by wet-chemical methods.^{21,22} Superconductive transition temperatures for the sintered pellets were determined by a standard four-probe technique. Once the high- T_c phases were characterized adequately, epoxy-encapsulated electrodes were fabricated from the ceramic pellets using the methodologies described previously.⁸⁻¹²

Results and Discussion

The high-temperature copper oxide ceramics lack many of the desirable properties which are normally associated with electrode materials. Thus, special methods are required to fashion electrodes from these brittle and reactive ceramic samples.⁸⁻¹² In the first step, the oxide superconductor is synthesized as a phase pure powder. The powder is compacted into a pellet using a hydraulic press and the specimen is heated close to its melting temperature so as to produce a pellet sample with mechanical integrity. Electrical contact is made to the pellet using silver paint and/or silver epoxy, and the assembly is placed into a plastic test tube; the tube is then filled with epoxy and cured. The bottom of the electrode assembly is sanded down to expose a rectangular region of the superconductor $\sim 1 \text{ mm} \times 3 \text{ mm}$. At this point, the electrode can be utilized as is; however, it is often desirable to further treat the surface so as to optimize the performance of the electrode.

As demonstrated in this paper, the method of surface treatment is vitally important in determining the quality of the electrochemical response acquired for high- T_c electrodes. Therefore, three different surface preparation techniques were examined here: (1) sanding the electrode surface at 550 rpm on a sanding wheel, followed by pol-

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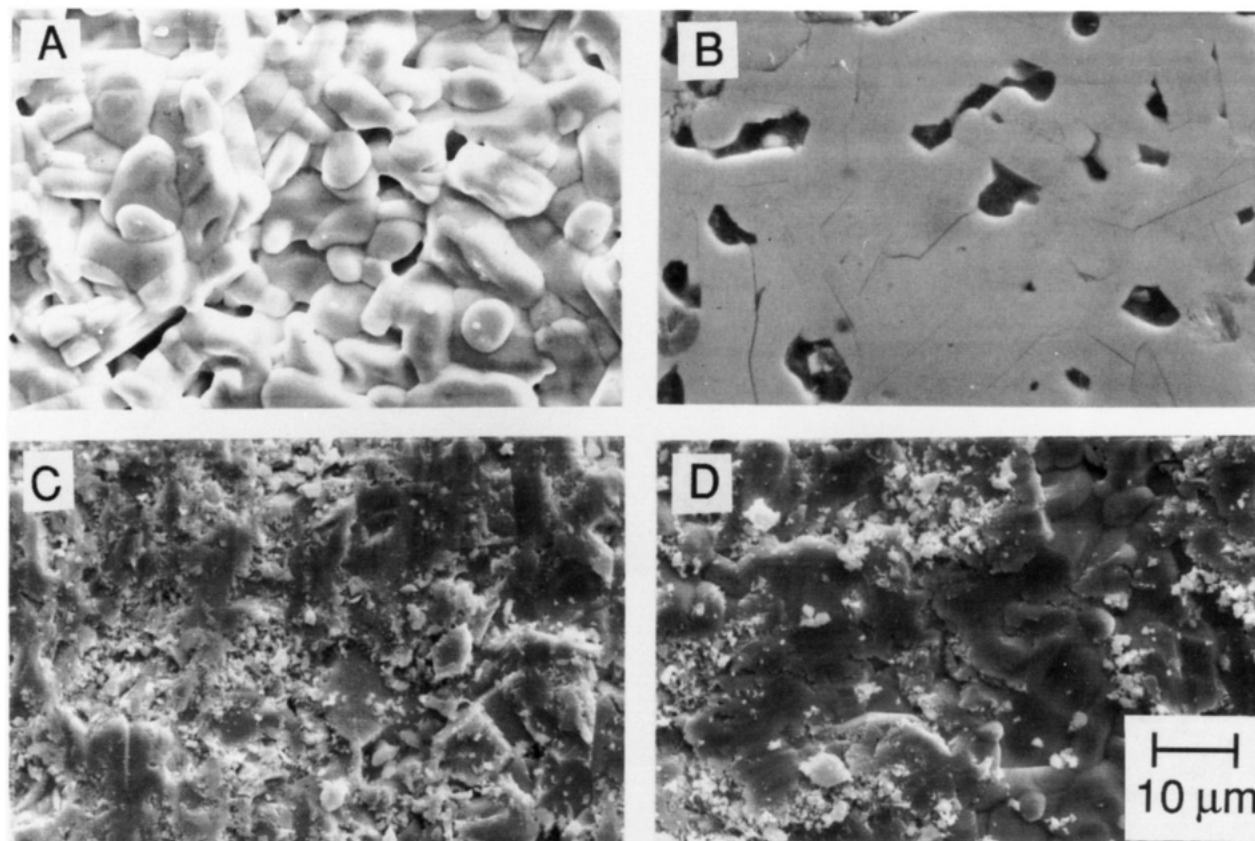


Figure 1. Scanning electron micrographs showing the morphologies of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramic pellets treated with the various surface preparation schemes. (A) Untreated ceramic pellet. (B) Interface sanded at 550 rpm followed by polishing with Al_2O_3 for 5 min (method 1). (C) Interface surfaced by sanding at 550 rpm (method 2). (D) Interface sanded at 550 rpm followed by scribing with a diamond pencil (method 3).

Table I. Summary of Data for the Copper Oxide Materials

material	structure	T_c (mid) (K)	TCNQ ^{0/-1} ΔE_p (mV)		
			$\text{Al}_2\text{O}_3/\text{H}_2\text{O}^b$	550 rpm sand ^c	diamond scribe ^d
A = $\text{YBa}_2\text{Cu}_3\text{O}_7$	orthorhombic	90	705	390	107
B = $\text{Ca}_{0.4}\text{Y}_{0.6}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.95}$	tetragonal	82	509	260	101
C = $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$	tetragonal	37		681	89
D = $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$	tetragonal	semiconductor	810	366	109
E = $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.25}\text{Y}_{0.75}\text{Cu}_2\text{O}_{8.37}$	orthorhombic	semiconductor	97	95	99
F = $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.75}\text{Y}_{0.25}\text{Cu}_2\text{O}_{8.24}$	orthorhombic	86	710	759	
G = $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.22}$ (N_2 quenched)	tetragonal	60	176	88	140
H = $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.37}$ (O_2 annealed)	tetragonal	metal	271	245	105
I = $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$	tetragonal	20	588	503	97

^aThe ΔE_p values presented here are for the first reduction wave of TCNQ (2.5 mM) recorded at 100 mV/s for the various copper oxide phases in 0.1 M $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$. ^bElectrodes surfaced by sanding at 550 rpm, followed by polishing for 5 min with $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$. ^cElectrodes surfaced by sanding at 550 rpm. ^dElectrodes surfaced by sanding at 550 rpm, followed by diamond scribing to remove the top layers of the electrode.

ishing the surface with $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$; (2) sanding the electrode surface at 500 rpm; (3) sanding the electrode surface at 550 rpm, followed by scribing the surface with a diamond pencil to remove the top layers of the electrode. Following the surface treatments, the electrodes were washed in dry CH_3CN to remove any debris generated in the previous steps. It should be emphasized that the above methods can be exploited in a relatively simple fashion so as to produce renewable high- T_c surfaces. As a surface becomes damaged, a fresh interface can be reestablished simply by sanding away the degraded layer and completing the final surface treatment once again. The use of the epoxy matrix serves to effectively fill the voids which exist on the outer portion of the pellet. Thus, problems normally associated with porous electrodes are eliminated in this fashion. Electron micrographs showing the surface morphology of $\text{YBa}_2\text{Cu}_3\text{O}_7$ samples generated with the

three electrode preparation methods are provided in Figure 1; a view of an untreated $\text{YBa}_2\text{Cu}_3\text{O}_7$ pellet is also provided for comparison purposes. In most cases, rough polycrystalline surfaces typical of ceramic pellets are noted. On the other hand, the Al_2O_3 polishing procedure produces a relatively smooth interface having only a few cracks and small pits. No traces of the accumulation of water degradation products were observed by SEM for samples treated in this fashion. However, despite the smoother surface texture, electrodes prepared via this procedure display relatively poor electrochemical characteristics (vide infra).

To evaluate the surface quality of the various oxide superconductor specimens, cyclic voltammetry was recorded for solution dissolved redox couples. The nine cuprate superconductor phases examined in this paper are listed in Table I along with data compiled for each specimen (throughout the paper, samples are identified using

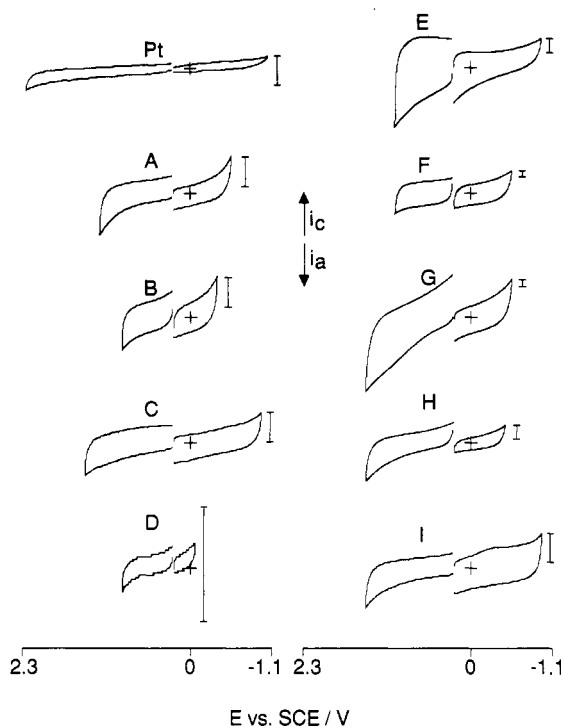


Figure 2. Background cyclic voltammograms recorded at 100 mV/s for diamond-scribed, epoxy encapsulated copper oxide electrodes in 0.1 M $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$: (A) $\text{YBa}_2\text{Cu}_3\text{O}_7$, (B) $\text{Ca}_{0.4}\text{Y}_{0.6}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.95}$, (C) $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, (D) $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$, (E) $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.25}\text{Y}_{0.75}\text{Cu}_2\text{O}_{8.37}$, (F) $\text{Bi}_2(\text{Sr}_{1.5}\text{Ca}_{0.5})\text{Ca}_{0.75}\text{Y}_{0.25}\text{Cu}_2\text{O}_{8.24}$, (G) $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.22}$, (H) $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.37}$, and (I) $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. All markers are 10 μA .

the scheme provided in this table). Carefully dried nonaqueous solvents such as acetonitrile containing tetraalkylammonium salts were employed so as to minimize the parasitic corrosion effects which occur for these materials when exposed to water. As we described previously,⁸⁻¹² freshly surfaced high- T_c electrodes in scrupulously dried nonaqueous solvents display electrochemical responses similar to those which can be obtained at noble metal electrodes. Under such conditions, high- T_c electrodes exhibit facile electron exchange between well-behaved redox couples such as TCNQ and the host electrode. However, when a thin insulating layer covers the electrode surface, the heterogeneous electron-exchange rate becomes sluggish, which results in a broad cyclic voltammogram response. Thus, according to the method of Nicholson and Shain,²³ the splitting in potential between the cathodic and anodic peaks, ΔE_p , can be exploited to evaluate the electron-transfer rate. For highly reversible redox couples, pristine electrode surfaces exhibit $\Delta E_p \sim 59$ mV (for one-electron-transfer events) and degraded surfaces exhibit $\Delta E_p > 59$ mV.

Electrochemical examination of these different materials has allowed us to explore issues related to the surface properties of high- T_c phases. However, prior to examining the faradaic response of the host electrodes, it is necessary to first examine the background scans in the absence of a redox species in the electrolytic fluid. Shown in Figure 2 are background scans recorded at all nine copper oxides for a solution of 0.1 M Et_4NBF_4 in dry CH_3CN ; for comparison purposes, data acquired at Pt are also illustrated. The superconductor electrodes were prepared as described above using a diamond-scribed technique to obtain a clean interface. The platinum electrode exhibits a potential

window of 2.3 to -1.1 V vs SCE, representing the limits of the electrolytic fluid. All nine of the copper oxides (scans A-I) have their own respective background limits within the potential window exhibited by Pt. The potential limits obtained for all the copper oxide samples are significantly less than those acquired for Pt, indicating that the oxide materials are susceptible to oxidative and reductive reactions outside their own respective potential limits. Redox reactions associated with the constituent atoms of the electrode material are likely to be responsible for this behavior. It must be noted that the background limits for the copper oxides shown here are not optimized, in that larger background limits have been recorded under more stringent conditions. The background limits and the ability to perform solution reduction/oxidation chemistry can be extended slightly to more extreme potentials if the electrodes are used immediately after electrode formation; it appears that the copper oxides degrade with aging in the epoxy matrix, commensurate with a decrease in the performance of the electrode.

Aside from the differences in the oxidative and reductive potential limits, the various oxide electrodes exhibit important differences. The $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$ phase (specimen D) displays a capacitive background 4 times smaller than any other specimen. Of all the samples examined here, $\text{La}_{1.5}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{7.18}$ is the least conductive. Thus, the rather small charging current exhibited by this sample is likely to be due to resistive losses occurring across the electrode specimen. The $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ phase (specimen I) displays a small cathodic faradaic peak that appears to be superimposed on the charging current for the background scan. This anomaly can be attributed most likely to an impurity on the surface of this material; in the past, we have been able to obtain background scans on this n-type superconductor without such a peak. Finally, the $\text{Tl}_{1.5}\text{Ba}_2\text{CuO}_{5.22}$ phase (specimen G) displays a sloping background indicative of a resistive surface layer. The accumulation of an impurity insulating surface layer may be responsible for this behavior (vide infra).^{22,24}

As mentioned above, cyclic voltammetry can be utilized to examine the surface quality of high- T_c samples. In the context of the present study, three different surface preparation techniques were examined for the treatment of the oxide electrodes. According to the first method, the electrode assembly is sanded down to expose a rectangular region of the copper oxide, followed by polishing the electrode surface for 5 min using $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$. The voltammograms of the nine electrodes prepared by this method for a solution of 2.5 mM TCNQ in 0.1 M $\text{Et}_4\text{NBF}_4/\text{CH}_3\text{CN}$ are displayed in Figure 3. The majority of the copper oxide electrodes display poorly resolved voltammetry as compared to that which can be acquired with the other surface methods (vide infra). For example, at Pt, where facile electron-transfer results, two peaks corresponding to the $\text{TCNQ}^{0/-1}$ and $\text{TCNQ}^{-1/-2}$ are readily resolved with ΔE_p values obtained close to 80 mV. The increase in ΔE_p above and beyond the theoretical value of 59 mV for these reversible couples can be attributed to uncompensated solvent resistance effects. Such resistive losses are commonly encountered with organic electrolytic fluids. No attempts have been made to compensate for such effects through the paper. The characteristics exhibited by the majority of the copper oxides illustrated in Figure 3 indicate that chemical degradation of the surface of these materials occurs for the $\text{Al}_2\text{O}_3/\text{H}_2\text{O}$ polishing method. Apparently, this treatment causes a degradation

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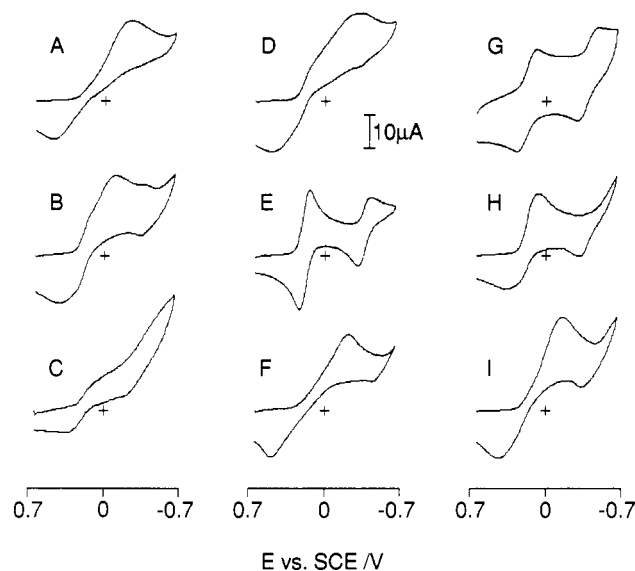


Figure 3. Cyclic voltammograms recorded at 100 mV/s for epoxy encapsulated copper oxide electrodes for 2.5 mM TCNQ in 0.1 M Et₄NBF₄/CH₃CN: (A) YBa₂Cu₃O₇, (B) Ca_{0.4}Y_{0.6}Ba_{1.6}La_{0.4}Cu₃O_{6.95}, (C) La_{1.85}Sr_{0.15}CuO₄, (D) La_{1.5}Ba_{1.5}Cu₃O_{7.18}, (E) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37}, (F) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.75}Y_{0.25}Cu₂O_{8.24}, (G) Tl_{1.5}Ba₂CuO_{5.22}, (H) Tl_{1.5}Ba₂CuO_{5.37}, and (I) Nd_{1.85}Ce_{0.15}CuO₄. The electrodes were surfaced by sanding at 550 rpm followed by polishing with Al₂O₃/H₂O for 5 min (method 1).

of the electrode surface leading to the formation of an insulating layer at the interface. This behavior is not surprising given the known reactivity of the high-temperature superconductors with water. However, the semiconducting Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37} (specimen E) displays a well-behaved voltammetric response even under these conditions. On the other hand, the superconducting Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.75}Y_{0.25}Cu₂O_{8.37} (specimen F) yields poorly resolved voltammetry. The ΔE_p values for the two samples differ greatly (see Table I) indicating that the surface of the semiconductor species is much less reactive to water than the superconductor species with the same structure. Differences in reactivity for these similar materials may be attributed to differences in oxide mobility in the respective lattices. Accordingly, the superconductor form possesses more order with respect to the oxide ions, and thus oxygen is lost more readily from superconductor samples than from the corresponding semiconductor samples. The high oxide mobility in the superconductor form may serve to promote internal redox reactions which facilitate the decomposition of the superconductor lattice.

The structurally similar materials Tl_{1.5}Ba₂CuO_{5.22} (specimen G) and Tl_{1.5}Ba₂CuO_{5.37} (specimen H) display pronounced differences in the voltammetry as seen in Figure 3. The Tl_{1.5}Ba₂CuO_{5.22} phase displays well-defined voltammetry for both the TCNQ^{0/-1} and the TCNQ^{-1/-2} waves. On the other hand, only the first wave is resolved for Tl_{1.5}Ba₂CuO_{5.37}. The higher apparent reactivity with water displayed by Tl_{1.5}Ba₂CuO_{5.37} may be traced to the higher formal valence exhibited by copper in this material. Finally, the surface of the La_{1.85}Sr_{0.15}CuO₄ sample (specimen C) appears to be completely destroyed as no resolved peaks are evident for the Al₂O₃/H₂O surface preparation technique.

Figure 4 illustrates the behavior of the electrodes for the second surface treatment in which the specimens are prepared by abrasive treatment at 550 rpm on a sanding wheel. The major difference between the first and second surface treatments is the elimination of the Al₂O₃/H₂O

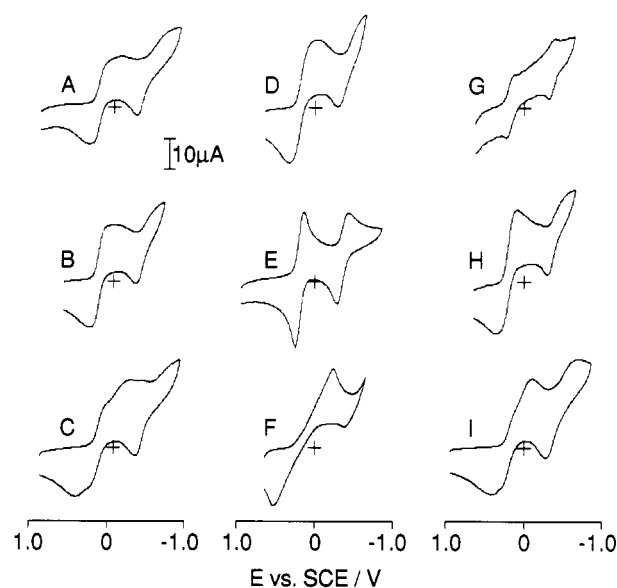


Figure 4. Cyclic voltammograms recorded at 100 mV/s for epoxy encapsulated copper oxide electrodes for 2.5 mM TCNQ in 0.1 M Et₄NBF₄/CH₃CN: (A) YBa₂Cu₃O₇, (B) Ca_{0.4}Y_{0.6}Ba_{1.6}La_{0.4}Cu₃O_{6.95}, (C) La_{1.85}Sr_{0.15}CuO₄, (D) La_{1.5}Ba_{1.5}Cu₃O_{7.18}, (E) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37}, (F) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.75}Y_{0.25}Cu₂O_{8.24}, (G) Tl_{1.5}Ba₂CuO_{5.22}, (H) Tl_{1.5}Ba₂CuO_{5.37}, and (I) Nd_{1.85}Ce_{0.15}CuO₄. The electrodes were surfaced by sanding at 550 rpm (method 2).

polishing step in the latter method; thus, the chemical reactivity of the electrode surface with water is reduced for the second surfacing method. For those samples which can tolerate brief exposure to water, the presence of water during the first surfacing technique may be beneficial in that the water may serve to moderate the local heating effects which often can be formidable during such treatments. With the elimination of water, there is an improvement in the quality of the voltammetry for the majority of the electrode specimens; the faradaic peaks are better resolved and the ΔE_p values are smaller.

As before, there are subtle differences between the quality of the voltammetry exhibited by the nine oxide specimens as illustrated in Figure 4. Again, Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37} (specimen E) displays the best voltammetric response with relatively small ΔE_p values. The La_{1.85}Sr_{0.15}CuO₄ sample (specimen C) has a secondary peak superimposed on the primary faradaic peak, likely due to an impurity at the surface of the electrode generated during the surface preparation.

Further improvement in the quality of the voltammetry is obtained with the third surface treatment method in which a diamond-scribe is utilized to prepare the electrode surface. Figure 5 illustrates the electrochemical responses for the oxide electrodes. For the majority of the specimens, this technique proves to be the best surface treatment. The resulting voltammetry is extremely well-resolved for eight of the nine copper-oxide materials. The majority of the electrodes display ΔE_p values of 100 (± 10) mV, indicating that this method produces relatively clean surfaces free of corrosion products. Only slightly better behavior is obtained at Pt electrodes. There are, however, a few exceptions where the oxide electrodes deviate from the ideal behavior. For example, Tl_{1.5}Ba₂CuO_{5.22} (specimen G) displays ΔE_p values about 40 mV greater than the other specimens. We speculate that a surface-localized impurity layer is responsible for this behavior. In fact, XPS measurements conducted on similar Tl-based cuprate samples revealed the presence of thallium-containing surface impurities with binding energies very close

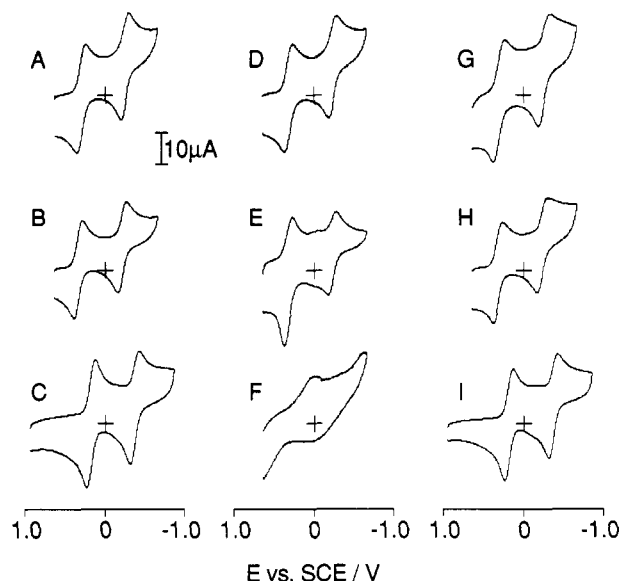


Figure 5. Cyclic voltammograms recorded at 100 mV/s for epoxy encapsulated copper oxide electrodes for 2.5 mM TCNQ in 0.1 M Et₄NBF₄/CH₃CN: (A) YBa₂Cu₃O₇, (B) Ca_{0.4}Y_{0.6}Ba_{1.6}La_{0.4}Cu₃O_{6.95}, (C) La_{1.85}Sr_{0.15}CuO₄, (D) La_{1.5}Ba_{1.5}Cu₃O_{7.18}, (E) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37}, (F) Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.75}Y_{0.25}Cu₂O_{8.24}, (G) Tl_{1.5}Ba₂CuO_{5.22}, (H) Tl_{1.5}Ba₂CuO_{5.37}, and (I) Nd_{1.85}Ce_{0.15}CuO₄. The electrodes were surfaced by sanding at 550 rpm followed by diamond scribing to remove the top layers of the electrode assembly (method 3).

to those observed for authentic Tl₂O₃ samples.^{25,26} The Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37} sample (specimen E) exhibits an anomalous wave between the TCNQ^{0/-1} and TCNQ^{-1/-2} cathodic waves. This effect is also observed for the other two surface methods and is most likely due to an impurity at the surface.

The Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.75}Y_{0.25}Cu₂O_{8.24} sample (specimen F) yields poorly resolved voltammetry even for the diamond-scribe technique. This behavior may be due to the fact that the processing temperature utilized to prepare the sample was very close to the melting point of the material. It is possible that a portion of the sample melted

and formed a liquid phase during the synthesis. Such a situation would result in the accumulation of impurities at the grain boundaries and yield nonhomogeneous surface in which electron transfer is inhibited.

Conclusions

In this paper, we have described methods to prepare electrodes from a wide variety of copper oxide materials and have shown that the electrochemical response of these electrodes is greatly dependent on the surface pretreatment. Moreover, we have demonstrated that the diamond-scribed technique yields the best resolved voltammetry for the majority of high-*T_c* phases examined here. The diamond-scribed technique produces the smallest ΔE_p values, indicating that this technique yields the highest quality superconductor interface. Both the Al₂O₃/H₂O and the 550 rpm abrasive sanding techniques yield surfaces which exhibit larger ΔE_p values, and voltammetry acquired at such surfaces is much less resolved for the majority of the copper oxide materials. Finally, it appears that the La_{1.85}Sr_{0.15}CuO₄ (specimen C) surface is the most sensitive with respect to the method of surface treatment, becoming totally destroyed when polished with Al₂O₃/H₂O and producing impurities with the sanding only technique. While the La_{1.85}Sr_{0.15}CuO₄ is the most sensitive to the method of surface treatment, it appears that Bi₂(Sr_{1.5}Ca_{0.5})Ca_{0.25}Y_{0.75}Cu₂O_{8.37} (specimen E) is the least sensitive. More thorough studies are now warranted to further deconvolute contributions to the surface reactivity due to copper valence, crystal symmetry, impurities, crystal microstructure, and corrosion reactivity. As we have shown in this paper, electrochemistry is a powerful method for studying such issues.

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