Electrochemical Oscillation in the Oxidation of Tritolylamines Using $YBa_2Cu_3O_{7-\delta}$ Ceramics Electrode in Oxygen Atmosphere

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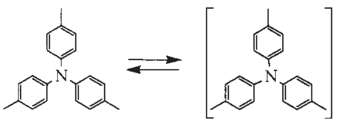
The electrochemical redox reaction of tritolylamine isomers was studied using polycrystalline $YBa_2Cu_3O_{7-\delta}$ (YBCO) pellets as electrodes. The oscillatory phenomena in which the anodic electrode of YBCO reacts between oxidation and reduction of the substrate in rapid alternation nonlinearly were observed. The cathodic reaction of YBCO forms cation radical species of the substrate.

The superconducting transition temperature (Tc), lattice constant, oxygen content, and oxygen site occupancies of the $YBa_2Cu_3O_{7-\delta}$ (YBCO) depend on the way of the sample preparation.[1–3] The superconductivity of YBCO is typically found for orthorhombic materials with oxygen contents between 6.5 and 7.0. As oxygen is removed from YBCO, Tc fall systematically from 92 K to zero. The material transforms from an orthorhombic to tetragonal structure as oxygen is depleted. The tetragonal phase having the oxygen contents of <6.5 tends to display either semiconducting or insulating behavior. A simple chemical model has been proposed to explain the variation of Tc with oxygen stoichiometry in YBCO, where the variation is primarily a carrier concentration effect with Tc displaying a dependence on the hole concentration.[4] In general, adding oxygen to YBCO increases the hole concentration. The coppers which can change valence state influences directly the hole concentration. $YBa_2Cu_3O_{6.5}$ corresponds to the point at which only Cu^{2+} is present. Coppers in YBCO are divalent and oxygens are O^{2-} unless charge balance requires oxidation state of Cu^{3+}. The hole concentration becomes equal to the concentration of Cu^{3+} because of the requirement of charge compensation. The orthorhombic YBCO structure consists of nearly square-planar CuO_2 layers weakly bonded through Cu–O–Cu bonds to one-dimensional CuO chains.[2] The CuO chains play a major role in the superconducting mechanism through the existence of mixed Cu^{3+}/Cu^{2+} ions.[1] The oxygen content in polycrystalline pellets of YBCO can be altered at room temperature by the reduction of YBCO as cathode in an electrochemical cell with a liquid electrolyte. The effective diffusion coefficient, 10^{-11}–10^{-12} cm^2/s, measured from the current decay at constant potential, explains the relatively facile movement of oxygen inside the YBCO grains.[5]

We studied electrochemical reactions between YBCO electrode and tritolylamine (TTA) isomers in oxygen atmosphere as a purpose for clarifying chemical property of YBCO. We report, for the first time, that the anodic reaction of YBCO gives a nonlinear phenomenon in electric current oscillation according to a reversible oxidation and reduction of TTA. The reaction of YBCO electrode with applied potential at -1.0 V vs Ag/Ag^+ forms cation radical species which are one electron-oxidation product of TTA.[6]



The orthorhombic YBCO electrode was prepared by sintering a commercial YBCO powder at 920 °C for 2 d. It was then annealed at 550 °C for 4 d, and then cooled slowly in O_2 flow (300 ml/min). The superconductive quality of the samples was confirmed by measuring the conventional direct-current four-probe resistivity and the alternating-current magnetic susceptibility from 80 to 300 K. Pellets of YBCO ($4 \times 12 \times 0.8$ mm^3) were used as working electrode. The counter electrode was a Pt wire, and an Ag/Ag^+ standard electrode was served as reference electrode. The TTA (1 mM) dissolved in electrolytic solution (0.1 M n-Bu_4NPF_6/n-butyronitrile) was aerated by bubbling oxygen prior to starting the experiment, and kept under oxygen during the experiment. The applied potential was varied between -1.0 and $+1.0$ V vs Ag/Ag^+, depending on the experiment. A commercial potentiostat was used for monitoring current. The electrochemical oxidation and reduction of TTA was monitored *in situ* by measuring absorbance at *ca.* 700 nm.

The visible absorption spectra of the TTA isomers under the cathodic polarization of -1.0 V with YBCO were shown in Figure 1a. These spectra were observed even in the electrolyte bubbled with N_2 gas. The reversible electrochromism was also observed in the change of the electronic absorption spectra, which were taken at the same time as the reversible cyclic voltammo-

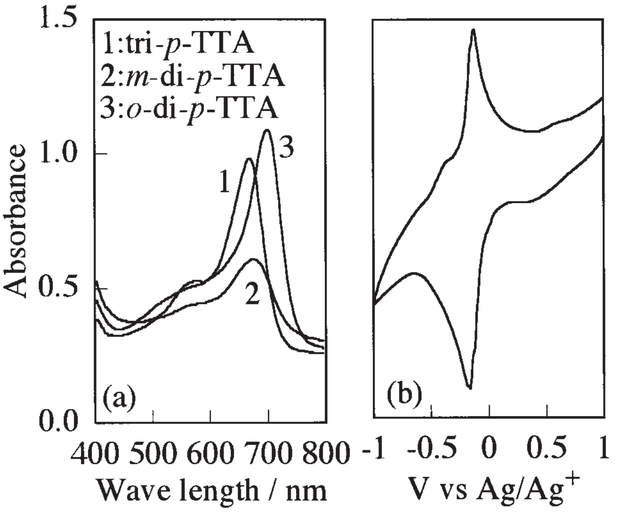


Figure 1. Electrochemical reaction of TTA isomers by the cathodic electrode of YBCO: (a) Absorption spectra of TTA isomers with applied potential of -1.0 V vs Ag/Ag^+, (b) Cyclic voltammogram of tri-p-TTA.

gram (CV) between -1.0 and $+1.0$ V (Figure 1b). The absorption maximum at *ca.* 700 nm in Figure 1a was attributed to TTA cation radicals ($TTA^{\bullet +}$). Oxidation-reduction potential ($E_{1/2}$) of tri-*p*-TTA was $+0.80$ V vs Ag/Ag^+ by the conventional CV measurement. However, the $E_{1/2}$ value of the tri-*p*-TTA measured from Figure 1b was -0.16 V vs Ag/Ag^+, using YBCO as the cathode electrode. Therefore, the observed $TTA^{\bullet +}$ must not be a direct electrochemical oxidation product. It seems to be formed by the reaction with secondary products in the result of the reduction of YBCO. The cathodic reduction of YBCO destroyed superconductivity phase. Both Tc(zero) value and conductivity of electrochemical reduced YBCO samples decreased. The electrochemically reduced YBCO exhibits a broadened transition to superconducting state.[7] The reaction that takes place at the YBCO cathode can be written as follows:

$$\delta Cu^{3+} + \delta O^{2-} \rightarrow \delta Cu^{2+} + \delta [O]$$

Here, Cu^{3+} is the hole and O^{2-} is an oxygen ion in the YBCO. [O] is a reactive oxygen species. The oxygen ion δO^{2-} inside the YBCO (δ is the number of oxygen ions) move to outmost layers of grains due to the electric field. Reactive oxygens are formed as a result that the oxygen ions release electrons inside YBCO phase. The cathodic reduction takes out holes from the valence band of YBCO by the released electrons. Reduction from Cu^{3+} to Cu^{2+} occurs simultaneously. The formed reactive oxygens react further TTA in solution.

On the other hand, the transition and conductivity properties of YBCO were not influenced by the electrode oxidation with $+1.0$ V vs Ag/Ag^+. As shown in Figure 2, a phenomenon of abnormal vibration was observed on an apparent current flowing through the electrochemical cell in oxygen atmosphere. That is, the direct current supplied through the cell was converted to the alternating one (0.24 Hz). In order to monitor this oscillation, we added TTA isomers to the electrolyte and measured *in situ* the visible absorption at λ_{max} (observed in Figure 1). As seen from Figure 2, the oscillation of the absorption which perfectly synchronized with the current signal was observed. However, almost no oscillation was observed in N_2 atmosphere. Therefore, the participation of a dissolved oxygen is indicated in such the oscillation. O_2 probably affects electrochemical oxidation of TTA by the YBCO electrode. From the experimental results, we assume the reason of oscillatory phenomenon as follows. The oxygen ions from the CuO chains in YBCO diffuse to Pt wire joined together to the electrode along supplied the voltage ($+1.0$ V). TTA is oxidized by the potential between YBCO electrode and counter electrode in the cation radical $TTA^{\bullet +}$. However, the O^{2-} diffusion of the grain inside has been blocked by the Pt wire. Such an electronic unstable state in grains is rapidly disappeared, and the O^{2-} diffused in the crystal returns to the original CuO chains. Simultaneously, the electrons accumulated in the YBCO grains discharge from the electrode surface. The released electrons rereduce the cation radical of TTA to its neutral molecule. Though molecular oxygen seems to be concerned in such the oxidation reaction of TTA, whether there is the involvement in the electrochemical oxidation of YBCO is uncertain. Further detailed study of the electrochemical oscillatory phenomenon observed for the YBCO electrode is in progress.

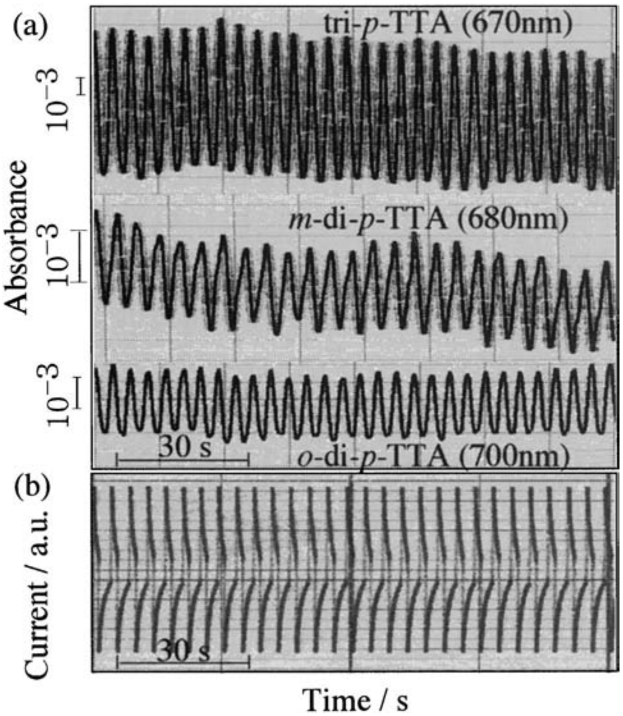


Figure 2. Oscillation of absorption (a) synchronized to vibration signal of electric current (b) by the anodic electrode of YBCO with applied potential of $+1.0$ V vs Ag/Ag^+.

In conclusion, the electrochemical redox reaction of TTA isomers using the YBCO electrode shows the behavior unlike usual electrochemical reaction. In the cathodic reaction of YBCO, the TTA in the electrolyte is oxidized in the cation radical $TTA^{\bullet +}$, and the superconductive phase of YBCO used for the electrode is destroyed. This reaction seems to be oxidation-reduction between YBCO and TTA with the diffusion of the oxygen ions on the CuO chains which supplies the superconductive carrier. On the other hand, oscillatory reactions that reversibly oxidize and reduce the substrate are observed in the anodic reaction of YBCO. The dissolved oxygen in the electrolyte is concerned in this nonlinear reaction.

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