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Investigation of the interface problem between high temperature superconductor and ionic conductors

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The charge carriers transfer process across the interface between a superconductor and an ionic conductor, around T_c is investigated. Low temperature electrochemical measurements are carried out on the interfaces between different polycrystalline high-T_c superconductors (HTSC) and $RbAg_4I_5$ and Ag^+ ion-conducting glass. The experiments cover a temperature range down to 10 K in the dc-frequency range. A transient technique in the time domain and electrochemical impedance spectroscopy (EIS) in the frequency domain are used to study the silver (Ag^+) deposition as the Faradaic charge transfer process at that interface. The results show significant enhancement of the charge transfer observed around the critical temperature. This was indicated by either an admittance peak in the transient measurements or a corresponding decrease of the polarization resistance (R_p) in EIS measurements. This enhancement of the charge transfer is correlated to the formation of Cooper pairs at $T \leqslant T_c$ and interpreted on the basis of a band structure model as a quantumelectrochemical phenomenon with the tunnelling of Cooper pairs through the electrochemical double layer.

1. Introduction

Since the discovery of a new class of oxide ceramics superconductors in 1986 by Bednorz and Müller [1], great efforts have been made in order to find new compositions with higher critical temperatures and improved electronic and magnetic properties. On the other hand, the interpretation of the pairing mechanism of HTSCs is still a matter of dispute.

Measurements of the charge transfer across the interface between HTSC and an adjacent phase containing occupied and unoccupied electronic states may lead to additional information about the pairing mechanism and the nature of the corresponding coupling.

Studies of charge carrier transfer processes across HTSC and semiconductor interfaces indicates a tunnelling process of charge carriers across the heterojunction when the HTSC is in the superconducting state [2]. Similar effects are also expected in electrochemical systems. These may give a new insight into the charge transfer mechanism, the change of energy barriers and proximity-like effects.

First, electrochemical studies on HTSC/solid electrolytes (SE) interface was carried out by the research group of Breiter, Lorenz and Saemann-Ischenko [2]. This field of electrochemical investigation at low temperatures around T_c is relatively new and the experiments are complicated by the low ionic conductivity of the electrolytes at these temperatures.

The mechanism of charge transfer process across the HTSC/SE interface can be studied electrochemically at low temperatures $T \leqslant T_c$ in order to get information about the double layer structure, participation of quasiparticles (electrons and holes) and correlated charge carriers (Cooper pairs) as well as ions with the charge transfer at temperatures above and below T_c. Besides this fundamental interest in this field, the knowledge of the surface behaviour, possible modifications and structure of HTSC surfaces even at low temperatures opens up new possibilities for the technical applications of HTSC materials.

In this paper, the results of low temperature electrochemical system HTSC/SE interfaces will be presented and an interpretation of the observed data will be given.

2. Experimental procedure

The solid electrolyte samples consisted of $RbAg_4I_5$ and Ag^+ glass ionic conductor tablets of 1 cm diameter and about 2 cm, 2 mm thickness respectively. The polycrystalline HTSCs samples of $YBa_2Cu_3O_{7-\delta}$, $Tl_2Ba_2CaCu_2O_8$ and $Tl_2Ba_2Ca_2Cu_3O_{10}$, served as working electrodes (WE). They were prepared from sinter-pressed tablets of 1 cm diameter and 0.13 cm thickness. The $RbAg_4I_5$ was prepared according to the standard procedure by melting and quenching the stoichiometric mixture of AgI and RbI with subsequent annealing for 16 h at $T = 438$ K [3]. The contact between HTSC and SE was made by pressing together the smooth and shiny surfaces of both ceramic materials considered. Silver paint at the back side of the SE served as the counterelectrode (CE). All measurements are performed potentiostatically in a two-probe technique.

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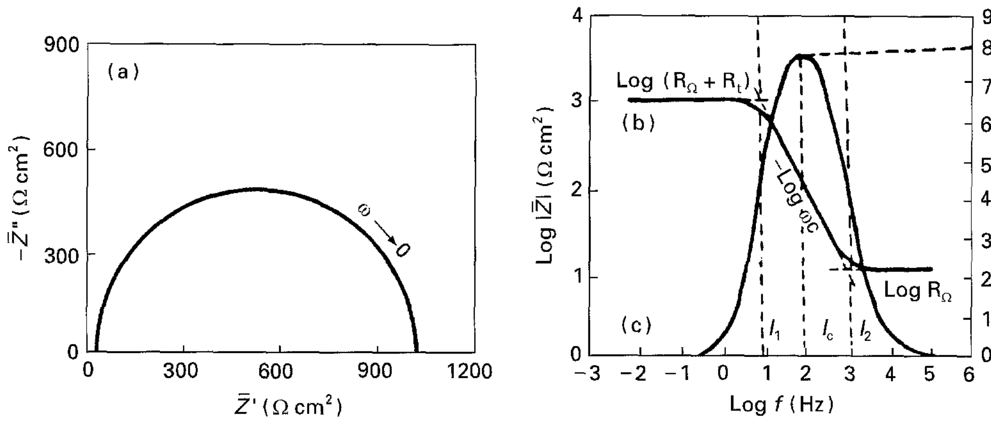

Figure 1 Electrochemical impedance measurements (a) Nyquist and (b), (c) Bode–Plot.

Electrochemical impedance spectroscopy measurements were carried out using a frequency response analyser (FRA) and a modified potentiostat (PAR 273) which allows measurement of low currents down to 10^{-12} A, with an additional external low-noise amplifications.

A cryostat based on a liquid helium cooling system was used to adjust the temperature of the sample under vacuum conditions with an accuracy better than 1 K. The measurements were carried out in the temperature range $19 \leqslant T \leqslant 298$ K.

The exchange current density i_0 of the system, is calculated either from electrochemical impedance spectroscopy data at low frequencies or from quasi-steady-state currents of the applied transient technique.

3. Construction of impedance hodograph for the electrochemical equivalent circuit

The most descriptive way of analysing the results of impedance and admittance measurements is by constructing hodographs [4], i.e. lines in the complex plane which describe the movement of the free end of the impedance vector during frequency variation. From the shape of the hodograph one can draw conclusions as to the equivalent circuit of the process being examined, and also to the process itself (Fig. 1). So, in the electrochemical system HTSC/SE, the kinetic reaction for the electrochemical cell will be described by the parameters; R_Ω the ohmic resistance of the SE, R_t the charge transfer resistance, C_{dl}, the double layer capacitance and Z_r which represents all resistances from the chemical reactions, mass transport, electrocrystallization, etc. The equivalent circuit consists of an ohmic resistance R_Ω connected in series with an RC parallel combination as shown in Fig. 2. The characteristic RC parameters as a function of the temperatures T calculated using a non-linear least square fit analysis [5] is applied to fit the experimental impedance data by the transfer function

$$Z(s) = R_\Omega + R_p(1 + sR_pC_{dl})^{-1} \tag{1}$$

where R_p denotes the polarization resistance and corresponds to R_t only for a purely charge transfer contolled electrode reaction. R_Ω and R_p are defined by the high and low frequency limits of $Z(s)$ respectively

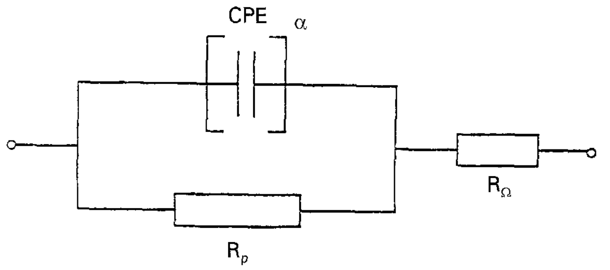

Figure 2 Equivalent circuit of the transfer function used for the fit of the experimental impedance data.

according to the following relations

$$R_\Omega = \lim_{s \to \infty} R_e\,[Z(s)] \tag{2a}$$

$$R_p = \lim_{s \to 0} R_e\,[Z(s)] \tag{2b}$$

To account for a possible frequency dispersion due to inhomogenity effects, a constant phase element $(s^\alpha C_{dl})^{-1}$ with $0 \leqslant \alpha \leqslant 1$ is used instead of $(s\,C_{dl})^{-1}$.

4. Electrochemical impedance spectroscopy measurements on HTSC/SE interfaces

The intrinsic ionic conductivities of the superionic conductors used are found to be temperature dependent as shown in Fig. 3. Obviously, the conduction mechanism of SEs is changed at about $T = 100 \pm 20$ K. Above this temperature, the conductance of silver ions is a thermally activated process with activation energies $E_a/\text{eV} = 0.20 \pm 0.03$ (α, $RbAg_4I_5$), 0.12 ± 0.01 (β, $RbAg_4I_5$), 0.47 ± 0.01 (γ, $RbAg_4I_5$), 0.13 ± 0.01 (Ag^+ ion-conducting glass), and 0.25 ± 0.05 (Agβ″, alumina [6, 7]) which agree well with previous results. At $T \leqslant 100 \pm 20$ K, a temperature independence with an apparent zero activation energy is observed. This clear change of the conduction mechanism might be caused by a tunnelling process of Ag^+ ions within the SEs, corresponding to a two-level tunnelling system (TLS-states). A "glass-like transition" T_g at $T = 110$ K is previously found for Na- and Ag-β″-alumina by Strom [8]. At $T < T_g$, a barrierless ionic motion of Ag-cations has been proposed.

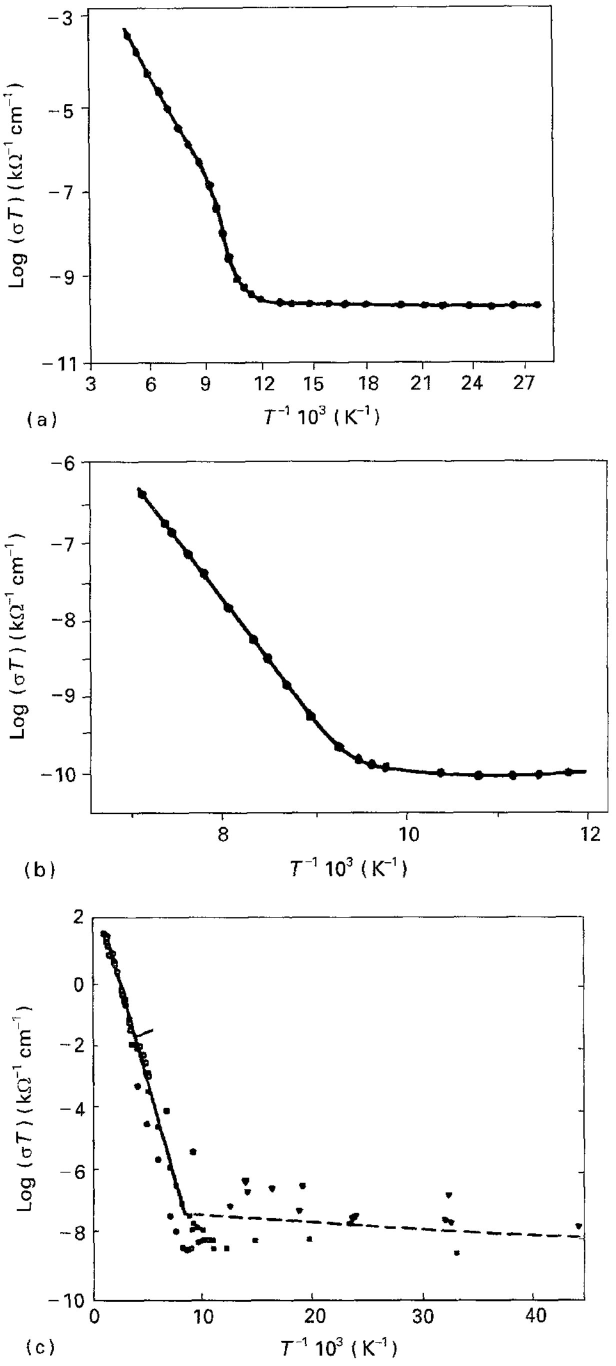

Figure 3 Temperature dependence of the specific conductivities of different solid electrolytes measured by EIS. Four-probe technique (a) $RbAg_4I_5$ $E_a = 0.14$ eV; (b) Ag^+ ion conducting glass $E_a = 0.13$ eV; (c) β″-alumina [6] $E_a = 0.25$ eV.

In general it must be recognized that the experimental overall impedance of the system Ag/HTSC/SE/Ag, consists of a series combination of the following components

$$Z = Z_{HTSC} + Z_{Ag/HTSC} + Z_{HTSC/SE} + Z_{SE} + Z_{SE/Ag} \tag{3}$$

The first two components are neglected with respect to the others. The impedance Z_{SE} corresponds to the frequency-independent ohmic resistance of the system and is given by the four-probe measurements.

Two-probe measurements (Fig. 4) have shown that the impedance of the Ag/SE interface is 1–2 orders of magnitude lower than that of the HTSC/SE interface.

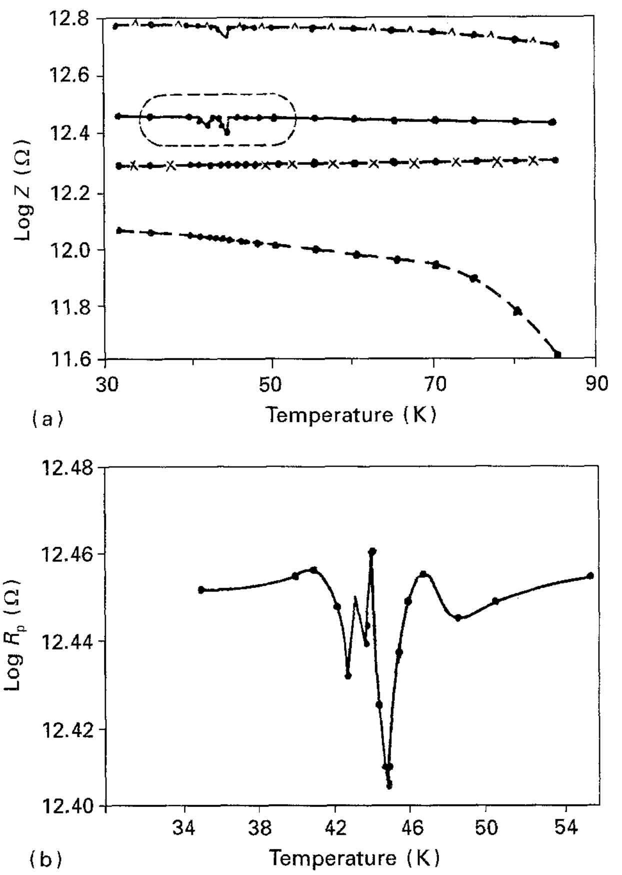

Figure 4 Two-probe measurements of the impedance Z and R_p versus temperature T for the system Ag/glass/Tl 2212/Ag. -Λ- Z (total); -•-Z (HTSC/SE); -×-Z (Ag/SE); -●-Z (SE).

Also, the non-monotonous temperature dependence around T_c corresponds to the HTSC/SE interface.

5. Discussion

The detection of an extraordinary temperature dependence or an enhancement effect of HTSC/SE interface around T_c may be interpreted as implying that the charge distribution at the interface and, therefore, the structure of the electrochemical double layer are changed in the presence of Cooper pairs at $T \leqslant T_c$ and that this situation may lead to either a kinetic or a proximity-like effect.

For the proximity-like effect, it is assumed that Cooper pairs can be injected into the SE, reducing only the ohmic resistance R_Ω of the SE which has been never observed. Transfer function analysis of electrochemical impedance spectroscopy measurements indicates that the experimental results cannot be explained on the basis of a proximity-like effect. The ohmic resistance, R_Ω, of the SE is estimated to be more than two orders of magnitude lower than the overall impedance of the system Ag/HTSC/SE/Ag [2]. Therefore, a proximity-like effect may have only minor impedance if it occurs.

For the kinetic effect, it is proposed that Cooper pairs can penetrate the electrochemical double layer causing a decrease of the charge transfer resistance R_t which is expected to depend inversely on the temperature (T) and inversely to be related to the exchange current density (i_0) of the Faradaic reaction occurring at the studied interface

n-type HTSC: $\mathrm{Ag^+(SE) + e^-(HTSC) = Ag(interface)}$

p-type HTSC: $\mathrm{Ag^+(SE) = Ag(interface) + P^+(HTSC)}$

according to the relation

$$R_t = (k_B T)/(Z e_0 i_0) \tag{4}$$

where k_B is the Boltzmann constant, Z and e_0 denote the ionic and the elementary charge, respectively.

In the case of a thermally activated charge transfer process of quasiparticles or ions, the current is strongly temperature dependent according to an Arrhenius-like equation

$$i_0 = i'_0 \exp(-E_a/k_B T) \tag{5}$$

where E_a denotes the activation energy of the charge transfer process of quasiparticles.

Therefore, the observed enhancement of the current at HTSC/SE interface around T_c cannot be explained only on the basis of a classical charge transfer process of quasiparticles across the interface. It can be assumed that Cooper pairs will not only change the structure of the electrochemical double layer at that interface, but also will penetrate through the double layer and decay into quasiparticles before occupying unfilled energy bands in the SE.

A necessary condition for such an enhanced charge transfer mechanism around T_c is the existence of energetically nearly equivalent states to be occupied by quasiparticles. Obviously, the condition for such a charge transfer is fulfilled for the HTSC in the superconducting state below T_c. Such states also have to exist in the SE and may be identified presumably with the energy levels in the LTS states of SEs below T_g as mentioned before.

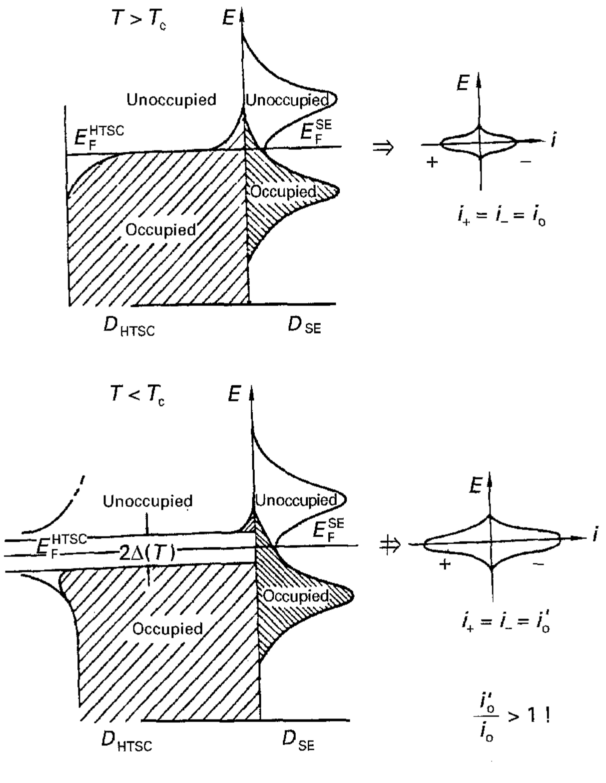

Figure 5 Schematic energy diagram of Fermi-particles at the superconductor/ionic conductor interface at electrochemical equilibrium [8]. (a) $T > T_c$, metallic state. (b) $T \leqslant T_c$, superconducting state.

The elecrochemical ionic conductivity of the system obeys the classical energy representation of Fermi particles at the interface at $T > T_c$. At $T \leqslant T_c$, the observed kinetic enhancement effect in the exchange current density cannot be explained because of the opening of the gap 2Δ which inhibits the charge transfer of quasiparticles as illustrated in a simplified band structure model (Fig. 5) according to Gerischer [9]. Therefore, the observed low-temperature effect on HTSC/SE interface is currently interpreted as a real quantumelectrochemical kinetic phenomenon caused by the formation of Cooper pairs (bosons) as correlated charge carriers within the HTSC at $T \leqslant T_c$ and their ability to cross the interface HTSC/SE, to contribute to the charge transfer process and to stimulate the interfacial Faradaic reaction.

6. Conclusion

The present low-temperature electrochemical impedance spectroscopy measurements have led to valuable information on the extraordinary charge transfer behaviour and the double layer capacity at HTSC/SE interfaces as well as on the intrinsic properties of the SE used. In particular, it was found that the superconduction transition of the HTSC at T_c yields to a structural change of the electrochemical double layer and an enhancement of the charge transfer kinetics of the Faradaic electrode reaction. Below T_c, the Faradaic reaction is no longer thermally activated and a completely different charge transfer mechanism with a prevailing tunnelling process of Cooper pairs, their decay into quasiparticles, and the occupation of TLS states in the SE must be taken into consideration.

The non-monotonous behaviour at the interfaces should be discussed in terms of quantum electrochemical kinetic phenomena on the basis of a band structure model.

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References

1. J. G. BEDNORZ and K. A. MÜLLER, *Z. Phys. B* (1986) 198.
2. M. W. BREITER, W. J. LORENZ and G. SAEMANN-ISCHENKO, *Surf. Sci.* **230** (1990) 213.
3. B. G. OWENS and G. R. ARGUE, *Science* **157** (1967) 308.
4. L. M. SOLOVÉVA, *Elektrokhimiya* **16** (1980) 407.
5. A. PINKOWSKI et al., *Electrochim. Acta* **34** (1989) 1113.
6. A. PINKOWSKI et al., *J. Electroanal. Chem.* **287** (1990) 203.
7. I. ENGELHARDT et al., *Electrochim. Acta* **37** (1992) 2129.
8. U. STROM, *Solid State Ionics* **8** (1983) 255.
9. H. GERISCHER, in "Physical chemistry", edited by H. Eyring, J. Henderson and W. Jost (Academic Press, New York, 1970) p. 463.

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