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APPLICATIONS OF DIRECT VOLTAMMETRY IN THE STUDY OF HIGH TEMPERATURE SUPRACONDUCTOR / REDOX ELECTROLYTE INTERFACE

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ABSTRACT. A new method based on direct voltammetry was used to study the variation of current density with temperature at the high temperature superconductor/ redox electrolyte interface (in the proximity of critical temperature).

For this purpose, we have solved the Volterra integral equation with known K(t,u) kernel and f(t) function, thus allowing the j(t) current density estimation.

From j(η) vs. η an explanation for the reversible solution form to a Butler-Volmer irreversible solution form trespassing in the case of critical temperature involvment, is suggested.

INTRODUCTION

In nonaqueous media direct voltammetry of Pb $|Bi_2\ Sr_2\ Ca\ Cu_2\ O_x$ (2212) phase is similar in appearence to that of noble metals [1].

Resonable results can be obtained, despite the distorsion induced by ohmic drop, in a nonstationary method.

A specific expresion of Volterra equation is considered for an inert electrodic material [2].

By solving this equation we found the current density j(t) in reversible and irreversible reactions cases (cathodic branch).

Until now there were not reported results about Tc estimation using nonstationary methods from classical point of view.

RESULTS AND DISSCUSIONS

In the Fredholm alternative [3] a Volterra integral equation is:

$$j_F(t) = \lambda \frac{j^0 N^*(t)}{\pi^{1/2}} \int_0^t \frac{j_F(u)}{(t-u)^{1/2}} du + f(t) \qquad (1)$$

where

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$$N^*(t) = \frac{\exp(-\beta f v t)}{F\sqrt{D_O}c_O} + \frac{\exp[(1-\beta) f v t]}{F\sqrt{D_R}c_R}\ ; \quad f(t) = j^0\{[\exp(-\beta f v t) - \exp[(1-\beta) f v t]]\}$$

$$\lambda = -1 \tag{1'}$$

D - diffusion coefficient; c - concentration, f = F/RT; T - temperature; t - time; $|v\ |t$ is the overtension (η) and $v < 0$.

If $D_0 = D_R = D$ and $c_0 = c_R = c$, by neglecting capacitive current, $j_F(t)$ is the measured current density in closed circuit conditions.

In this case (1') is:

$$N^*(t) = \overline{N}\exp(\beta f|v|t)[1+\exp(-f|v|t)]\ ;\ f(t) = j^0\exp(\beta f|v|t)[1-\exp(-f|v|t)]$$

$$\overline{N} = \frac{1}{F\sqrt{Dc}}\ ;\ f = \frac{F}{RT} \tag{1''}$$

We can write integral eq. solution in serial form:

$$j(t)=j_0(t)+\lambda j_1(t)+ \ldots +\lambda^k j_k(t)+ \ldots \tag{2}$$

where:

$$j_0(t)=f(t)=j^0\exp(\beta f|v|t)[1-\exp(-f|v|t)] \tag{2'}$$

$$j_{k+1}(t) = \frac{j^0 N^*(t)}{\pi^{1/2}}\int_0^t \frac{j_k(u)}{(t-u)^{1/2}}du \tag{2''}$$

and for j_1 (t) result:

$$j_1(t) = \frac{j^0 N^*(t)}{\pi^{1/2}}\int_0^t j^0\exp(\beta f|v|u)[1-\exp(-f|v|u)](t-u)^{-1/2}du \tag{3}$$

In proximity of t, $(t - u)^{-1/2} \to \infty$ and: $\exp(\beta f|v|u[1-\exp(-f|v|u)] \to$
$\exp|\ \beta f|v|t\ [1-\exp(-f|v|t)]\ |$.

It was possible to be applied an average theorem for eq.(3), and we found:

$$\int_0^t j^0\exp(\beta f|v|u)[1-\exp(-f|v|u)](t-u)^{-1/2}du \cong j^0\exp(\beta f|v|t)[1-\exp(-f|v|t)]\cdot$$

$$\cdot\int_0 (t-u)^{-1/2}du \cong j^0\exp(\beta f|v|t)[1-\exp(-f|v|t)]2\sqrt{t} \tag{4}$$

with

$$\int_0^t (u-0)^m(t-u)^n du = (t-0)^{m+n+1}\frac{\Gamma(m+1)\Gamma(n+1)}{\Gamma(m+n+2)} \tag{5}$$

$(t>0;\ m>-1;\ n>-1)$

where $\Gamma(\ )$ function is:

$$\Gamma\left(n\right)=\int_{0}^{\infty}u^{n-1}\exp\left(-u\right)du\;;\;n\neq 0,-1,-2,-3,... \qquad (6)$$
$$\Gamma\left(n+1\right)=n\Gamma\left(n\right)\;;\;\Gamma\left(1\right)=1\;;\;\Gamma\left(1/2\right)=\pi^{1/2}$$

Using (4) and (5):

$$j_1\left(t\right)=\left[j^0N^*\left(t\right)\right]j^0\exp\left(\beta f\left|v\right|t\right)\left[1-\exp\left(-f\left|v\right|t\right)\right]\frac{1}{\Gamma\left(1/2+1\right)}t^{1/2} \qquad (7)$$

The little error occuring by averaging procedure from (4), failed, because odd therms in serial form (2) appear with (-) and even therms appear with (+).
Generally:

$$j_k\left(t\right)=\left[j^0N^*\left(t\right)\right]^k j^0\exp\left(\beta f\left|v\right|t\right)\left[1-\exp\left(-f\left|v\right|t\right)\right]\frac{t^{k/2}}{\Gamma\left(k/2+1\right)} \qquad (8)$$

By using (2") in the same averaging conditions we obtained:

$$j_{k+1}\left(t\right)=\left[j^0N^*\left(t\right)\right]^{k+1} j^0\exp\left(\beta f\left|v\right|t\right)\left[1-\exp\left(-f\left|v\right|t\right)\right]\frac{t^{\left(k+1\right)/2}}{\Gamma\left[\left(k+1\right)/2+1\right]} \qquad (8')$$

and (8) is indeed a general expression.
Finaly the current density is:

$$j\left(t\right)=j^0\exp\left(\beta f\left|v\right|t\right)\left[1-\exp\left(-f\left|v\right|t\right)\right]\left\{1+\left\{\lambda j^0\overline{N}\exp\left(\beta f\left|v\right|t\right)\left[1+\exp\left(-f\left|v\right|t\right)\right]\right\}\cdot\right.$$
$$\left.\cdot\frac{t^{1/2}}{\Gamma\left(1/2+1\right)}+\ldots+\left\{\lambda j^0\overline{N}\exp\left(\beta f\left|v\right|t\right)\left[1+\exp\left(-f\left|v\right|t\right)\right]\right\}^k\frac{t^{k/2}}{\Gamma\left(k/2+1\right)}+\cdots\right\} \qquad (9)$$

A (9) serie is convergente and deriving this expression, after few algebric operation finaly results [3]

$$\frac{1}{\left(\lambda j^0\overline{N}\right)^2}\left[\frac{dj\left(t\right)}{dt}-\frac{\beta+\left(1-\beta\right)\exp\left(-f\left|v\right|t\right)}{1-\exp\left(-f\left|v\right|t\right)}f\left|v\right|j\left(t\right)\right]=\left\{1+2\left[\beta-\frac{\exp\left(-f\left|v\right|t\right)}{1+\exp\left(-f\left|v\right|t\right)}\right]\cdot\right.$$
$$\left.\cdot f\left|v\right|t\right\}\exp\left(2\beta f\left|v\right|t\right)\left[1+\exp\left(-f\left|v\right|t\right)\right]^2 j\left(t\right)+\left\{1+2\left[\beta-\frac{\exp\left(-f\left|v\right|t\right)}{1+\exp\left(-f\left|v\right|t\right)}\right]f\left|v\right|t\right\}\cdot \qquad (10)$$
$$\cdot\exp\left(2\beta f\left|v\right|t\right)\left[1-\exp\left(-2f\left|v\right|t\right)\right]\frac{1}{\lambda\overline{N}\pi^{1/2}t^{1/2}}$$

This is an ordinary diferential equation of first order for direct voltammetry.

a) current density for reversible redox reactions.

In this case $j^0 \to \infty$ and from (10) (with λ = -1) we have:

$$j(t) = \frac{1-\exp(-f|v|t)}{1+\exp(-f|v|t)} \frac{F\sqrt{D}\,c}{\pi^{1/2}t^{1/2}} \tag{11}$$

Equation (11) can be written

$$j(\eta) = \frac{F\sqrt{D}\,c\,v^{1/2}}{\pi^{1/2}} \cdot \text{th}\left(\frac{f\eta}{2}\right)\frac{1}{\eta^{1/2}} \tag{12}$$

(using overtension η)

b) current density for irreversible redox reactions.

With $j^0 \to 0$, from eq. (10)

$$\frac{dj(t)}{dt} = \left[\beta + \frac{\exp(-f|v|t)}{1-\exp(-f|v|t)}\right] f|v|\,j(t) \tag{13}$$

and by integration:

$$j(t) = j^0 \exp(\beta|v|t)[\,1-\exp(-f|v|t\,] \tag{14}$$

or $$j(\eta) = j^0 \exp(\beta\eta)[\,1-\exp(-f\eta\,)] \tag{14'}$$

By deriving the eq. (12) is obtained:

$$4f\eta\exp(-f\eta)-1+\exp(-2f\eta) = 0 \tag{15}$$

or: $$\text{sh}(f\eta) = 2f\eta \tag{15'}$$

and after numerical computation a maximum at:

$$\eta_p=2{,}18 \cdot RT/F \tag{16}$$

dependent of the temperature.

Let's consider the diffusion coefficient at different temperatures of: 2 mM Cp_2* Fe in 0,2 M Bu_4NPF_6, 1/2 (PrCN/EtCl) solvent mixture [4].

Numerical computations was applied to eq.(12). This procedure generated nonlinear j vs. η plots for 50 mV/s scan rate (see fig.1) at low temperature conditions.

Initialy at 273 K j vs. η is a reversible shape, but finaly at about 100 K appears change. By decreasing the temperature both value j(η) and η_{peak} change.
$\eta_{peak} \to \eta_{Tc}$ (for critical temperature), and the reversible current density j(η) should became a Butler -Volmer irreversible type.

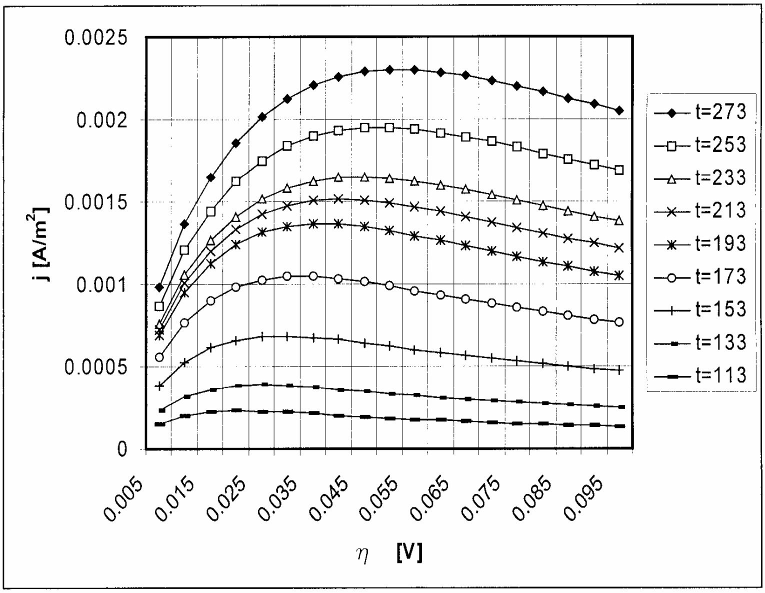

Fig.1. j vs. η plots (50 mV/s scan rate) in different temperature conditions between 113 K and 273 K

In critical conditions (T_c) the numerical estimation show that one can write:

$$FD^{1/2}c|v|^{1/2} \, . \, \pi^{1/2} = j^0 \exp (\beta\eta_{Tc})[\, 1+\exp(-f\eta_{Tc}\,)] \, . \, \eta_{Tc}^{\;1/2}$$

From this eq. it is possible to calculate the critical temperature in classical treatement.

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