A model for understanding the temperature change of an alternate hot and cold micro-band graphite electrode

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Abstract

A model is established for understanding the temperature change of an alternate hot and cold micro-band graphite electrode. It consists of two symmetrically placed thermoelectric coolers with an embedded graphite sheet as interlayer. By measuring the open circuit behaviors of a standard redox couple, the electrode surface temperature can be detected. And the electrode surface temperature can be regulated from 40 °C to −10 °C in aqueous solution without freezing. The model is described as $Q_h = \gamma_h \Delta T$, $Q_c = \gamma_c \Delta T$, where the temperature change (ΔT) of electrode surface is assumed to be proportional to power of heating (Q_h) or cooling (Q_c). In addition, the diffusion activation energy of ferricyanide ion is firstly achieved by extending the temperature range from above zero degree down to the supercooled temperature (−10 °C) with this specially designed electrode. Diffusion coefficient of ferricyanide ion is ca. $0.22 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at −10 °C, and activation energy is 23.2 kJ mol^{−1}. The experimental data are consistent with data obtained by Stokes-Einstein equation for the determination of diffusion coefficient and activation energy.

Keywords: Model; Alternate hot and cold micro-band graphite electrode; Supercooled temperature; Ferricyanide; Diffusion coefficient; Activation energy.

1. Introduction

Since the development by Gründler in 1993 [1–2], temperature modulation

electrodes are becoming more popular for electrochemical detection systems. Principles and analytical applications of them can be found in reviews [3–7]. There are many advantages for them: affecting thermodynamic and kinetic parameters of the electrode reaction, accelerating the redox reaction rates, and so on [8–11]. In recent years, the cavitation phenomena, dielectrophoretic and electrothermal effects can be found on heated electrodes [12–14]. However, those electrodes' surface temperature can't be cooled down. The electrode worked in the supercooled solution, whose temperature is below its normal freezing point, is called supercooled electrode [15]. The electrode that can be heated and chilled is called alternate hot and cold electrode [16]. The surface temperature of both electrodes [15–16] can be cooled down to $-13\text{ }^{\circ}\text{C}$ in aqueous solution. But there is no theoretical explanation about the heating or cooling “mechanism” for both electrodes. Due to the high surface roughness, high conductivity, rapid thermal response, good thermal stability and easily being modified, graphite is usually used as an electrode material [17–18]. Herein, a model is established for understanding the temperature change of an alternate hot and cold micro-band graphite electrode (MBG-AHCE).

A variety of system designed for detecting temperature dependence of diffusion coefficient of the ferricyanide and ferrocyanide ion at elevated temperatures have already been described in literatures [19–22]. Here MBG-AHCEs were applied to detect the activation energy and diffusion coefficient of the ferricyanide ion by extending the temperature range from above zero degree down to the supercooled temperature ($-10\text{ }^{\circ}\text{C}$), which has not been detected before.

2. Materials and methods

2.1. Materials

Chemical agents were purchased from Sinopharm Chemical Reagent Co. Ltd. Graphite sheet (thickness ca. $25\mu\text{m}$) was purchased from AOQ Electronic Technology Co., Ltd. Copper foil tape (thickness ca. $50\mu\text{m}$) was purchased from Hengte Adhesive products Co., Ltd. Digital multimeter, direct current power, TECs, epoxy resin and

electrochemical analyzer were the same with the literature [16].

2.2. Fabrication of MBG-AHCEs

The fabrication process of MBG-AHCEs is shown in Fig. 1A. Using the thermal grease, two symmetrically placed TECs were tightly bonded together with graphite sheet (width ca. 1600 μ m, thickness ca. 25 μ m) and copper foil tape welded with copper wire as an embedded interlayer. Then the junction of TECs and the graphite sheet was coated with epoxy resin. Prior to experiment, MBG-AHCEs were polished, then rinsed with double-distilled water and sonicated before used.

2.3. Experimental equipment

An electrochemical cell with a traditional three-electrode configuration was used. A platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The cell was kept in ice water bath, maintaining the temperature of the bulk solution.

2.4. Temperature characterization

The temperature of electrode surface was measured by electrochemistry method: the temperature-dependent open circuit potential of a reversible redox couple has been applied to test the model developed for thermal perturbations [23]. Temperature characterization of the electrode was similar to the previous literature [2], by using the temperature shift of equilibrium electrode potential of a standard redox couple equimolar in 5 mM ferricyanide and ferrocyanide with 4 M sodium perchlorate as supporting electrolyte. 4 M sodium perchlorate was used as supporting electrolyte in temperature characterization because it will not freeze at $-18\text{ }^{\circ}\text{C}$. The temperature-potential coefficient of this redox couple is 1.46 mV K^{-1} [16]. Using the temperature coefficient, open circle potential can be converted directly into temperature changes of the electrode/electrolyte interface.

3. Results and discussion

3.1. Performance of MBG-AHCEs

The MBG-AHCE was fabricated as shown in Fig. 1A. As can be seen from Fig. 1B, the temperature of MBG-AHCEs can be adjusted from ca. $-10\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$ and the equation of the fitting curve is $T = 35.5I^2 + 39.5I + 1.4$ ($R^2 = 0.9989$), where T is the surface temperature of electrode, I is the current. The performance of them was shown in Fig. 1C. The temperature of MBG-AHCEs can be heated up or cooled down easily. And the thermal stability was tested by using different currents applied to TECs. At same current, good stability and reproducibility can be obtained. When alternating the current, electrodes can achieve a new temperature platform in a relatively short period of time (20s ~ 30s).

3.2. A model for understanding the temperature change of MBG-AHCEs

MGB-AHCEs were constructed based on TECs. The cooling/heating power of a TEC can be expressed as below [26]:

$$Q_c = Q_P - Q_J - Q_K = N(\alpha_p - \alpha_n)I(\Delta T_c + T_s) - UI/2 + K\Delta T_c \quad (1)$$

$$Q_h = Q_P + Q_J - Q_K = N(\alpha_p - \alpha_n)I(\Delta T_h + T_s) + UI/2 - K\Delta T_h \quad (2)$$

wherein Q_P is the thermol power of Peltier Effect, Q_J is the joule thermol power, Q_K is the thermol power of thermal conductance. N is the number of p-n couples, and its value is 7 in our experiment. α_p ($230\mu\text{V/K}$) and α_n ($-220\mu\text{V/K}$) [27] are the Seebeck coefficient of p-type and n-type semiconductor. ΔT_c and ΔT_h is the temperature difference for cooling and heating process, respectively. And they are defined as $\Delta T_c = T_c - T_s = T_c - T_h$ and $\Delta T_h = T_h - T_s = T_h - T_c$. As shown in Fig. 2A, T_s ($1\text{ }^{\circ}\text{C}$) is the temperature of the ice-water bath solution. For cooling/heating process, T_s is approximately equal to T_h or T_c , respectively. U and I is the electrical voltage and current, respectively. K is the total thermal conductance and its value can be calculated from the following equation[26]:

$$K = kA/L \quad (3)$$

where k ($2.0\text{ W K}^{-1}\text{m}^{-1}$) [28] is the coefficient of thermal conductivity, A (24 mm^2) is the cross-section area of the TEC, L (2.3 mm) is the length of the thermoelectric

element. So K is 20.9 mW K^{-1} in our experiment.

A linear approximation for the heat transfer was assumed to predict the temperature change of the electrode:

$$Q_c = \gamma_c \Delta T_c \quad (4)$$

$$Q_h = \gamma_h \Delta T_h \quad (5)$$

where γ_c and γ_h is the linear coefficient for equation (4) and (5), respectively. As shown in Fig. 2B, according to the experimental data, the value of γ_c is -0.0023 ($R^2 = 0.9717$,) and γ_h is 0.0045 ($R^2 = 0.9724$).

Combining equation (1) with (4) and equation (2) with (5), respectively, the model temperature difference ΔT_{mod} can be deduced as below:

$$\Delta T_{mod-c} = \frac{N(\alpha_p - \alpha_n)IT_s - UI/2}{\gamma_c - N(\alpha_p - \alpha_n)I - K} \quad (6)$$

$$\Delta T_{mod-h} = \frac{N(\alpha_p - \alpha_n)IT_s + UI/2}{\gamma_h - N(\alpha_p - \alpha_n)I + K} \quad (7)$$

wherein ΔT_{mod-c} and ΔT_{mod-h} are the temperature difference for cooling/heating process, respectively. ΔT_{mod} was calculated as shown in Fig. 2C according to U , I and γ_c/γ_h . As can be seen from Fig. 2D, the linear slope k_c is 1.0487 ($R^2=0.9924$) and k_h is 0.9712 ($R^2=0.9988$) in the cooling/heating process, which shows excellent consistence between model and experiment on the error below 5%. Hence for a certain TEC, ΔT can be calculated from U , I and γ_c/γ_h according to equation (6) and (7). So the surface temperature of electrodes can be obtained from ΔT and T_s . Compared with the calibration curve as shown in Fig. 1B, the model gives a novel approach with theoretical explanations to obtain the surface temperature of electrodes.

3.3. Determination of diffusion activation parameters of ferricyanide

The electrochemical properties of ferricyanide ion were investigated by MBG-AHCEs with the surface temperature adjusted from -10°C to 40°C . Fig. 3A shows CVs obtained at MBG-AHCEs in the presence of $5 \text{ mM K}_3[\text{Fe}(\text{CN})_6] + 1.0 \text{ M KCl}$ solution at different temperatures. The CVs of ferricyanide exhibited S-shaped curve characteristic.

For micro-band electrode, current and time follow the below relationship at long time zone [29],

$$i = \frac{2\pi nFADC_o}{w \ln(64Dt/w^2)} \quad (8)$$

wherein, n is the number of electron transfer, A is the electrode area, D is the diffusion coefficient, C_o is the oxidation state of the species concentration, w is the width of the micro-band electrode and t is the time. According to the steady state current i , diffusion coefficient of ferricyanide can be obtained.

Stokes-Einstein relationship was proposed to give an approximate method to analyze the diffusion of spherical particle in dilute solution [30]:

$$D = \frac{kT}{6\pi r\mu} \quad (9)$$

where k is the Boltzmann constant, μ is the macroscopic dynamic viscosity of the solution, r defines the molecular ‘effective’ radius.

Viscosity data of water can be found from literatures [31–32]. $\text{Fe}(\text{CN})_6^{3-}$ can be seen as a positive octahedron structure whose radius r can be obtained from bond lengths of Fe-CN and C-N which are acquired from the literature [33]. As can be seen in Fig. 3C, D_{exp} and D_{S-E} was diffusion coefficient obtained by experiments and Stokes-Einstein equation, respectively. They are consistent with each other on the error below 7% (the slop of line $k = 0.9366$ in Fig. 3.C) and other groups (Table 1). And diffusion coefficient of ferricyanide ion is $0.22 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at supercooled temperature (-10°C). As shown in Fig. 3D, according to diffusion coefficient and temperature data, the relationships can be described as follows: $\ln D_{exp} = -2.465 - 2788/T$ ($R^2 = 0.9986$) and $\ln D_{S-E} = -3.115 - 2588/T$ ($R^2 = 0.9960$).

It was assumed that diffusion coefficient of ferricyanide was temperature-dependent according to the Arrhenius equation [34–35]:

$$D = D_o \exp^{-E_a/RT} \quad (10)$$

where D_o is an empirical coefficient, E_a is the activation energy for diffusion, R is the universal gas constant and T is the absolute temperature. According to slopes of lines in Fig. 3D, $E_{a(exp)} = 23.2 \text{ kJ mol}^{-1}$ and $E_{a(S-E)} = 21.5 \text{ kJ mol}^{-1}$ can be achieved, which are in agreement with each other. Where $E_{a(exp)}$ and $E_{a(S-E)}$ was obtained by experiments and

Stokes-Einstein equation, respectively. Our activation energies for diffusion and the data of literature [19] are higher than most values reported by other groups (Table 1) indicating that temperature had a smaller effect on diffusion in our experiments according to equation (10). The higher values are because of MBG-AHCEs and thermostated electrodes in literature [19] working without relative motion between electrode surface and solution which increasing the difficulty of atomic transition.

Table 1

Summary of temperature dependence of diffusion activation parameters of the ferricyanide ion from this and other representative work.

Temperature modulated mode ^a	Temperature range ^b (°C)	$D @ 25\text{ °C}$ (cm ² s ⁻¹)	E_a (kJ mol ⁻¹)
A(this work)	-10 ~ 40	0.74×10 ⁻⁵ , 0.22×10 ⁻⁵ (-10 °C)	23.2
B[19]	25 ~ 90	0.85×10 ⁻⁵	32.1
C[21]	30 ~ 90	0.65×10 ⁻⁵ (30 °C)	15.1
C[24]	10 ~ 30	0.72×10 ⁻⁵	13.1
C[25]	23 ~ 43	0.67×10 ⁻⁵	17.0
(Not described)[20]	24 ~ 50	0.67 ~ 0.74×10 ⁻⁵	17.1 ~ 19.6

^a Method of temperature control: A—TECs to heating or cooling the electrode surface; B—resistive heating of electrode surface; C—thermostated electrolyte (either by thermostated water jacket, immersion resistive heater, or convective “heat gun”);

^b Temperature range for the determination of diffusion activation parameters of ferricyanide ion.

4. Conclusions

In summary, a model is established for understanding the temperature change of MBG-AHCEs. MBG-AHCEs with thermal stability were successfully fabricated. The electrode temperature can be regulated from ca. 40 °C to −10 °C in aqueous solution. Compared with the calibration method, the model gives a novel approach with theoretical explanations to obtain the surface temperature of electrodes. The activation energy and diffusion coefficient of ferricyanide ion are achieved by extending the temperature range from above zero degree down to the supercooled temperature (−10 °C) with this specially designed electrode. The experimental data are consistent with data obtained by Stokes-Einstein equation for the determination of diffusion coefficient and activation energy.

Conflict of interest

There is no conflict of interest.

Acknowledgments

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Captions

Fig. 1. (A) Fabrication process of MBG-AHCEs. SC represents semiconductor. Inset: the MBGE surface photograph. (B) Relationships between temperature and current. (C) Relationships between Temperature and time for MBG-AHCEs, $-0.4\text{A} \sim 0.6\text{A}$ represent different currents applied to TECs.

Fig. 2. (A) The scheme of cooling/heating process. (B) Dependence of ΔT_{exp} at MBG-AHCEs on the cooling/heating power Q . (C) Dependence of ΔT_{mod} at MBG-AHCEs on U and I . (D) Correlation between ΔT_{exp} and ΔT_{mod} .

Fig. 3. (A) CVs at MBG-AHCEs in 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 1.0 M KCl aqueous solution. Scan rate: 5 mV/s. (B) Chronoamperometry at MBGE in 5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ + 1.0 M KCl aqueous solution. (C) Correlation between D_{exp} and D_{S-E} . (D) Relationship between $\ln D$ and T^{-1} . From a to h, it represents electrode temperature $-10\text{ }^\circ\text{C}$, $-5\text{ }^\circ\text{C}$, $1\text{ }^\circ\text{C}$, $10\text{ }^\circ\text{C}$, $20\text{ }^\circ\text{C}$, $25\text{ }^\circ\text{C}$, $30\text{ }^\circ\text{C}$, $40\text{ }^\circ\text{C}$, respectively.