



Short communication

## Supercooled electrodes



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### ABSTRACT

A supercooled disk electrode is fabricated, around which the temperature of aqueous solution is below its normal freezing point. The supercooled electrode demonstrates thermal stability and its surface temperature can be adjusted by changing an additional heating current. Theoretical simulation shows that the supercooled region is restricted within a small volume around the disk electrode. The electrochemical behavior of cytochrome c was investigated at supercooled electrode for the first time.

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## 1. Introduction

Since their development by Gründler in 1993 [1,2], heated electrodes have attracted great interests. The quickly elevated electrode temperature can affect thermodynamic and kinetic parameters of the electrode reaction, especially through thermal induction of a stirring effect, accelerating the redox reaction rates [3–6]. A summary of principles and analytical applications of heated electrodes can be found in reviews [7–11]. In recent years, the cavitation phenomena at heated micrometer-sized electrodes have been found and dielectrophoretic and electrothermal effects can be generated on heated disk microelectrodes [12–14].

Many articles about temperature modulation electrodes can be found, however, the research of cooled electrodes had been a blank. As early as 1964, Conway et al. studied the hydrogen evolution reaction and isotope effects in methanol solution at  $-150\text{ }^{\circ}\text{C}$  [15]. A more systematic study of the low temperature electrochemical experiments had been published by Van Duyne and Reilley in 1972 [16–18]. In low temperature electrochemical studies, two ways were taken in order to maintain the electrolyte solution state. One is using the organic solvents whose freezing point are low enough, and the other one is using high concentrations of salts or acid solution to lower the eutectic point of the mixed solution. Stimming et al. adopted  $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$  as the electrolyte to study the hydrogen evolution reaction and the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  reaction at low temperature [19,20]. Low temperature electrochemistry in non-aqueous solvent is important since selectivity over reaction products, mechanistic

pathways and kinetics may be affected significantly [21–23]. It was shown that working at low temperatures further increases the large potential window of the electrolytic solution [24,25].

It still remains a mystery that some organism can still be alive under extreme condition. For example, many species of polar fishes live in the environment of  $-1.9\text{ }^{\circ}\text{C}$  [26] and excised peripheral nerves from several species of mammals continue to operate when supercooled to as low as  $-6\text{ }^{\circ}\text{C}$  [27]. Hence, studying the activity of biological macromolecules at supercooled electrode is interesting. However, very limited lifetime for its intrinsic metastability makes supercooled water difficult for scientific studies [28–30]. Using the heated electrode technology, superheated water with temperature above the boiling point can be obtained [31–33]. Inspired by the superheated water, in this work, a novel device which can cool the aqueous solution around gold disk electrode (GDE) below its normal freezing point without using organic solvents or high concentrations of salts was created. Herein the electrode worked in the supercooled solution is called supercooled electrode. The supercooled electrode demonstrates thermal stability and the surface temperature at GDE can be adjusted by changing heating currents. The electrochemical behavior of cytochrome c is investigated in this extreme condition.

## 2. Materials and methods

### 2.1. Materials

Horse heart cytochrome c (type VI, molecular weight 12384) was purchased from Sigma. 4,4'-Bipyridyl was obtained from Aladdin Industrial Corporation. All the reagents were of analytical grade and received from Sinopharm Chemical Reagent Co. Ltd. Aqueous

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solutions were prepared with purified water from a Millipore Milli-Q system. The cyclic voltammetry measurements were performed with an electrochemical analyzer (CHI660d, Chenhua, China). Direct current power (ATTEN PPS3003S) was purchased from Shenzhen Atten Technology Co., Ltd.

## 2.2. Fabrication of the gold disk electrode

A gold wire (50  $\mu\text{m}$  radius) ca. 4 mm was connected with a copper wire (0.36 mm diameter) by silver conductive glue, and then coated with epoxy resin. After 24 h, the copper wire was wound by a thinner copper enameled wire (75  $\mu\text{m}$  radius) and the approach of heating coils has been used before [34,35]. Then the electrode was put into a PTFE pipe, and sealed with epoxy resin. The prepared electrode was fixed to plastic bottle (1 L volume) whose outer layer was covered with polyurethane foam.

## 2.3. Experimental setup

The electrochemistry cell was kept in circulating water in order to maintain the temperature of the bulk solution. This comes next to the method with a cryostat and heated Pt microwires proposed by Gründler [36]. A small beaker containing the same solution was connected to the cell through a salt bridge. The platinum foil and the saturated calomel electrode were used as the counter and the reference electrode, respectively. The temperature of the electrode surface was measured by following the temperature-dependent change of the open-circuit potential of a reversible redox couple [33] and the temperature-potential coefficient of this redox couple is  $1.56 \text{ mV K}^{-1}$  [2].

## 2.4. Theoretical simulation

Simulations of the temperature distribution of water around GDE surface were carried out using Fluent. The vertical cross-section with dimensions 3 cm (horizontal)  $\times$  3 cm (vertical) was simulated. The GDE (radius 50  $\mu\text{m}$ ) was placed in the middle of the water's top edge. The geometry and meshing were created by GAMBIT modeling and meshing program, using a graded mesh with a spacing of 1  $\mu\text{m}$  at the disk surface and expanding to 50  $\mu\text{m}$ . The temperature-dependent viscosity, density, specific heat, and thermal conductivity of water were input to Fluent as data tables using published values [37–40]. Because of the low temperature of the supercooled water, laminar flow was assumed as the viscous model. The temperature of GDE surface was  $-13 \text{ }^\circ\text{C}$  and boundary conditions (vertical and bottom edges) applied were  $25 \text{ }^\circ\text{C}$ . The value for the heat flux of the top edge is zero. Simulations using the successive substitution solver converged smoothly.

## 3. Results and discussion

### 3.1. Steady supercooled region around a gold disk electrode

The schematic diagram of the supercooled device is shown in Fig. 1. The cooling source is provided by liquid nitrogen trapped in a plastic bottle, which coated with polyurethane foam as thermal insulation. Within this thermal insulation layer, a narrow passage for heat transfer is bridged through a thin gold wire, with one end of disk into the aqueous solution and with another connected to a copper rod inserting in the liquid nitrogen. An enameled heating coil twining round the copper rod is used as a heater to adjust the temperature around GDE in the aqueous solution by changing the heating current.

The simulated temperature and velocity vector distribution around the interface of the GDE in the water at a vertical cross-section through the axis of the cylinder is shown in Fig. 2A. The color scale indicates temperature and shows that there is a supercooled region with temperature below  $-2 \text{ }^\circ\text{C}$  around GDE. The arrows represent velocity vector of the

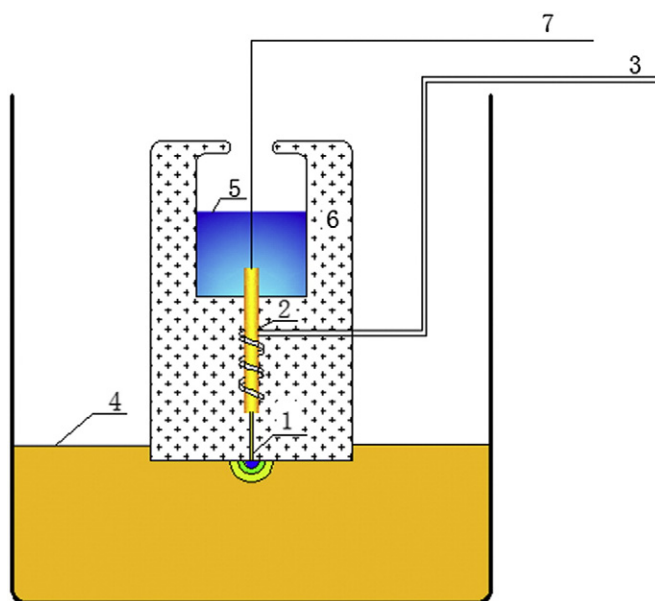


Fig. 1. Schematic diagram of the supercooled device: (1) gold wire; (2) enameled heating coil; (3) connecting to a direct current power; (4) aqueous solution in cell; (5) liquid nitrogen in the plastic bottle; (6) polyurethane foam; (7) connecting to a potentiostat.

fluid of the natural convection resulted from the temperature difference. The direction of the fluid is from top to bottom and from outer to inner, which is just the opposite of that for the heated electrode [41].

In Fig. 2B, the marked shadow representing the supercooled region is restricted within a radius of ca. 60  $\mu\text{m}$  around the GDE. The velocity distribution around the interface of GDE and water at a cut plane through the axis of GDE is shown in Fig. 2C. The fluid velocity is very much slower in the cold region near the surface of GDE than that in the hot region far from GDE.

For the heated disk electrode [31], it can maintain a high surface temperature (more than  $200 \text{ }^\circ\text{C}$ ) for a long time without boiling the aqueous solution. The reason of forming the superheated and supercooled water around disk electrodes is not clear at present. It might attribute to the exiting of temperature gradient and the mass transfer inside this small region.

The performance of this device producing supercooled region was shown in Fig. 3. When liquid nitrogen is poured in the thermal insulated plastic bottle, temperature at the GDE surface ( $T_{GDE}$ ) is rapidly decreased from the room temperature (point 'a') to a supercooled region. The detected lowest temperature of supercooled electrode is about  $-15 \text{ }^\circ\text{C}$ . It is not applicable when ice is formed on the GDE surface as  $T_{GDE} < -15 \text{ }^\circ\text{C}$  in this experiment. Switching on the heating current of the coil '3' (Fig. 1) leads to a temperature jump at point 'b'.  $T_{GDE}$  can be adjusted with heating currents from room temperature to the supercooled region, and changed approximately linearly with the heating power (inset in Fig. 3A).

The thermal stability was tested at different temperatures adjusted by heating currents. A steady-state of supercooled water around the GDE can be achieved for more than 2 h until the liquid nitrogen is evaporated up (Fig. 3B). In the steady stage of the heating, the temperature fluctuation was ca.  $2 \text{ }^\circ\text{C}$ .

### 3.2. The electrochemical behavior of cytochrome c at supercooled electrode

We choose the cytochrome c, a relatively abundant electron-transferring protein in all animals, plants and aerobic microorganisms, as an example to study its electron transfer at supercooled electrode. Cyclic voltammograms of cytochrome c at the GDE as  $T_{GDE}$  are changed

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