



A Sensitive Dissolved Oxygen Sensor Based on a Charge-Transfer Complex Modified Electrode

TU Yifeng

Institute of Analytical Chemistry, College of Chemistry and Chemical Engineering,
Dushu Lake Campus, Suzhou University, Suzhou Industrial Park, Suzhou, 215006, P.R.China
Tel: 86-512-65880356; Fax: 86-512-65101162; Email: tuyf@suda.edu.cn

Received: 28 January 2006 /Accepted: 24 February 2006 /Published: 27 February 2006

Abstract: A charge-transfer complex was modified on the graphite paste electrode for making a sensitive dissolved oxygen sensor. It was composed of copper with two ligands of phenanthroline and 1,2-dicyano-1,2-dithiol- ethane. Because of the low redox potential of the core ion and the pull and repulsive effect from the ligands, the redox of modified complex took place under lower potential and it could selectively catalyze the reduction of dissolved oxygen. The slope of the chronocoulometric curve of the sensor proportionally responded on the content of dissolved oxygen from 0 to 16 mg/L within 1–2 seconds. It was applied to detect the dissolved oxygen in tap water and the campus river for 3.0mg/L and 5.1mg/L. This sensor responded the dissolved oxygen with high selectivity, wide linear range, high accuracy, excellent stability and fast speed. It's very possible to act as a practical sensor for the detection of dissolved oxygen in field.

Keywords: Dissolved oxygen, Sensor, Charge-transfer complex, Chemical modification

1. Introduction

The dissolved oxygen (DO) is a comprehensive quality index of environmental water. Its level and the variation can reflect the content of oxygen consuming pollutants and the self-depurating ability of the surface water [1]. The Winkler titration [2] and the Clark oxygen electrode [3] are the typical methods for determining the DO. The studies to develop the more sensitive, precise and rapid responding DO sensors are meaningful for applying on-line or in field. The chemical modification [4] is an effective approach to improve the characters of electrode mainly to enhance the sensitivity and selectivity. This paper will report a copper complex modified electrode that sensitively catalyzed the redox of DO. The complex composed of three components with copper as the core element and two ligands of phenanthroline and 1,2-dicyano-1,2-dithiol-ethane. Due to the pull and repulsive effect for electrons from the ligands, the complex have the property of charge transfer [5, 6]. Its reversible redox reaction carried out under lower potential and there would be a parallel catalyzing from dissolved oxygen. This modified electrode could be applied as a DO sensor because of its rapid response of slope of chronocoulometry in linear range of dissolved oxygen from 0 to 16 mg/L.

2. Experimental

2.1 Instruments and Chemicals

A BAS-100A Electrochemical Analyzer (Bioanalytical System Inc., USA) was applied to control the three-electrode cell with a Ag/AgCl reference electrode and a Pt wire auxiliary electrode in all of electrochemical studies.

The complex of copper-phenanthroline-1,2-dicyano-1,2-dithiol-ethane was synthesized in lab. The spectral pure graphite powder of 70 μ m of diameter was used to construct the carbon paste electrode for applying as the base electrode of the sensor.

Other chemicals included epoxy resin, relevant solidifier and DMF were used.

2.2 The fabrication of the sensor

The DMF solution of complex was blended into the graphite powder. When the solvent was volatilized, churned up them with the epoxy resin and solidifier. Then filled the paste into a glass tube with a copper conducting wire. Polished and cleaned the surface thoroughly when the paste was dried absolutely.

2.3 Characterizing properties of the sensor

The cyclic voltammetry, bulk electrolysis and chronocoulometry were applied to study the electrochemical properties, the electrochemical reaction mechanism and the analytical merits of the sensor.

3. Results and Discussion

3.1 The electrochemical properties of the sensor

On the cyclic voltammetric curve of the sensor, there is a couple of redox peak around the potential of 0V. Under the slow scan rate of 2mV/s, the reduction peak obviously exhibited double steps of mono-electron reduction (Fig. 1) that were measured by semi-logarithm analysis and coulometric electrolysis. By the results of that the peak currents were proportional to the scan rate and the *i*-*t* curve didn't obey the Cottrell equation, the peak potentials were proportional to the natural logarithm of the scan rate, it was proved that the electrochemical reaction of the sensor was typically an adsorbing controlled process [7]. The electrochemical reaction could be expressed as follow equations:

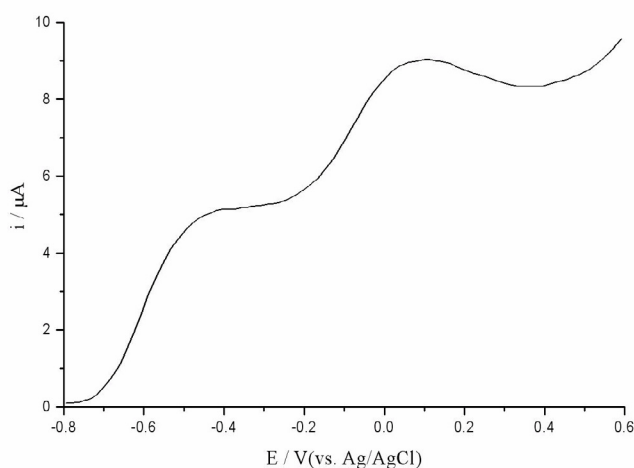
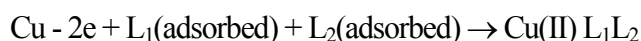
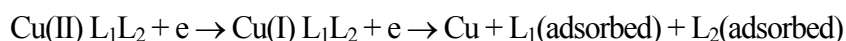
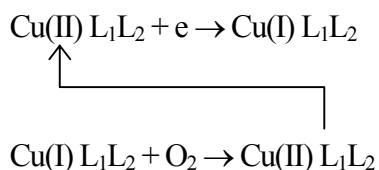


Fig. 1. The linear scanning voltammogram under low scan rate of 2mV/s.

3.2 The catalytic effect from the DO

If there were oxygen molecules in the solution, the reduction current of first step remarkably increased meanwhile there couldn't observe the second step reduction peak and the oxidation peak anymore. It revealed that there must

be a parallel catalytic reaction [8, 9] occurred to catalyze the first step of the reduction of the complex:



The table 1 showed the difference of the response upon the DO between the sensor and the bare graphite paste electrode.

Table1: *The difference of the response of DO sensor and bare electrode*

| Electrode | DO sensor | Graphite paste electrode |
|-------------------------------|---------------|--------------------------|
| Deoxygenated | 0.015 μ A | 0.21 μ A |
| Saturated with O ₂ | 1.50 μ A | 0.57 μ A |
| Multiples of current | 100 | 2.7 |

3.3 The analytical characteristics of the sensor

The sensor could be applied to detect the DO with the method of chronocoulometry [10] at the potential of -0.3V , the slope of the i - Q curve was proportional to the content of DO:

$$\text{Slope} = 2nAF(D/t)^{1/2}C_{\text{DO}} = KC_{\text{DO}}$$

It is an excellent basis to build up the rapid response of the sensor in 1–2 seconds due to that the chronocoulometry is speedy. The slope was determined by the diffusion of oxygen and the detection was carried out in quiescent state. It happened in 1-2 seconds therefore didn't destroy the equilibrium of the oxygen. Within the range of the content of dissolved oxygen from 0 to 16 mg/L that was calibrated by titration, there was a regression equation of $S = -0.19 + 0.157\text{DO}$ with the regression coefficient of 0.998 (Fig. 2). The sensor has the excellent reproducibility of RSD of 1.8% ($n=20$) and the good stability due to that the complex was very difficult to dissolve into water. The cyclic voltammetric curve of the sensor after months use was absolutely same as its original curve. The measures of polish and wash could recover the properties of the sensor if it was polluted.

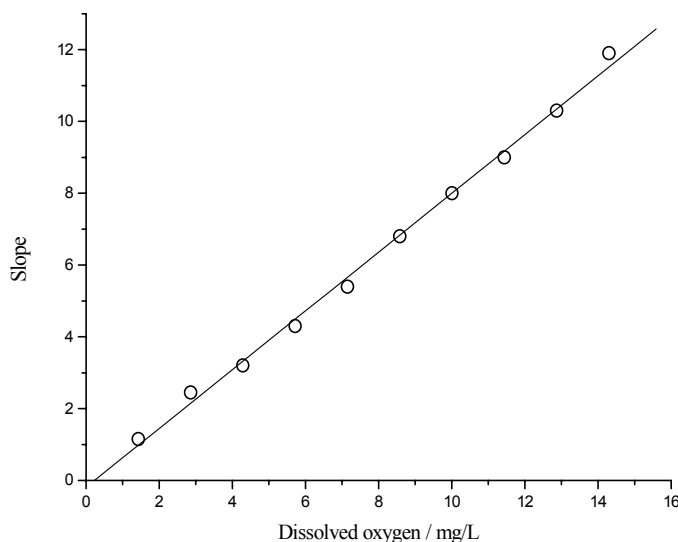


Fig. 2. The calibration curve of the dissolved oxygen sensor

3.4 The influence facts to the sensor

The acidity and the temperature of the solution influenced the response of sensor. The slope increased obviously due to the catalyzing in whole range of the pH especially in the range from 7.0 to 9.0, it could be see in Fig. 3. The influence from the temperature could be seen in Fig. 4.

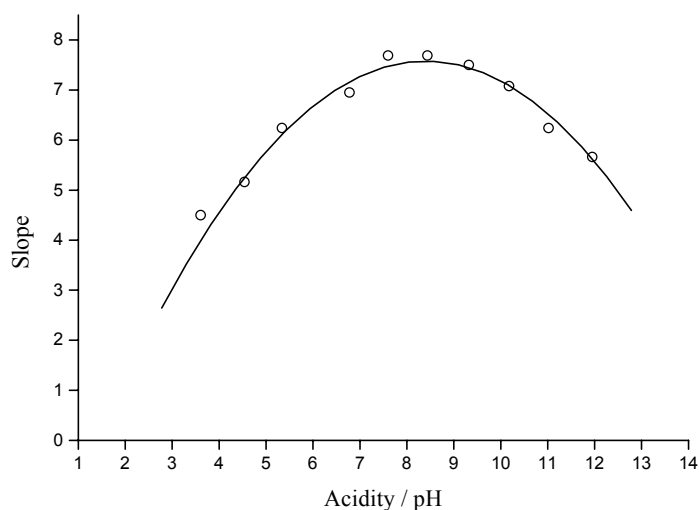


Fig. 3. The influence of the pH value to the response of DO sensor.

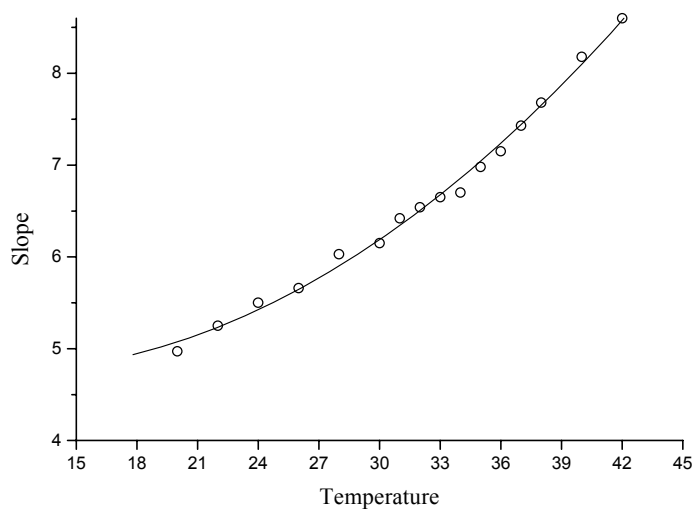


Fig. 4. The influence of the temperature to the response of DO sensor

3.5 The application of the sensor

The sensor was applied to detect the dissolved oxygen in tape water and our campus river for 3.0mg/L and 5.1mg/L.

4. Conclusion

This sensor responded the dissolved oxygen with high selectivity, wide linear range, high accuracy, good stability and fast speed. Due to it was structured upon the charge transfer complex of copper, it could work at potential of -0.3V that was lower than Clark oxygen electrode for 0.5V . It had provided an extra advantage for improving the selectivity side by side with the intrinsic selectivity of complex. So the sensor has better anti-jamming ability than Clark oxygen electrode. The rapid period of chronocoulometric detection in 1-2 seconds that didn't destroy the equilibrium of the oxygen and the higher analytical merit of sensor resulted in the high sensitivity and accuracy of determination. Furthermore, the determination could be carried on in origin water samples needn't to add any reagent. It's very possible to develop a practical sensor for the detection of dissolved oxygen on-line or in field.

References

- [1]. Allaby M, *Dictionary of the Environment*, 2nd Ed., London: Macmillan Reference Books, 1983: p.161
 - [2]. Winkler L W, *Berlin. Deut. Chem. Ges.*, 1888, 21:2843
 - [3]. Carritt D E and Kanwisher J W, *Anal. Chem.*, 1959, 31:5
 - [4]. Murray R W, in Bard A J ed. *Electroanalytical Chemistry* v. 13, New York: Marcel Dekker Inc., 1966: p.191
 - [5]. Davison A, Edelstein N, Holm R H and Maki A H. *Inorganic Chemistry*, 1963, 2(6):1227
 - [6]. Gao Xiaoxia, *Introduction of Electroanalytical Chemistry*. Beijing: Science Press, 1986, p.342
 - [7]. Vogler A, Kunkely H, Hlavatsch J And Merz A. *Inorganic Chemistry*, 1984, 23(4): 506
 - [8]. Galus Z. *Fundamentals of Electrochemical Analysis*, New York: John Wiley and Sons Inc., 1976: p.311
 - [9]. Gao Xiaoxia, *Chemical Bulletin*, 1962, 1:18
 - [10]. Anson F C, *Anal. Chem.*, 1966, 38: 54
-