# Construction of Carbon Paste Coated Wire Ion-Selective Electrode for Chloride and Its Application to Environmental Water Analysis

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A carbon paste coated-wire ion-selective electrode for chloride (carbon chloride-CWE) was constructed using epoxy resin, ion-exchanger and carbon powder as a polymer membrane. Its utility, the composition of a polymer membrane, the response characteristics, and the selectivity were examined and applied to the environmental water analysis. The carbon chloride-CWE was prepared using a silver wire, which was covered with silver chloride and then coated with epoxy resin into which chloride ion-exchanger and carbon powder were previously incorporated in advance. The response of the carbon chloride-CWE was Nernstian for $1.0 \times 10^{-2}$–$2 \times 10^{-5}$M chloride and the useful pH range from $10^{-2}$M Cl⁻ to $10^{-4}$M Cl⁻ was 3.0-9.0. Furthermore, the selectivity of chloride over iodide, bromide, and cyanide was much improved compared with those for a solid state epoxy body chloride electrode and a liquid membrane chloride electrode. The carbon chloride-CWE was applied to determine Cl⁻ in tap and ground water. The obtained results were in good agreement with those by the established methods such as spectrophotometric or other chloride-selective electrode methods.

## Introduction

The interest in ion-selective electrodes as an analytical method has dramatically increased over the last decade. The interest in ion-selective electrodes has led to the development of new sensor materials which show selectivity for a variety of anions, cations, and new methods for the construction of electrodes from these materials.

Coetzee and Freiser[1] have developed PVC-CWE (CWE, coated wire electrode) by mixing a liquid anion-selective ion-exchanger with PVC and applied to various anions. Suzuki *et al.*[2] have prepared epoxy-CWE to determine various anions using epoxy resin as a supporting material. Ishiwada *et al.*[3] constructed chloride-CWE by mixing a liquid ion-exchanger with epoxy resin in copper wire, which had been coated with silver paste following silver chloride. These CWEs have limited to relative reponse, characteristics, and selectivity. A calcium ion-selective electrode using a graphite rod with calcium exchanger in PVC have been reported by Ansaldi and Epstein[4]. Mesaric and Dahmen[5] constructed carbon paste electrode for halide and silver ion. Lee and his coworkers[6] constructed a carbon paste nitrate-CWE by coating a copper wire with ion-selective electroactive paste which was a mixture of graphite powder, epoxy resin, liquid ion-exchanger, and plasticizer.

This work reports the behavior of a carbon paste coated wire chloride ion-selective electrode (carbon chloride-CWE) which was prepared by coating cloride ion-selective electroactive paste on a silver chloride pretreated silver wire. The electroactive paste was made from epoxy resin, liquid anion-exchanger, and graphite powder. Among the advantages of this carbon chloride-CSE over commercial chloride electrodes are easy of construction, increased sturdiness, portability, and economy.

## Experimental

**Apparatus.** All electromotive force (EMFs) were measured with an Orion microprocessor ionalyzer (Model 901) using an Orion double junction electrode (Model 90-02) as

**Table 1.** Response Characteristics in the Carbon Paste Chloride-CWE

| Composition of membrane[a] (in ratio of A:B:C) A:B:C | Region of linear response | | | |
|---|---|---|---|---|
| | Slope[b] (mV/log C) | Low conc. limit (M) | Upper conc. limit (M) | Resistivity[c] ( cm) |
| 1:1:0 | $56.0 \pm 0.4$ | $5 \times 10^{-5}$ | $4 \times 10^{-2}$ | $1.2 \times 10^{8}$ |
| 1:2:0 | $43.1 \pm 0.6$ | $1 \times 10^{-4}$ | $4 \times 10^{-2}$ | $3.8 \times 10^{7}$ |
| 2:1:0 | $44.1 \pm 1.1$ | $1 \times 10^{-4}$ | $4 \times 10^{-2}$ | $1.7 \times 10^{8}$ |
| 1:1:0.1 | $56.4 \pm 0.5$ | $4 \times 10^{-5}$ | $4 \times 10^{-2}$ | $2.1 \times 10^{7}$ |
| 1:1:1 | $57.1 \pm 0.5$ | $3 \times 10^{-5}$ | $5 \times 10^{-2}$ | $6.7 \times 10^{6}$ |
| 1:1:2 | $58.3 \pm 0.6$ | $2 \times 10^{-5}$ | $7 \times 10^{-2}$ | $4.3 \times 10^{6}$ |
| 1:1:3 | $56.1 \pm 0.9$ | $4 \times 10^{-5}$ | $6 \times 10^{-2}$ | $3.4 \times 10^{6}$ |
| 1:1:4 | $54.9 \pm 0.5$ | $5 \times 10^{-5}$ | $5 \times 10^{-2}$ | $2.4 \times 10^{6}$ |

[a]A: Epoxy resin; B: Ion-exchanger; C: Carbon powder. [b]The ± means standard deviation in slopes obtained for more than 10 electrodes. The resistivities of the polymer membrane without ion-exchanger and carbon powder was $3.2 \times 10^{-14}$ $\Omega$cm. Those of the polymer membrane in which epoxy resin and ion-exchanger were incorporated in the ratio of 5:1 and 10:1 were $6.2 \times 10^{9}$ and $1.3 \times 10^{11}$ $\Omega$cm, respectively. [c]The resistivities were measured at 18 °C and 55% relative huminity.

the reference electrode. Resistance of polymer membrane were measured with a Keithley solid state electrometer Model 610 C). The glass cell thermostat was maintained at 25 ± 0.5 °C using a Haake constant temperature circulator (Model T31).

**Materials and Reagents.** Aliquat 336s (trioctylmethyl-ammonium chloride), n-decanol, triethylenetetramine (TETA), and tetrahydrofuran (THF) were obtained from Tokyo Kasei Co., Ltd. Epoxy resin, bisphenol A, and amorphous graphite powder (200 mesh) were purchased from Shell and Pyungtaick Mining Co., respectively. Unless otherwise noted, all reagents used in this study were of reagent grade.

To prepare 0.1M chloride standard solution, 0.7462g of potassium chloride (Junsei Chemicals) was dissolved in deionized water. All working chloride solution were prepared by successive dilution of 0.1M chloride standard solution. Ion-exchanger was prepared by dissolving 0.004g Aliquat 336s in 9.96g of n-decanol.

**Construction of Carbon Chloride-CWE.** The epoxy resin was incorporated with liquid ion-exchanger, graphite powder, and TETA as hardner disolved in THF solvent. After thorough mixing, the solution was allowed to stand for 2-3 hr in air. When an appropriate viscosity was attained, a silver wire (0.5 mm in diameter) which had been pretreated with AgCl by dipping 2-3 times in 0.5 M KCl and 0.5 M. AgNO$_3$ solutions, respectively , was dipped 10 mm in length in the solution for uniform coating, and then allowed to stand overnight in air. Performance characteristics of the prepared electrodes were subsequently investigated.

Prior to each EMF measurement, newly prepared electrode should be preconditioned by soaking it in deionized water for about 30 minutes. The electrode may be stored at dry state for a long period while not in use, but it should be reconditioned prior to re-use. All EMF were measured under strictly controlled conditions by immersing the electrode to a constant depth into an exact solution volume, 20 ml. During EMF measurement, the solution was stirred at a
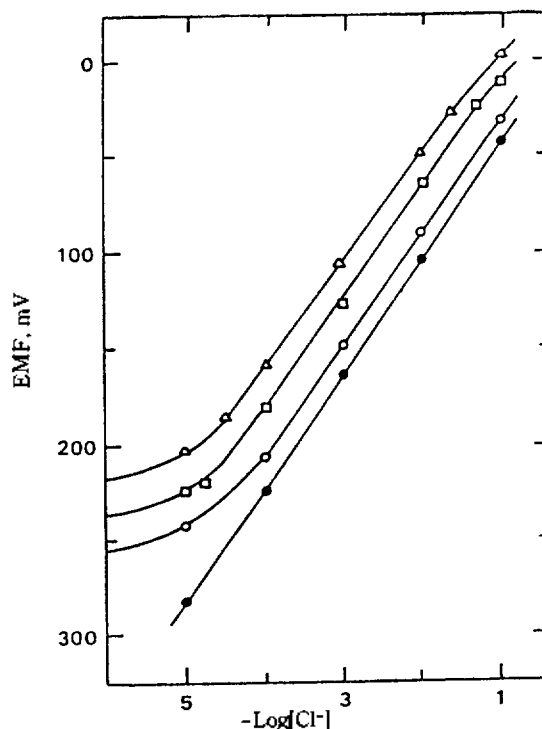


**Figure 1.** EMF-logarithmic concentration curves of chloride ion-selective electrodes. $\triangle$: chloride-CWE, $\square$: carbon paste chloride-CWE, $\bigcirc$: Orion-ISE, $\bullet$: theoretical nernstian slope (59.2 mV/ log [Cl$^-$]).

constant rate. The cell temperature was controlled at 25 ± 0.5 °C by keeping the cell in a thermostat.

## Results and Discussion

**Response Characteristics.** The polymer membrane of the chloride-CWE was made of epoxy resin and a liquid ion-exchanger. The best performance was obtained when one part of epoxy resin was mixed with one part of liquid ion-exchanger.

In most case of the chloride-CWE, there was 56 mV change for every decade change in activity. Graphite powder was added into the membrane of the best composition to increase the conductivity of of membrane. The resultant ratio of the best composition was 1:1:2 (epoxy resin: ion-exchanger: graphite powder). And the best electrode response was a 58.3 mV for every decade change in activity, which is pretty close to the 59.2 mV change expected for the ideal behavior. These are listed in Table 1. With the best composition, the linear response range was more extensive than any other conditions. The addition of graphite powder seems to increase a conductivity of the polymer membrane. In Figure 1 the calibration curve of the carbon chloride-CWE is compared with those of others including an orion chloride ion-selective electrode (Model 94-17B).

The effect of the polymer membrane thickness (0.1-1.0 mm) on the electrode responses was investigated by varying membrane thickness and the results were shown in Figure 2. 0.20-0.30 mm appeared to be of optimal thickness in terms of physical strength and response characteristics. When the membrane was thicker than 0.30 mm, the response is decreased rapidly and when thinner than 0.15 mm, the resistivity

*Carbon Paste Coated Wire Cl⁻ Electrode*

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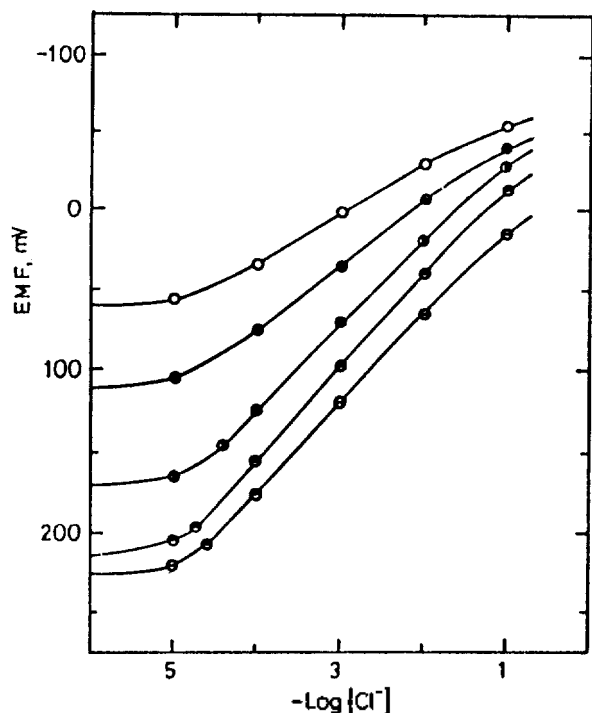


**Figure 2.** Effect of thickness of polymer membrane on carbon paste chloride-CWE. ○: 0.1 mm, ●: 0.25 mm, ◐: 0.4 mm, ◉: 0.6 mm, ⊖: 1.0 mm.

**Table 3.** Comparison of Analytical Results on Ground Water[a]

| Running No. | Concentration of Cl⁻ (ppm) | | |
|---|---|---|---|
| | Orion-ISE method | Spectrophotometric method[b] | Present work |
| 1 | 31.8 | 30.8 | 32.1 |
| 2 | 31.5 | 31.2 | 31.7 |
| 3 | 31.7 | 31.1 | 31.9 |
| 4 | 31.7 | 31.0 | 31.6 |
| 5 | 32.0 | 31.4 | 31.8 |
| Mean | 31.74(a) | 31.10(b) | 31.82(c) |
| S.D. | ±0.17 | ±0.22 | ±0.20 |
| C.V.(%) | 0.54 | 0.71 | 0.63 |
| Relative error(%) | 0.25 (c−a)/a × 100 | 2.32 (c−b)/b × 100 | 0.63 |

[a]Ground water sample were taken from Yonsei Univ. in 9th Feb., 1988. [b]Mercuric thiocyanate method.

became poor because of the impairment of the membrane. Typical electrode response time at each concentration level from $10^{-1}$ to $10^{-5}$M KCl ranged from 30 to 70 sec. The potential variation of the carbon chloride-CWE was within ± 0.2 mV. It is necessary to restandardize for each test to get the reliable results using these electrodes. When the EMF was measured with several identical electrodes the same response was obtained for up to 6 weeks.

**Resistivity of Polymer Membrane.** Table 1 shows the resistivity variation as a function of the polymer membrane composition of the carbon chloride-CWE. As the amount of epoxy resin was increased, the resistivity of the membrane also increased. When epoxy resin was mixed with graphite

powder at the ratio of 1:0.1 − 2, more graphite powder caused less resistivity. However, when the ratio of graphite powder to epoxy resin was over 2, both the resistivity and the response slope of the electrode were reduced because the surface of the polymer membrane was not uniform. As the result, the response of the carbon chloride-CWE was considerably improved compared to the epoxy chloride-CWE in which graphite powder was not incorporated.

**Effect of Interfering Anion.** The effect of foreign ions on the response of the electrodes was investigated by potentiometric measurements of the solution of $10^{-3}$ M KCl containing 0.09 M interfering anion of interest. Selectivity coefficients were calculated from the following Eisenman equation[7]:

$$\Delta E = (\text{slope}) \log [1 + K_i \frac{a_i^{1/z}}{a_{ci}}]$$

where $a$ and $Z$ are the activity and the charge of the interfering anion, respectively. The calculated selectivity coefficients are summarized in Table 2. The selectivity of chloride over iodide, bromide, and cyanide for the carbon

**Table 2.** Selectivity Coefficients $K_j$, for the Carbon Paste Chloride-CWE

| Interferants | CWE | | | | Orion-ISE[e] | Liquid membrane[b] | Liquid membrane[d] |
|---|---|---|---|---|---|---|---|
| | Carbon paste[a] | Epoxy[b] | Epoxy[c] | PVC[d] | | | |
| I⁻ | 0.80 | 3.7 | 1.1 | — | 2.53 | 2.3 | — |
| ClO₄⁻ | 1.01 | 3.4 | 1.3 | — | 0.043 | 1.1 | — |
| ClO₃⁻ | 0.28 | — | — | — | 0.044 | — | — |
| NO₃⁻ | 0.96 | 3.3 | 1.7 | 2.0 | 0.043 | 2.0 | 3.0 |
| NO₂⁻ | 0.99 | 1.2 | 1.1 | — | 0.036 | 0.49 | — |
| SO₄²⁻ | 0.0071 | 0.010 | 0.016 | 0.12 | 0.0053 | 0.0059 | 0.061 |
| Br⁻ | 0.44 | — | — | 1.2 | 2.15 | — | 2.7 |
| CN⁻ | 0.78 | — | — | — | 2.40 | — | — |
| F⁻ | 0.59 | — | — | — | 0.036 | — | — |
| H₂PO₄⁻ | 0.43 | — | — | — | 0.061 | — | — |
| HCO₃⁻ | 0.19 | — | — | — | 0.030 | — | — |
| CH₃COO⁻ | 0.11 | — | — | — | 0.034 | — | — |

[a]Present work. [b]Data from ref. 2. [c]Data from ref. 3. [d]Data from ref. 7. [e]Solid state electrode (experimental data in this research). Reference and Interfering solution, $10^{-3}$M KCl. Electrode response in series of pure test solution, -58.3 mV/10 fold in concentration.

**Table 4.** Comparison of Analytical Results on Tap Water[a]

| Running No. | Concentration of Cl⁻ (ppm) | | |
|---|---|---|---|
| | Orion-ISE method | Spectrophotometric method[b] | Present work |
| 1 | 13.0 | 12.7 | 13.2 |
| 2 | 13.3 | 13.1 | 13.4 |
| 3 | 13.1 | 13.0 | 13.1 |
| 4 | 13.2 | 13.0 | 13.0 |
| 5 | 13.0 | 12.9 | 13.1 |
| Mean | 13.12(a) | 12.94(b) | 13.16(c) |
| S.D. | ±0.13 | ±0.15 | ±0.13 |
| C.V.(%) | 0.99 | 1.17 | 0.98 |
| Relative error(%) | 0.30 (c-a)/a × 100 | 1.70 (c-b)/b × 100 | |

[a]Tap water sample were taken from Yonsei Univ. in 9th Feb., 1988.
[b]Mercuric thiocyanate method.

chloride-CWE was much greater than those for either solid state epoxy body chloride electrodes or liquid membrane chloride electrodes.

Analysis of water samples. Carbon chloride-CWE was ap-plied to the determination of chloride ion in tap and ground water. The analytical results are given in Table 3 and 4 along with those obtained by other methods. The results were in excellent agreement (RSD, 3.0%) with those by other es-tablished methods such as spectrophotometric or other chloride selective electrode method.

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# Theoretical Studies on the Potential Energy Profiles for Proton Transfer Reaction in Formamide Dimer

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Theoretical studies on the proton transfer reaction in a formamide dimer have been done by Ab initio SCF calculation. In this study, we have shown several effects on the potential energy profile of the proton transfer in a formamide dimer, such as the effect of a basis set, the effect of a geometry optimization, and the effect of a distance between proton-donor and proton-acceptor.

## Introduction

There are many studies on the hydrogen bonding[1-8]. Especially, proton transfer reactions in biomolecules are very important to understand many biological phenomena[9]. Precise potential energy profiles of proton transfer reactions may give many informations to deduce the possibility of the proton transfer. Therefore, in this study, we have chosen a formamide dimer as the model of an asymmetric double pro-ton transfer reaction and obtained potential energy profiles for the proton transfer reaction by ab initio SCF calculations. Several effects on the proton transfer reaction have been tested in order to know how the potential energy profiles have been changed according to the conditions. The effect of a basis set on the potential energy profile of the proton transfer reaction has been checked by varying the basis set, such as STO-3G, 3-21G, and 4-31G. The effect of a geomet-ry optimization and that of a distance between proton-donor and proton-acceptor have been also checked by adopting the geometry optimization or not and varying the distance be-tween proton-donor and proton-acceptor respectively.

## Method of Calculations

Ab initio SCF calculations have been performed to obtain the potential energy profiles for the proton transfer in a for-