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DETECTION OF CHLORIDE ION CONCENTRATION USING CHRONOPOTENTIOMETRY

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ABSTRACT

In this paper, a novel approach is reported for the electrochemical measurement of chloride ions using chronopotentiometry. A current pulse is applied at the Ag/AgCl working electrode and the potential change is measured with respect to another identical Ag/AgCl electrode in the bulk electrolyte. The potential difference, given by the Nernst equation, follows an inverse logarithmic trend versus the Cl^- ion concentrations. The sensitivity of the response is tuneable through the applied current pulse and the corresponding concentration window. The potential response is also influenced by the pH of the electrolyte, this effect is pronounced at low concentration of Cl^- ions (< 1 mM KCl) and high pH values (>12 pH). The advantage of this approach is that a bare Ag/AgCl electrode can be used as a pseudo-reference electrode. Additionally tuneable sensitivity is obtained and the dissolution of sparingly soluble AgCl membrane is counteracted. This system can be used for long term application like in-situ measurement of Cl^- ions in concrete.

KEYWORDS

Chronopotentiometry, stimulus/response, differential potential, Ag/AgCl pseudo-reference electrode.

INTRODUCTION

Presence of chloride ions in reinforcement concrete is the major cause of concrete deterioration [1]. The threshold amount of chloride ions in concrete initiates pitting corrosion of reinforcement steel and results in localized structural failure [1]. A real time service life model of concrete structure is inevitable to precisely predict the maintenance cycle of concrete structures. The knowledge of chloride ion concentration in concrete is an important input for such model.

For more than two decades electrochemical sensors have been designed for in-situ measurement in concrete. Most of the reported electrochemical sensors were based on the potentiometry [2] where the half-cell potential of a silver/silver chloride (Ag/AgCl) electrode was measured w.r.t a reference electrode at equilibrium [2]. The reference electrode needs to be embedded inside concrete near the working electrode to reduce errors due to diffusion potential [2]. The limiting factor of this approach is the long term stability of the reference electrode. Therefore for applications such as in-situ measurement in concrete, an electrochemical system is desired where a stable reference electrode is not required.

An alternative to this static approach (potentiometry) are dynamic measurements, i.e. detecting the response of a system in equilibrium to an applied stimulus [3]. The idea is to use a chemical stimulus technique where a controlled stimulus defines the condition at the working electrode depending on the concentration of the analyte (e.g. Cl^- ions). In such a system, the change in the measured response is independent of the reference system.

The aim of this work is to develop a Cl^- ion sensor based on a dynamic electrochemical measurement using chronopotentiometry. In such measurement, the stable reference electrode is no longer required, a bare Ag/AgCl electrode can be used as a pseudo-reference electrode. A current stimulus is applied at the Ag/AgCl working electrode and the corresponding potential difference is measured simultaneously.

THEORY

A Ag/AgCl electrode is a redox electrode of the second kind. When it is immersed in a solution containing Cl^- ions, equilibrium occurs between AgCl salt and Cl^- ions at the electrode surface, which gives rise to the half-cell potential. The concentration of Cl^- ions in the electrolyte determines the half-cell potential, given by the Nernst equation, eq.(1).

$$\mathrm{V_{Ag/AgCl}} = \mathrm{V^{o}_{Ag/AgCl}} - \frac{\mathrm{RT}}{\mathrm{F}}\ln\alpha_{\mathrm{Cl^-}} \tag{1}$$

$$\mathrm{Ag + Cl^- \rightarrow AgCl + e^-} \tag{2}$$

Here, $V^{o}_{Ag/AgCl}$, R, F, T and α_{Cl} are the standard potential of Ag/AgCl, gas constant, Faraday constant, absolute temperature and activity of the Cl^- ions, respectively. In chronopotentiometry, a constant current is applied at the working electrode (WE) and the potential change is measured with respect to a reference. In case of a Ag/AgCl WE, an anodic current pulse initiates the Faradaic reaction, given in eq.(2), at the surface of the WE. The Cl^- ions near the WE are consumed during this reaction, resulting in a local depletion of Cl^- ions near the electrode surface [4]. The expression for the concentration of Cl^- ions at the surface of Ag/AgCl WE (x = 0) is given in eq.(3) [3].

$$\mathrm{C(0,t)} = \mathrm{C^*}\left(1 - \frac{2\mathrm{j}(1-\mathrm{t^{e}_{Cl}})}{\mathrm{FC^*}}\sqrt{\frac{\mathrm{t}}{\mathrm{D\pi}}}\right) \tag{3}$$

Here, t^{e}_{Cl}, C^*, D are the transport number of Cl^- ion, bulk Cl^- ion concentration and diffusion coefficient, respectively. The time, during the applied current pulse, at which the Cl^- ion concentration near the WE surface reaches zero is called the transition time, τ. The applied current pulse and the corresponding concentration gradients give rise to a potential difference (ΔV) at the WE with respect to a reference electrode (RE). This potential difference is the sum of the ohmic drop due to impedance of electrolyte ($V_{\Omega,e}$), of the growing layer of

AgCl salt on the WE ($V_{\Omega,a}$) and the half-cell electrode potential ($V_{Ag/AgCl}$) due to the change in Cl^- ion concentration. Therefore:

$$\Delta V = V_{\Omega,e} + V_{Ag/AgCl} + V_{\Omega,a} \tag{4}$$

For high background-electrolyte concentration (0.5 M KNO_3) the ohmic drop, $V_{\Omega,e}$, can be neglected. The ohmic drop due to the AgCl deposition, $V_{\Omega,a}$, depends on the initial thickness of the AgCl layer. The further rise in this potential during the current actuation is very small, ca. 1 $mV{\cdot}s^{-1}$, estimated at the current density of 25 $A{\cdot}m^{-2}$ [3], therefore this potential change can also be neglected. The ΔV is calculated from the Nernst equation, see eq.(5), where the Cl^- ion concentration is evaluated from eq.(3).

$$\Delta V = -\frac{RT}{F}\ln\left(1 - \frac{2j}{FC^*}\sqrt{\frac{t}{D\pi}}\right) \tag{5}$$

The potential difference, ΔV, in eq.(5) does not depend on the reference potential, therefore a bare Ag/AgCl electrode in the bulk electrolyte can serve as a pseudo-reference electrode. The schematic of this approach is shown in Figure 1. At zero current condition, the potential difference is ideally zero (same half-cell potential). During the current pulse, applied w.r.t. a counter electrode (CE), the potential at the WE changes, due to Cl^- ions depletion whereas the half-cell potential of the Ag/AgCl pseudo-reference electrode remains the same. This change in potential, ΔV, is a function of Cl^- ion concentration in the bulk electrolyte, as elaborated from eq.(5).

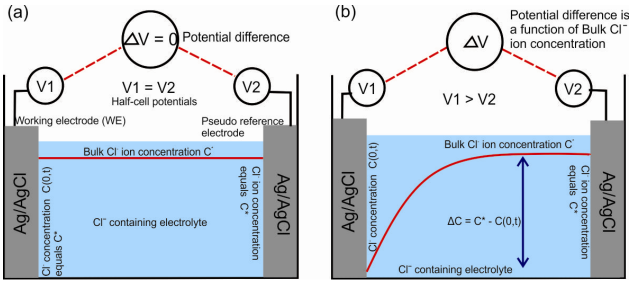

Figure 1: The schematic of the chronopotentiometric approach with Ag/AgCl as pseudo-reference electrode. (a) At zero current condition, the half-cell potential of the WE and pseudo-reference electrode is the same, therefore the potential difference, ΔV, is zero. (b) During the current pulse at the WE, applied w.r.t. to a counter electrode, not included in this figure, the Cl^- ions deplete near the WE surface, resulting in a concentration profile w.r.t the bulk electrolyte.

This approach is only valid if the potential difference, ΔV, is measured within the transition time, τ. Eq.(6) outlines the selection criteria for the current densities, j, and the actuation time, t, to ensure measurements within the transition time. The detection ranges of Cl^- ion concentrations and the corresponding current densities are given in Table 1.

$$j < 0.5\, FC^*\sqrt{\frac{D\pi}{t}} \tag{6}$$

Table 1: The selected current densities, j, for different Cl^- ion concentrations for the actuation time of $t = 5$ s, as elaborated from eq.(6).

No.	$[Cl^-]$ range (mM)	Current density, j ($A{\cdot}m^{-2}$)
1	0.1 to 1	0.15
2	1 to 10	1.5
3	10 to 100	15

The Ag/AgCl electrode is an ion selective electrode which shows higher selectivity to Cl^- ions than other interfering ions; for instant Br^-, I^-, OH^- ions [2]. The influence of interfering ions is quantified by the selectivity coefficient. For analytical applications the selectivity coefficient of interfering ions is preferably small (ideally zero), but in the presence of higher concentrations of the interfering ions as compared to primary ions, this effect become pronounced [2]. In concrete pore solution the most notable interfering ions are OH^- ions (pH of the electrolyte), which are hydration product from $Ca(OH)_2$, NaOH and KOH [2]. The effect of pH is trivial if the ratio of Cl^- to OH^- ions satisfies eq. (7). The selectivity coefficient of Ag/AgCl electrode for OH^- ions in aqueous solution, $k_{(Cl^-,\, OH^-)}$, is reported as $2.4{\cdot}10^{-2}$ [5].

$$\frac{[Cl^-]}{[OH^-]} \gg k_{Cl^-,OH^-} \tag{7}$$

EXPERIMENTAL

Ag/AgCl electrode fabrication

The Ag/AgCl electrode was fabricated by electro-deposition of silver chloride over a silver wire (0.5 mm dia.). The Ag wire (area ca. 19.5 mm^2) was chloridized in a 0.1 M HCl solution for 20 min at a current density of 13.3 $A{\cdot}m^{-2}$, and a compact layer of AgCl (thickness ca. 5 µm) was formed at the surface of the Ag wire. The non-anodized area of the electrode was protected through heat shrink tubing. The Ag/AgCl electrode was then stored in 1 M KCl solution.

Chemicals

The Ag wire ≥99.99% trace metals, the potassium chloride BioXtra, ≥99.0%, the potassium hydroxide 90% pure reagent grade and the potassium nitrate > 99% reagent grade were ordered from Sigma-Aldrich. The electrolyte solutions were prepared with KCl and KNO_3 in milli-Q water.

Measurement setup

The chronopotentiometric measurements were performed using a VSP potentiostat from Biologic Instruments. The WE terminal of the potentiostat was connected to the Ag/AgCl electrode (19.5 mm^2), the reference terminal was connected to another identical Ag/AgCl electrode (pseudo-reference electrode) and the CE terminal was connected to 60 mm^2 Pt counter electrode. The schematic of the setup is shown in Figure 2. The distance between the Ag/AgCl WE and the Pt CE is ca. 1 cm whereas the distance between the WE and the pseudo-reference electrode is ca. 2.5 cm in a glass beaker of 5 ml capacity.

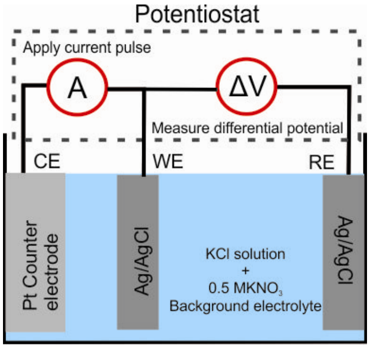

Figure 2: Schematic representation of the experimental setup for the chronopotentiometric measurements.

RESULT AND DISCUSSIONS

Chronopotentiogram of Ag/AgCl electrode

Figure 3 shows a typical chronopotentiogram of the Ag/AgCl WE electrode w.r.t to another Ag/AgCl electrode in a 10 mM KCl solution at a current density of 35 A·m^{-2}. Initially, before the current is applied, the electrode potential of the Ag/AgCl electrode is ca. 5 mV (ideally zero) due to a nearly identical half-cell potential of the WE and the pseudo-reference electrode in the bulk electrolyte. A current pulse of 35 A·m^{-2} is applied at t = 0 s which results in a rapid ohmic rise of ca.100 mV. After the initial ohmic rise the potential, ΔV, increases at a relatively lower rate (first plateau) due to the Cl$^-$ ion depletion near the WE electrode surface, region A in Figure 3. As the Cl$^-$ ions deplete completely near the WE, the slope of ΔV reaches its maximum, region B in Figure 3, corresponding to the transition time. After this point a new plateau is reached (after 2.6 s), this plateau is attributed to the other faradaic reaction, i.e. the formation of silver oxide (Ag_2O). The theoretical curve, based on eq.(5), is also plotted in Figure 3 after the initial ohmic rise (100mV).

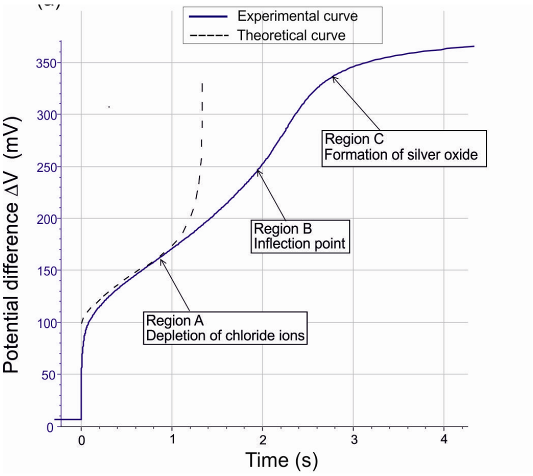

Figure 3: The experimental and theoretical chrono-potentiogram of the Ag/AgCl WE. A current pulse of 35 A·m^{-2} is applied between WE and CE in a 10 mM KCl and 0.5 M KNO_3 bulk electrolyte. The potential, ΔV, of Ag/AgCl WE is measured w.r.t another identical Ag/AgCl pseudo-reference electrode.

The transition time in this case is ca. 2.0 s, measured experimentally, whereas the theoretical value is 1.2 s. For the differential measurements, region A is of prime interest, as the potential change, in this region, is a function of Cl$^-$ ion concentration, eq.(5).

Figure 4 shows the potential response for different Cl$^-$ ion concentrations at a current density of 15 A·m^{-2} for 5 s. The ohmic drop at this current density is in the range of 30 to 40 mV. Before the applied current pulse, the potential difference, ΔV, for all the concentrations is nearly zero. At t > 0, the potential changes as a function of locally decreasing Cl$^-$ ion concentration. The potentials are measured at t = 5 s. For each Cl$^-$ ion concentration, the actuation time (t = 5 s) is within the corresponding transition time. The potential difference decreases with the increase in Cl$^-$ ion concentration, see Figure 4.

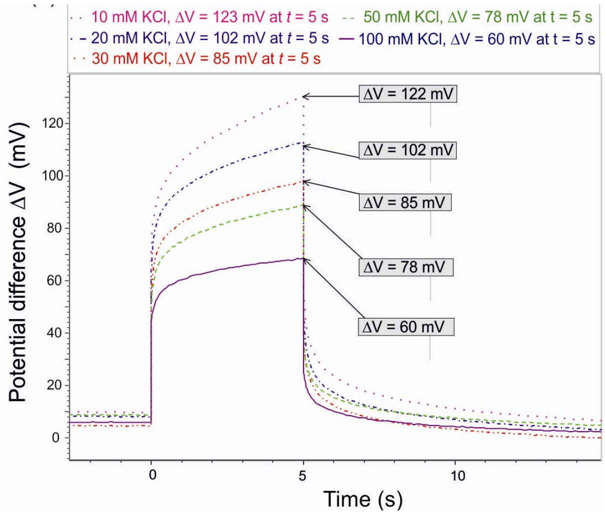

Figure 4: The potential difference, ΔV, for different concentrations of Cl$^-$ ions. A current pulse of 15 A·m^{-2} is applied between 0 to 5 s, not included in this figure, and the potential is measured w.r.t a Ag/AgCl pseudo-reference electrode. The potential ΔV decreases with the increase in Cl$^-$ ion concentration.

Calibration curve for chloride ions measurement

Figure 5 shows the calibration curves for different Cl$^-$ ion concentrations ranges at different applied current densities, given in Table 1. The theoretical curves from eq.(5) are also plotted with the respective experimental curves. At higher current densities, the operational range of this system shifts to higher concentration regions, in accordance with eq.(6) and Table1, see Figure 5. The detection range of the system is tuneable and is a function of the applied current pulse. The experimental curve follows the trend of the theoretical curve, the potential difference, ΔV, shows an inverse logarithmic response for different Cl$^-$ ion concentrations in the bulk electrolyte. The deviation from the theoretical curve is due to the ohmic drop at high current densities, e.g. in case of Figure 5b and Figure 5c the ohmic drop is ca. 30 mV and ca. 55 mV, respectively.

Effect of the pH

Figure 6 shows the effect of pH on the potential difference, *ΔV*, at different Cl^- ion concentrations. The applied current densities are selected according to the condition stated in eq. (6). The effect of pH is pronounced at low Cl^- ion concentrations (< 1mM) and at high pH (pH > 12), see Figure 6. This is due to the fact that the condition stated in eq.(7) no longer holds true, e.g. at 0.1mM $[Cl^-]$ and pH 12, $[Cl^-]/[OH^-] = 1\cdot10^{-4}/1\cdot10^{-2} = 1\cdot10^{-2}$, being smaller than $k_{(Cl^-,\ OH^-)}$ (ca.$2.4\cdot10^{-2}$, [5]). Therefore, for this setup, the lower detection limit for Cl^- ion concentrations in aqueous solution at pH > 12 is 1 mM. For in-situ measurement in concrete this lower detection limit moves to even lower value due to relatively smaller value of $k_{(Cl^-,OH^-)}$ inside concrete(ca. $4\cdot10^{-3}$, [2]). The change in potential at high pH, in the absence of Cl^- ions, is also attributed to the damage of the AgCl membrane by the formation of oxides [2].

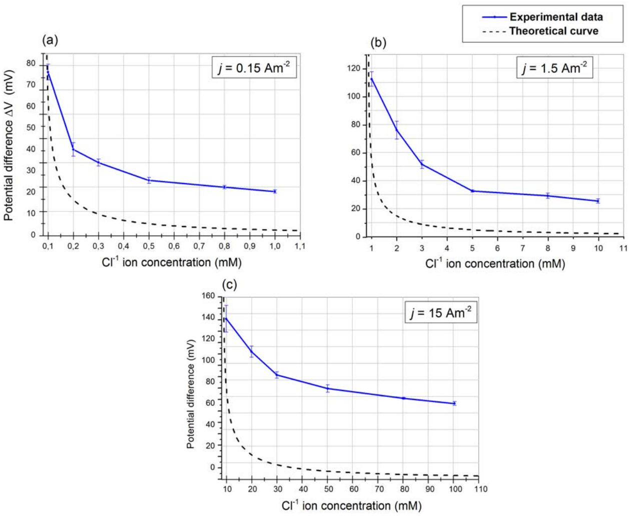

Figure 5: The calibration curve of the potential difference, ΔV, at different Cl^- ion concentration range. For each concentration range the corresponding current densities, for optimal sensitivity, were calculated from eq.(6).

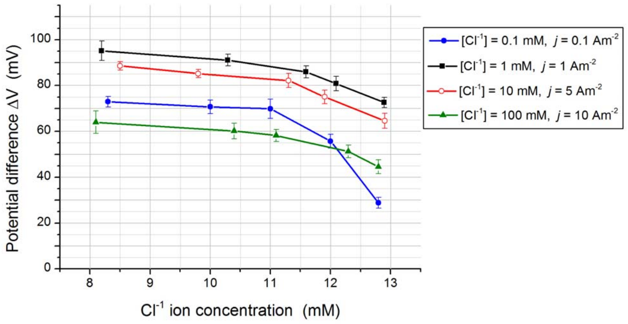

Figure 6: Effect of pH on the potential response of Ag/AgCl electrode. Different current densities were used for different Cl^- ion concentrations of electrolyte, to satisfy eq.(6).

CONCLUSION

The chronopotentiometric approach can be successfully used for the detection of Cl^- ions, in an aqueous solution, without using a conventional liquid-junction-reference-electrode. When a current pulse (stimulus) is applied at the Ag/AgCl WE electrode, the change in the electrode potential (response), due to the depletion of Cl^- ions, becomes a function of Cl^- ion concentration in the bulk electrolyte. In such approach, a bare Ag/AgCl can serve as a pseudo-reference electrode, therefore this sensor is suitable for long term applications. The theoretical expression for the potential difference was derived from the Nernst equation. The calculation partially agreed with the experimental observations. The deviation from the theoretical curve is attributed to the ohmic drop during the applied current pulse. The potential difference for different concentration of Cl^- ions showed an inverse logarithmic behaviour i.e. the potential decreases with the increase in Cl^- ion concentration. The sensitivity of the response is tuneable and it is a function of the applied current pulse and the corresponding detection range of Cl^- ion concentration. The pH of the electrolyte has an influence on the sensor response, the potential response is not stable at high pH values (pH > 12) and low Cl^- ion concentrations (< 1 mM). The pH of the electrolyte defines the lower detection range of the sensor. It is worthwhile to investigate this measurement approach inside concrete structures.

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REFERENCES

[1] A. Moncmanová, *Environmental deterioration of materials* vol. 21: Wit Pr/Computational Mechanics, 2007.

[2] U. Angst, B. Elsener, C. K. Larsen, and Ø. Vennesland, "Potentiometric determination of the chloride ion activity in cement based materials," *Journal of Applied Electrochemistry,* vol. 40, pp. 561-573, 2010.

[3] P. Bergveld, J. Eijkel, and W. Olthuis, "Detection of protein concentrations with chronopotentiometry," *Biosensors and Bioelectronics,* vol. 12, pp. 905-916, 1997.

[4] J. B. Allen and R. F. Larry, "Electrochemical methods: fundamentals and applications," *Department of Chemistry and Biochemistry University of Texas at Austin, John Wiley & Sons, Inc,* 2001.

[5] Y. Umezawa, CRC Handbook of ion-selective electrodes: selectivity coefficients: CRC Press Boca Raton, FL, 1990.

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