



A chronopotentiometric approach for measuring chloride ion concentration



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ARTICLE INFO

Article history:

Received 28 March 2013

Received in revised form 27 May 2013

Accepted 14 July 2013

Available online 23 July 2013

Keywords:

Chloride ion detection

Chronopotentiometry

Stimulus/response approach

Ag/AgCl pseudo-reference electrode

Concrete structures

ABSTRACT

In this paper, a novel approach is reported for the electrochemical measurement of chloride ions in aqueous solution. This sensor is based on the stimulus/response principle of 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 is related to the Cl^- ion concentration via the Nernst equation and follows an inverse logarithmic trend. By varying the applied current pulse, the sensitivity of the sensor is tunable to different concentration ranges. The potential response is also influenced by the pH of the electrolyte, this effect is pronounced at lower concentration of Cl^- ions (<1 mM KCl) and at high pH values (>12 pH). The advantage of this approach is the use of a bare Ag/AgCl electrode as a pseudo-reference electrode, which enables this system for long term application such as the in situ measurement of Cl^- ions in concrete.

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1. Introduction

The major cause of deterioration in reinforcement concrete is due to the presence of chloride ions in the concrete itself [1,2]. When the amount of chloride ions increases beyond a certain threshold, pitting corrosion of the steel reinforcements initiates and ultimately results in localized structural failure [3]. This is particularly a problem in structures near salt water or which are exposed to de-icing salt. In 2011, the U.S.A. Federal Highway Administration stated that 11% of the national bridges are structurally defective [4] mainly due to degradation from chloride ions. Delayed maintenance could result in the collapse of these structures and human casualties, but unnecessary upkeep increases both costs and CO_2 emissions. To precisely predict the optimal time for maintenance of these structures, a service-life model of the concrete is required [5] and the chloride ion concentration is an essential parameter.

The well-established method for chloride ion detection in concrete requires destructive sampling of structures and time-intensive laboratory processing [6,7]. In contrast, a non-destructive in situ monitoring provides fast measurements, data reliability and

real time ingress profile without destroying the structures [8]. In recent years many groups have investigated in situ measurement of chloride in concrete using mainly electrochemical [9–11] and optical methods [12–14]. However, optical methods have bulky setups, are difficult to integrate as a standalone system and have other disadvantages such as the photo bleaching of dyes (optical transducers) and the leaching of transducer (polymer matrix) due to the high pH environment inside concrete.

While electrochemical sensing is the preferred and most researched method, many devices are only suitable for in situ measurements in a laboratory setting and no solution for long-term measurements in concrete structures currently exists (with a required sensing period of 20 years or more). Most of the reported electrochemical sensors use potentiometry [8,11,15–17] where the half-cell potential of a silver/silver chloride (Ag/AgCl) electrode is measured with respect to a reference electrode at equilibrium. This method requires the reference electrode to be embedded inside concrete (near the Ag/AgCl working electrode) to reduce errors due to diffusion potential [18]. The limiting factor of this approach (for in situ measurement in concrete) is the long term stability of the reference electrode and the drift in potential [19]. Therefore, to design an electrochemical sensor capable of measuring a real-time Cl^- ion concentration in concrete over the span of decades, a system that is not dependent on a stable reference electrode is desired.

Potentiometry is a static (zero current) approach and the alternative to this is a dynamic measurement approach (e.g. chronopotentiometry) which involves measuring the response of an equilibrated system to an applied stimulus [20,21]. In this technique, a controlled, chemical stimulus defines the condition at the

Abbreviations: WE, working electrode; RE, reference electrode; CE, counter electrode.

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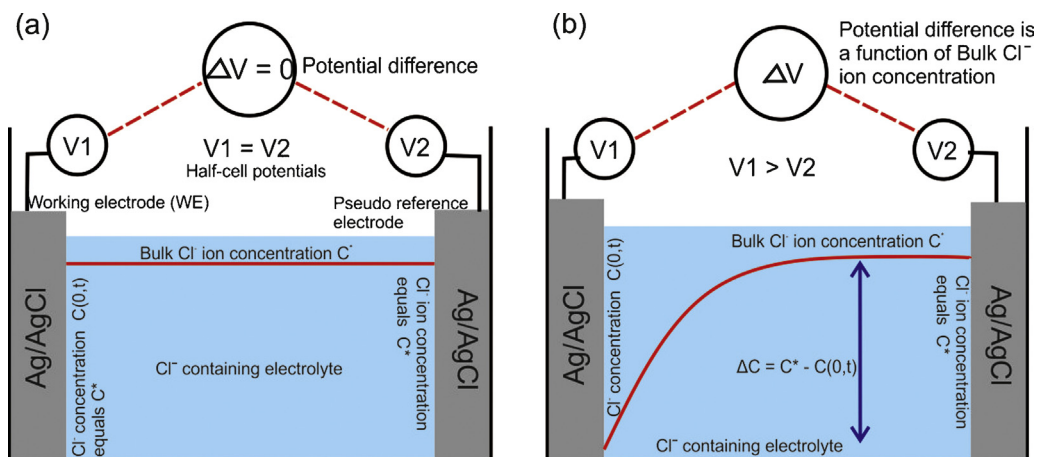


Fig. 1. The schematic of the chronopotentiometric approach with Ag/AgCl as pseudo-reference electrode. (a) At zero current condition, the half-cell potential of the WE and pseudo-reference electrode is the same, therefore the potential difference, ΔV , is zero. (b) During the anodic current pulse at the WE, applied w.r.t. 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. The half-cell potential at the WE changes whereas the potential at pseudo-reference electrode remains the same.

working electrode, depending on the analyte concentration (in this case, Cl^- ions). A chemical stimulus approach provides improved sensitivity and system robustness by avoiding drift of the potentiometric response [19,22]. Moreover, the dynamic measurement technique can eliminate the dependence of potential measurement on the stable reference electrode.

The aim of this work is to develop a Cl^- ion sensor based on chronopotentiometry where the conventional (liquid junction) reference electrode is replaced by a bare Ag/AgCl “pseudo-reference” electrode. A current stimulus is applied at the Ag/AgCl working electrode and the corresponding potential difference is measured simultaneously. This resulting potential difference will vary depending on the Cl^- ion concentration in the bulk electrolyte, thereby enabling long-term, in situ measurement of Cl^- ions in concrete structures without the need for stable reference electrodes. This method can be used for the in situ measurement of Cl^- ions in concrete structures. The theoretical background of this approach along with the experimental evaluation in aqueous solution containing chloride ions are presented in detail.

2. Theory

A Ag/AgCl electrode is a redox electrode of the second kind. When immersed in a solution containing Cl^- ions, electrochemical 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):

$$V_{\text{Ag/AgCl}} = V^\circ_{\text{Ag/AgCl}} - \frac{RT}{F} \ln \alpha_{\text{Cl}^-} \quad (1)$$

Here, $V^\circ_{\text{Ag/AgCl}}$, R , F , T , α_{Cl^-} are the standard electrode potential of Ag/AgCl, general gas constant, Faraday constant, absolute temperature (K) 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 electrode; the measured potential response is called chronopotentiogram. In the case of a Ag/AgCl WE, an anodic current pulse initiates the Faradaic reaction, Eq. (2), at the surface of the WE. The Cl^- ions near the WE are consumed during this reaction, locally depleting Cl^- ions near the electrode surface [23]. This results in a concentration gradient that gives rise to a potential difference (ΔV) at the WE with respect to the RE. The expression for

ΔV , in the case of high background electrolyte concentration (0.5 M KNO_3) is given in Eq. (3), from the Appendix.



$$\Delta V = -\frac{RT}{F} \ln(1 - \sqrt{(t/D\pi)2j/FC^*}) \quad (3)$$

Here, C^* is the bulk Cl^- ion concentration in the electrolyte, j the current density, t the pulse time and D the diffusion coefficient. Since the potential difference, ΔV , in Eq. (3) does not depend on the reference potential, a bare Ag/AgCl electrode in the bulk electrolyte can serve as a pseudo-reference electrode. The schematic of this approach is shown in Fig. 1. Both Ag/AgCl electrodes are in the same bulk electrolyte. At zero current condition (Fig. 1a), the potential difference is ideally zero (same half-cell potential). During the current pulse (Fig. 1b) applied via a counter electrode (CE), the potential at the WE changes due to the depletion of Cl^- ions 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. (3).

However, this approach is only valid if the potential difference is measured within the time it takes for the Cl^- ion concentration at the electrode surface to reach zero, defined as the transition time (τ) [23]. After the transition time, additional Faradaic reactions occur (e.g. oxide formation) which invalidate Eq. (3). The selection criteria for the current densities, j , and the current-pulse time, t , to ensure measurements within the transition time is outlined in Eq. (4).

$$j < 0.5 FC^* \sqrt{(t/D\pi)} \quad (4)$$

This boundary condition is evaluated from the logarithmic-term $(1 - \sqrt{(t/D\pi)2j/FC^*})$ of Eq. (3). The theoretical curve of this logarithmic-term versus the Cl^- ion concentrations of the bulk electrolyte is shown in Fig. 2 for three different current densities. The logarithmic-term values between 0 and 1 give the operational range of this sensor. The sensitivity changes at different values of the Cl^- ion concentration. In this work the concentration range of the Cl^- ions are selected for values between 0.13 and 0.9 of the logarithmic term to achieve relatively high sensitivity. The sensor then has different sensitivities for specific Cl^- ion concentration ranges depending on the applied current density. The detection ranges of Cl^- ion concentrations and the corresponding optimal current densities are given in Table 1 for current-pulse time, $t = 5$ s.

The Ag/AgCl electrode is an ion selective electrode which has higher selectivity to Cl^- ions than other interfering anions (for instance Br^- , I^- , OH^- ions) [8]. These interfering ions also contribute

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