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No more conventional reference electrode: Transition time for determining chloride ion concentration

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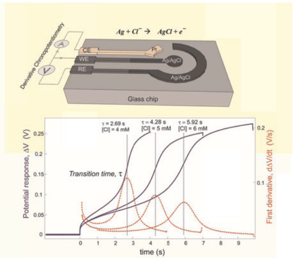
HIGHLIGHTS

- Concentration of chloride ions was measured using chronopotentiometry.
- The transition time of the Ag/AgCl electrode determines the Cl^- ion concentration.
- The square root of the transition time is proportional to the $[Cl^-]$.
- Any metal wire can be used as a pseudo-reference electrode.
- There was no inherent drift over two weeks measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

Ion selective electrodes (ISE) are used extensively for the potentiometric determination of ion concentrations in electrolytes. However, the inherent drift in these measurements and the requirement of a stable reference electrode restrict the feasibility of this method for long-term in-situ applications. This work presents a chronopotentiometric approach to minimize drift and avoid the use of a conventional reference electrode for measuring chloride ion concentration. An anodic current pulse is applied to a Ag/AgCl working electrode which initiates a faradaic reaction that depletes the chloride ions near the electrode surface. The rate of change in potential at the Ag/AgCl electrode, due to chloride ion depletion, reaches an inflection point once the chloride ions deplete completely near the electrode surface. The moment of the inflection point, also known as the transition time, is a function of the chloride ion concentration and is described by the Sand equation. It is shown that the square root of the transition time is linearly proportional to the chloride ion concentration. Drift in the response over two weeks is negligible: 59 μM/day when measuring 1 mM of Cl^- ions using a 10 A m^{-2} current pulse. The transition time at a specific ion concentration can be tuned by the applied current pulse, e.g., in a solution containing 5 mM chloride ions, the transition times with current pulses of 10 and 20 A m^{-2} are 1.56 and 0.25 s, respectively. The moment of inflection determines the response, and thus is independent of the absolute potential of reference electrode. Therefore, any metal wire can act as a pseudo-reference electrode, enabling this approach for long-term and integrated-sensor applications such as measurement inside concrete structures.

1. Introduction

Ion selective electrodes (ISE) are one of the most prevalent electrochemical sensors in analytical chemistry and date back to the early 20th century [1,2]. Their high selectivity toward specific

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Abbreviations: RE, reference electrode; WE, working electrode; CE, counter electrode; DEM, dynamic electrochemical measurement.

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ions make them suitable for many analytical applications. The half-cell potential of ISEs is a function of the ionic activity in the electrolyte, as derived from the Nernst equation [3]. Typically, the open circuit potential of the ISE is measured with respect to a reference electrode, which is called potentiometry [4]. This method is routinely used in some clinical [5,6] and environmental applications [7,8]. Despite the simple measurement setup and the low energy consumption of the potentiometric method, it is unfeasible for long-term and remote sensing applications [9]. This is due to the requirement of a long-term-stable reference electrode and drift in the potential response over time [10].

Dynamic electrochemical measurements (DEM) are well known for counteracting drift in electrochemical measurements because they measure a system's response to an applied stimulus [9–11]. Chronopotentiometry is an example of DEM, where an applied current pulse stimulates a faradaic reaction which depletes ions near the working electrode and changes its the potential [12]. This measured potential change relates to the applied current pulse and the concentration of the electrolyte [13]. When the ions involved in the reaction at the electrode surface have completely depleted, the potential increases rapidly and jumps to a higher value (creating an inflection point), where a second faradaic reaction then occurs [14]. The moment of this inflection point, also known as the transition time [15,16], is a characteristic of the analyte concentration [3,17] and is given by the Sand equation. This approach has been used to determine different ions concentration [16–18] and the pH of electrolytes [19,20].

Chloride ions are one of the major contributors to degradation of reinforcement-concrete [21,22]. The presence of these ions initiate pitting corrosion in the reinforcement steel and ultimately results in the failure of the construction [23]. Thus, the chloride ion concentration inside concrete is a crucial parameter to predict the service life of a structure [24,25]. Several groups have investigated the in-situ measurement of chloride using potentiometry based on Ag/AgCl ISE [26–28]. Despite promising results, this approach is limited to lab-scale measurements because drift in the reference potential causes flawed data. A transition time approach based on DEM as described could counteract such drift. This approach has been previously reported by Meyer et al. [16]. Here, we demonstrated the advantage of this approach by shunning the liquid-junction reference electrode and instead using any metal wire as a pseudo-reference electrode. This allows the detection of chloride ions concentration for long term and in-situ applications, e.g., measurement inside concrete structures.

This work presents a chloride ion concentration sensor based on chronopotentiometry using the transition time of a Ag/AgCl WE. A current pulse is applied between the Ag/AgCl WE and CE and the potential is measured w.r.t a pseudo-reference electrode. The maximum of the first derivative of the potential response during the applied current pulse gives the transition time. Since only the rate of change in the potential is of interest, the absolute potential values are irrelevant. Therefore, any conducting electrode can be used as a pseudo-reference electrode. The feasibility of this approach will be demonstrated by using several electrodes as pseudo-REs to measure the transition time. Furthermore, the effect of Cl^- ion concentration and current density is discussed. Measurements are also taken to ensure the technique appropriately avoids inherent drift.

2. Chronopotentiometric response of a Ag/AgCl electrode

The half-cell potential of a Ag/AgCl electrode is a function of chloride ion concentration, as described by the Nernst equation. When an anodic current pulse is applied to a Ag/AgCl WE (in a Cl^- ion containing electrolyte), the faradaic reaction given in Eq. (1) takes place, consuming Cl^- ions at the electrode surface. Depletion of Cl^- ions at the Ag/AgCl WE occurs when the electrochemically imposed ion flux can no longer be maintained by the Cl^- ions near the electrode surface [29]. The time it takes for the Cl^- ions to deplete completely near the Ag/AgCl WE surface is called the transition time [3], τ.

$$Ag + Cl^- \rightarrow AgCl + e^- \tag{1}$$

Beyond the transition time, the Cl^- ion flux to the electrode surface is not sufficient to satisfy the applied current. Therefore, the electrode potential shifts to a higher value where another faradaic reaction occurs, e.g., the formation of silver oxide. A schematic of the Cl^- ion concentration profile near the WE during the applied current pulse is shown in Fig. 1a. The corresponding potential response of the Ag/AgCl WE along with its first derivative are illustrated in Fig. 1b. There are three distinct regions of the response curve, each corresponding to different conditions near the WE. Region A depicts the change in the potential due to the depletion of Cl^- ions (corresponding to Eq. (1)). The change in potential in this region is a function of Cl^- ion concentration in the bulk electrolyte. Region B is characterized by the steep rise in the potential and contains the transition time. Here, the rate of change of the potential is maximum (inflection point) [18] as given by the peak of the first derivative of the potential response (see Supplementary Information S1). Region C denotes the beginning of a second faradaic reaction and the potential jumps to another plateau.

Supplementry material related to this article found, in the online version, at http://dx.doi.org/10.1016/j.aca.2013.12.001.

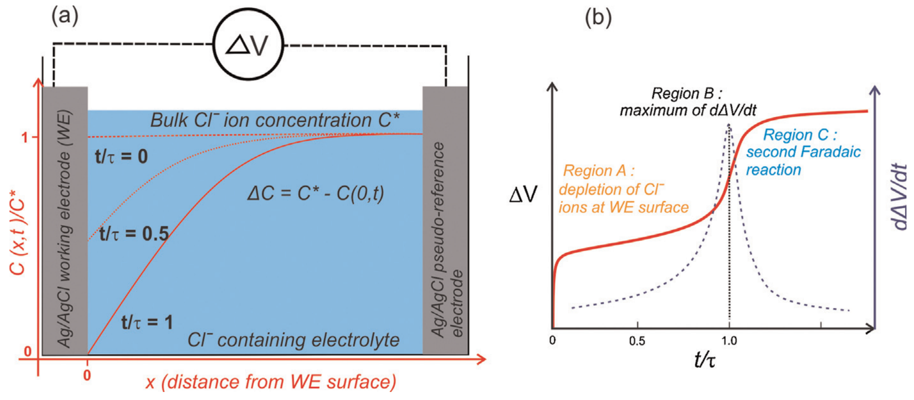

Fig. 1. (a) Schematic of the Cl^- ion detection approach. During an applied current pulse at the WE w.r.t a CE (not included in this figure), chloride ions deplete at the Ag/AgCl WE, resulting in the illustrated Cl^- ion concentration profile. (b) Schematic figure of the ΔV and $d\Delta V/dt$ response. The solid line (—) and dashed line (–) represent ΔV and $d\Delta V/dt$, respectively. τ is the transition time and t is the duration of the applied current pulse.