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Activated Carbon as a Pseudo-reference electrode for Potentiometric Sensing inside Concrete

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Abstract

The half-cell potential of the Activated carbon (AC), due to its high double layer capacitance (EDL), remains stable in high ionic electrolyte. The open circuit potential (OCV) of the AC, with EDL of 40 – 50 F, shows a stable potential (10 mV variation) over two weeks in the cement pore solution (sat. $Ca(OH)_2$). The OCV is less sensitive to the pH change from pH 8 to 12 (range inside concrete). The potentiometric response of a Ag/AgCl vs. AC pseudo-reference shows a near-Nernstian response (-51 mV/decade). The AC electrode can be proposed as a pseudo-reference for the potentiometric monitoring inside concrete.

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Keywords: Activated carbon; open circuit potential; pseudo-reference electrode; potentiometric measurement; concrete structures

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1. Introduction

Corrosion of the reinforcement steel is the major cause of concrete structural failure. The presence of Cl^- ions, in the concrete, accelerates the rate of corrosion [1]. The non-destructive and on-site monitoring of the corrosion rate is inevitable to assess the structural integrity of the infrastructures. Potentiometry is commonly used to measure the corrosion potential of the steel and aggressive ions such as chloride inside concrete [1]. The open circuit potential (OCV) of a Ag/AgCl electrode determines the Cl^- ion concentration. To reliably measure the OCV of the working electrode, i.e. Ag/AgCl or reinforcement steel, a stable reference electrode is inevitable [1]. The currently available conventional liquid junction reference electrodes are not feasible for long-term usage (> 20 year) inside concrete. Several groups reported metal-metal oxide (MMO) [2] electrodes as a pseudo-reference electrode (PRE) for the potentiometric measurement inside concrete. But these electrodes are strongly pH dependent (theoretical sensitivity

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= -59 mV/pH).In contrast, the activated carbon (AC) electrode is relatively inert to the pH change and ionic composition of the electrolyte. AC electrodes are commonly used for super capacitors due to their high surface area (> 1000 m^2/g) [3]. This results in a higher electrical double layer (EDL) capacitance, C_{DL}. As a consequence, any reduction or oxidation charge, dQ, at its surface offers negligible change in its electrode potential, ΔE, since $\Delta E = dQ/C_{DL}$. Hence, the electrode potential remains relatively stable to the changes in the concentration of redox active species [3] in the higher ionic electrolyte as compared to MMO electrodes. Concrete pore solution is composed of a saturated solution of $Ca(OH)_2$ and other ions. The usage of the AC electrode as a PRE in the concrete pore solution is studied. The characterization of the AC electrode, the stability of its electrode potential toward ionic composition, pH and long term measurement is evaluated. Furthermore the calibration curve of the [Cl^-] using a Ag/AgCl (Cl^- ion selective) electrode vs. AC PRE is also evaluated.

2. Material and Methods

2.1. Activated carbon (AC) electrode preparation

The AC electrode was prepared by rolling a Kynol activated carbon fabric around a graphite rod, see fig. 1. The Kynol AC fabric (Carbon content: 100%, product code: ACC-507-15) was ordered from Kynol Europa GmbH, Germany. The specific area, provided by the manufacturer, is 1500 m^2/g (weight = 120 g/m^2). The higher surface area is due to its high micro and nano-porosity, see SEM image in fig. 2. The apparent area of the electrode is 37.5 cm^2 (0.48 g). The graphite rod was used as a contact to connect the AC with the potentiostat terminals. The AC fabric was adhered to the graphite by a carbon/graphite paste (fig. 1b). Fig. 1c shows the finished electrode.

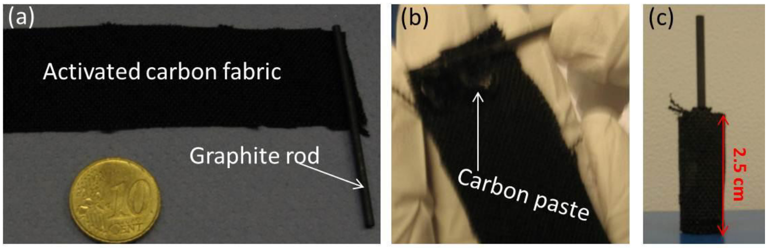

Figure 1: Preparation of AC electrode. (a) AC electrode fabric with graphite rod. (b) Rolling of AC electrode fabric around the graphite rod, here carbon paste is used for adhesion of AC to graphite rod. (c) The AC electrode ready to be used.

2.2. Chemicals and equipment

The graphite rods, 2 mm dia. and 100 mm length were ordered from Goodfellow Cambridge Ltd., UK. The graphite/carbon paste was ordered from Gwent group, UK. Potassium chloride (BioXtra, ≥ 99.0%), potassium hydroxide (90% pure reagent grade), Calcium hydroxide (99.995% trace metal basis) and potassium nitrate (>99% reagent grade) were ordered from Sigma–Aldrich, the Netherlands. The Ag/AgCl liquid junction reference electrode (model MF-2079) was ordered from BASi, USA. The electrochemical measurements were performed using a VSP potentiostat from Biologic Science Inst., France. The Ag/AgCl electrode was fabricated by anodization (@ 0.5 mA/cm^2 for 20 mins) of a Ag wire in 0.1 M HCl electrolyte. All measurements were carried out at room temperature, 21 °C.

3. Results and discussion

3.1. Capacitance of the AC electrode

The EDL capacitance of the AC electrode can be estimated by cyclic voltammetry. A potential sweep, with specific scan rates (1 and 0.1 mV/s), is applied to the AC electrode and the current through the electrode is measured. The capacitance is then estimated by dividing the measured current by the scan rate, $C = i/(dV/dt)$. Fig.

2d shows the capacitance measurement from the cyclic voltammogram in 3 M KCl electrolyte. The capacitance at 0.1 and 1 mV/s is ~50 and ~40 F, respectively. The capacitance, C_{DL}, is higher at lower scan rate (0.1 mV/s) as ions have more time to transport in the nano-pores giving the higher surface area.

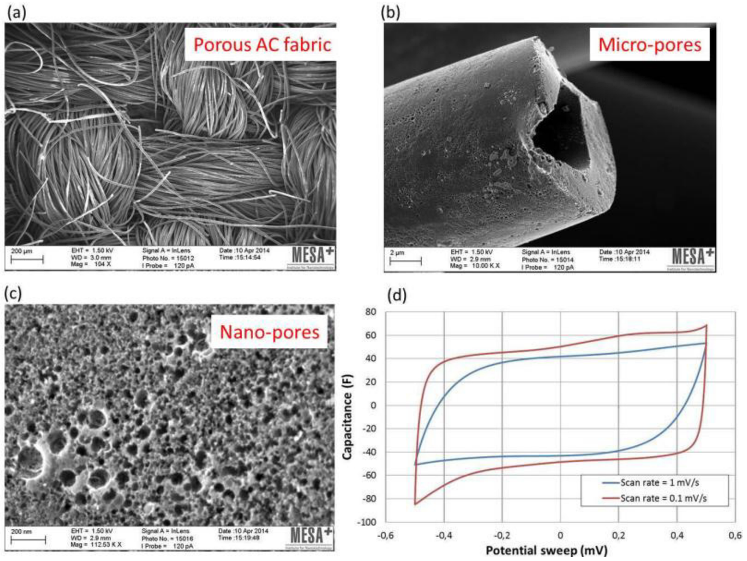

Figure 2: (a) SEM image of the porous AC fabric composed of carbon-tube threads. (b) SEM image of one of the carbon tubes in the AC fabric, micro pores can be seen. (c) SEM image (magnified view) of one of the carbon tubes in the AC fabric with nano-pores. (d) The capacitance of the AC electrode evaluated from the cyclic voltammogram at different scan rates (0.1 and 1 mV/s), in 3 M KCl solution.

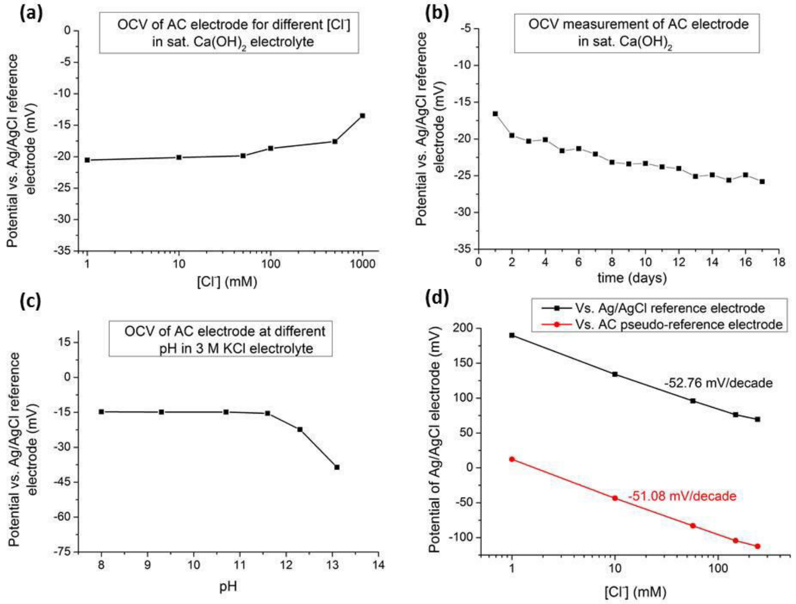

Figure 3: Potentiometric measurement. (a) Effect of changing the $[Cl^-]$ on the OCV of the AC electrode in the pore solution. (b) OCV measurement of the AC electrode for two weeks in the pore solution. (c) The OCV of the AC electrode for different pH in 2 M KNO_3 background electrolyte. (d) Calibration curve of the Ag/AgCl electrode vs. AC electrode and the conventional liquid junction reference electrode for different $[Cl^-]$ in 2 M KNO_3 background electrolyte.

3.2. Open circuit potential (OCV) of the AC electrode

The AC electrode is proposed to be used as a pseudo-reference electrode inside the concrete to measure Cl^- ion. Its half-cell potential should not be affected by the presence of Cl^- in the pore solution (sat. $Ca(OH)_2$). Fig. 3a shows the effect of the [Cl^-] concentration on the OCV of the AC electrode. The potentials were measured against a Ag/AgCl liquid junction reference electrode. Before each measurement, the AC electrode was preconditioned overnight in the electrolyte. In fig. 3a, the potential is relatively stable, the OCV changes by 7 mV to the 3 order change in the [Cl^-]. To observe the long term stability, the OCV of the AC electrode was measured in the pore solution for two weeks, see fig. 3b. Every day the measurements were performed for 8 hours. The potential stabilizes with time and drifted within ~15 mV (0.8 mV/day drift) over two weeks. The pH of the electrolyte has an effect on the OCV of the AC electrode, see fig. 3c. The effect is pronounced at higher pH (pH > 12) as the potential decreases significantly (~20 mV). From pH 8 to 12 the OCV is relatively stable ($\Delta V < 1$ mV). The AC electrode is less sensitive to pH in this range as compare to metal-metal oxide electrodes.

3.3. Potentiometric response of the Ag/AgCl vs. AC pseudo-reference

To observe the functionality of the AC electrode, as a pseudo-reference for the potentiometric monitoring of Cl^- ions, the OCV of Ag/AgCl was measured vs. AC PRE. Fig. 3d shows the calibration curve, which indeed shows a Nernstian response of Ag/AgCl (sensitivity = -51.08 mV/decade). For comparison, the calibration curve against. a Ag/AgCl liquid junction reference electrode is also measured, fig. 3d. The OCV vs. the AC pseudo-reference shows a constant offset (~177 mV) with respect to the conventional reference electrode. This shows that the half-cell potential of the AC pseudo-reference is relatively stable during the potentiometric measurement of the Cl^- ions. The AC electrode can indeed be used as a PRE for Cl^- ion monitoring.

Conclusion

The activated carbon electrode can be used as a PRE for the potentiometric monitoring of Cl^- ions in concrete. For higher ionic electrolyte concentration, the half-cell potential of the AC electrode remains stable. The CV measurement shows the high EDL capacitance (40 – 50 F) of the AC electrode. The high capacitance is due to the high micro and nano-porosity of the AC electrode. The high capacitance resists the change in the OCV due to any charge transfer at the electrode surface. For the simulated pore solution the AC electrode showed stable OCV (ΔV within 10 mV) for measurement over two weeks. Furthermore, the OCV of the AC electrode was relatively inert against the pH change (pH 8 to 12) of the electrolyte as compare to the MMO PRE. This is the typical pH range inside the concrete. The potentiometric measurement of [Cl^-], using a Ag/AgCl electrode vs. the AC showed a near-Nernstian response (sensitivity = -51.08 mV/decade). Therefore, the AC PRE can be a favorable alternative to other PRE, such as MMO electrode, for potentiometric measurement of Cl^- ions inside concrete.

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