Activated carbon as a pseudo-reference electrode for electrochemical measurement inside concrete

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HIGHLIGHTS

- Activated carbon (AC) material is proposed as a pseudo-reference electrode.
- Kynol based activated carbon, which has surface area >1500 m^2, is used.
- The high EDLC capacitance neutralizes the change in open circuit potential.
- Application: pseudo-reference in potentiometric measurement inside concrete.
- The open circuit potential of AC electrode is stable w.r.t. pH changes up to pH 12.

ARTICLE INFO

ABSTRACT

The application of Kynol based activated carbon (KAC) as a pseudo-reference electrode for potentiometric measurement inside concrete is presented. Due to its high surface area the activated carbons has a large electrical double layer capacitance (EDLC > 50 F g^{-1}) and are used as electrode material for super capacitors. The change in potential of an electrical double layer capacitor is given by $\Delta E = dQ/C_{DL}$, where E (V) is the potential, Q (C) is the charge and C_{DL} (F) is the EDLC. Therefore any small amount of oxidation/reduction reaction as well as adsorption/desorption of charge (dQ) at the KAC will be neutralized by its large capacitance C_{DL} and its potential will not change significantly. The open circuit potential (OCP) of the KAC with an EDLC of 90–110 F g^{-1}, shows a stable potential (drift < 0.2 mV/day over two weeks) when immersed in the concrete pore solution. The OCP is stable w.r.t. pH changes up to pH 12. The nature of the ions does affect the OCP in the pore solution only at higher concentrations. The AC electrode is proposed as a feasible alternative for a pseudo-reference electrode in concrete.

1. Introduction

In electrochemical measurements a long-term stable reference electrode has always been a topic of interest [1–4]. This is even more pronounced in the case of potentiometric measurements where the half-cell potential of a working electrode is measured against a reference electrode [2,5–7]. The drift in reference potential adds an error to the measurements [8]. In regard to a redox electrode, such as an Ag/AgCl electrode (Nernstian slope = −59 mV/decade), a change of 8.9 mV in reference potential means a twofold error in the determination of concentration [9].

For a continuous long-term potentiometric measurement a stable reference electrode is inevitable [9–11]. Such an application is the in situ monitoring of chloride ions and corrosion in concrete

structures. The chloride ions are responsible for rebar corrosion in concrete causing structural degradation [12]. A threshold amount of chloride ions triggers rapid corrosion of rebar, which can result in ultimate failure of the structure [13,14]. Currently, to determine the [Cl^-] [15,16] and corrosion [17–19], the half-cell potential of an Ag/AgCl electrode and the reinforcement steel is measured against a reference electrode (usually a liquid junction reference), respectively. The conventional liquid junction electrodes, such as CSE, are used as an external electrode for potential mapping of reinforcement steel using the ASTM C876 standard [20]. The working electrodes (Ag/AgCl and reinforcement steel) are embedded inside the concrete whereas the reference electrode is kept outside since its reference solution should be refreshed over time to keep a stable potential. This adds a dynamic diffusion potential to the measurement [21] causing errors. Furthermore, conditioning of the concrete sample is required to develop an ionic connection between the working and reference electrode. For reliable, rigorous

and continuous potentiometric measurement in real concrete structures a stable embeddable reference electrode is crucial.

Several solutions of embeddable pseudo-reference electrodes in concrete [22] have been proposed such as metal/metal oxide (MMO) electrodes (e.g., Mn/MnO$_2$ [23,24] and metal oxide activated titanium rod electrodes [25]). These electrodes are sensitive to pH change and therefore vary over time due to pH changes in concrete. Due to carbonation, the pH inside concrete may vary from 12.5 to 9 [26]. Still, for some onset corrosion measurement, while the pH remains constant, these electrodes can be used as a pseudo-reference. However, for long term monitoring the pseudo-reference should be inert to the change in pH and ionic composition in the concrete pore solution. The concrete pore solution is composed mainly of saturated Ca(OH)$_2$ [15,27]. This high ionic concentration of the pore solution can be utilized for designing a stable pseudo-reference electrode.

Carbon material is well known for its inert behavior in the presence of aggressive ions in concrete such as hydroxide and chloride [22,28]. When activated at elevated temperature (typically above 700 °C) this material becomes highly porous, also known as activated carbon (AC) [29]. Due to its higher surface area, the activated carbon electrode, when immersed in an electrolyte, forms a huge electrical double layer capacitance (EDLC > 50 F g^{-1}) [30]. Activated carbon electrodes are therefore commonly used as an electrode material for super capacitors [31]. The high surface area of an AC electrode comes from its micro and nano-porosity. The large EDLC can be utilized to stabilize the potential of AC electrode in high ionic electrolytes. In our case, there is no active redox species for activated carbon electrode and its potential is derived from the polarization of the electrode in the presence of the double layer capacitance. The potential change, ΔE, across the double layer capacitor is given by $\Delta E = dQ/C_{DL}$, where dQ and C are the change in charge and the capacitance, respectively. Any change in the charge due to any small amount of oxidizing/reducing species or adsorption/desorption reaction (dQ) will be neutralized by the large C_{DL} in the denominator. Therefore, the electrode potential of an AC electrode will remain relatively steady against the change in the concentration of ions in a higher ionic electrolyte as compared to commonly used MMO electrodes. Ruch et al. reported the use of AC electrode as a pseudo-reference electrode in ionic liquid by using the same principle [32]. The use of an AC electrode as a pseudo-reference electrode can be justified in high ionic electrolyte, especially in the absence of potential determining redox species. The feasibility of an AC electrode as a pseudo-reference electrode for potentiometric measurement inside concrete is demonstrated. The EDLC and characterization, stability of electrode potential toward ionic composition and pH of the electrolyte are evaluated. Furthermore, the long-term measurement in concrete pore solution is studied.

2. Materials and method

2.1. Activated carbon material

In this work a Kynol based activated carbon of type ACF-1603-15 from Kynol GmbH Hamburg is used. According to the manufacturer this activated carbon contains 100% carbon which is derived from a novoloid fiber precursor [33]. It is a fabric-like material with a specific surface area larger than 1500 m^2 g^{-1}. Unlike most of the available AC material [29,34] it consists of 100% carbon with no polymeric impurity added. According to the supplier the novoloid fiber is first sewed together to form polymer fabric and then carbonized and activated at elevated temperatures (typically up to 2000 °C). The resulting AC material is a porous carbon flexible fabric which can be compacted into small volumes, as shown in Fig. 1a. The SEM image of the Kynol AC fabric at different magnifications is shown in Fig. 1b–d. The spaghetti of micro carbon tubes of ca. 10 μm is visible in Fig. 1b which gives the bulk-porosity to this material. When zooming in on a carbon tube the micropores and nano-pores are clearly visible, see Fig. 1c and d. Each carbon

tube shows randomly distributed micro and nano-pores of diameter down to ca. 1 nm. The pores on each carbon tube are not connected within the bulk material which will reduce any intercalation problem for such electrode. For further details on the fabrication and mechanical properties of Kynol activated carbon see its datasheet in the Supplementary information S1 and S2, provided by the supplier.

2.2. Electrode fabrication

The Kynol AC fabric is compacted to form an electrode for electrochemical measurement. A graphite rod (2 mm diameter, 5 cm length) is used as a current collector. The electrode fabrication process is shown in Fig. 2. The fabric is rolled around the carbon rod and a graphite/carbon paste is used for adhesion between the fabric and the carbon rod and also among the different layers of fabric as shown in Fig. 2a and b. The graphite paste should be carefully applied as an excess amount of graphite/carbon paste can block the pores and decrease the specific surface area of the electrode. The finished electrode is shown in Fig. 2b and will be referred to as AC electrode from now on. The AC electrode is dried at room temperature for 24 h followed by an immersion step into DI water for 24 h. Finally N$_2$ purging is applied to remove the trapped oxygen.

2.3. Measurement in concrete

To evaluate the performance of the AC electrode in concrete, it was embedded inside a concrete sample. For simplicity and the proof of concept, a mortar sample is used. The sample was prepared at Microlab TU Delft, The Netherlands according to the recipe mentioned in Table 1 with a water to cement ratio (w/c) of 0.5. During casting, the AC electrodes of various sizes (350 and 30 F) are immersed in the concrete sample. Moreover, for comparison a graphite rod (1.2 cm^2) and an Ag/AgCl electrode are embedded in the same sample. After drying, the sample is placed in an electrolyte (pore solution = sat. Ca(OH)$_2$) and the open circuit potentials (OCP) of the electrodes are measured against a double junction Ag/AgCl reference electrode, see Fig. 3.

2.4. Chemicals and equipment

Calcium hydroxide (99.995% trace metal basis), potassium nitrate (>99% reagent grade), potassium chloride (BioXtra, ⩾99.0%) and potassium hydroxide (90% pure reagent grade) were ordered from Sigma–Aldrich, The Netherlands. A double junction Ag/AgCl reference electrode Z113107 model is ordered from Sigma–Aldrich, The Netherlands. The carbon rods (Ultrafine 1–5 μm, 99.997%, model C007911) were ordered from Goodfellow Cambridge Ltd., UK. The graphite/carbon paste model C10903P14 is ordered from Gwent Group, UK. The electrochemical characterization and measurements were performed using a VSP potentiostat with internal impedance of >1 TΩ from Biologic Science Inst., France. The Ag/AgCl electrode was made by anodization an Ag wire in 0.1 M HCl electrolyte for 20 min. at a current density of 0.5 mA cm^{-2}. The Ag wire model 265608 (wire, diam. 1.0 mm, 99.9% trace metals basis) was ordered from Sigma–Aldrich, The Netherlands. All measurements were carried out at room temperature (ca. 21 °C) unless stated otherwise.

3. Results and discussion

3.1. Cyclic voltammogram of AC electrode (capacitance measurement)

The EDLC of the AC electrode is determined from cyclic voltammetry measurements. A potential range of −0.5 to 0.5 V is applied to the AC working electrode at various scan rates (1 and 0.1 mV s^{-1}) in 3 M KCl electrolyte. Another AC electrode is used as a counter electrode and an Ag/AgCl wire is used as a reference electrode. The CV curve is normalized by dividing all the current values by the scan rate [30,35]. After normalization the y-axis of the CV corresponds to the capacitance of the AC electrode as $C = i/(dV/dt)$. The normalized CV of the AC electrode at scan rate of 1 and 0.1 mV s^{-1} is shown in Fig. 4a. Theoretically, the scan-rate-normalized CV curves should be the same for both scan rates, which is not the case. The EDLC is determined to be ca. 40 F (93 F g^{-1}) and ca. 45 F (104 F g^{-1}) for 1 and 0.1 mV s^{-1} scan rates, respectively. The decrease in capacitance at higher scan rate can be explained by the kinetics limitation of the adsorbing/desorbing ions and/or by the transmission line behavior of the porous electrode [30,36]. At lower scan rate (0.1 mV/s) ions have more time to reach the nano-pores and thereby accessing the larger surface area of the electrode thus increasing the EDLC. Moreover, the