



## Potential of zero charge of glassy carbon at elevated temperatures



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### ARTICLE INFO

#### Article history:

Received 9 September 2013

Received in revised form 23 January 2014

Accepted 19 March 2014

Available online 1 April 2014

#### Keywords:

Potential of zero charge

Glassy carbon

EIS

Electrochemical sensor

### ABSTRACT

Glassy carbon (GC) electrodes are often used in electrochemical studies such as those focusing on electrochemical sensor development. The application of a GC electrode as a sensor for particle–wall interaction studies requires knowledge of the potential of zero charge (PZC), which defines the sign of the surface charge on the electrode. This work presents the temperature dependency of the PZC for a GC electrode at temperatures up to 473 K in 10  $\mu$ M, 1 mM, 5 mM and 10 mM NaClO<sub>4</sub> and NaF solutions. Electrochemical impedance spectroscopy was used to measure the potential at which the differential capacitance reaches its minimum. It was found that the PZC of GC changes linearly with temperature with an average temperature coefficient of 0.71 mV K<sup>-1</sup> and varies from 285  $\pm$  5 to 415  $\pm$  5 mV (vs. SHE<sub>298</sub>) when the temperature increased from 298 to 473 K.

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### 1. Introduction

Glassy carbon (GC) electrodes have been used extensively in electrochemical studies and electroanalytical chemistry in both aqueous and organic solutions. Owing to GC's versatile properties such as high corrosion resistance, high temperature stability and low residual current, it is used as an indicator/sensor electrode [1–3]. All of these applications are governed by the formation of the electrical double layer (EDL) at the electrode/electrolyte interface [4,5]. For all studies associated with the EDL, one of the fundamental parameters is the potential at which the electrical double layer collapses and the surface has no excess charge. This is called the potential of zero charge (PZC) and it coincides with the potential at which the differential capacitance ( $C_{diff}$ ) reaches its minimum [6]. The PZC provides information about the structure of the electrode/solution interface, potential ranges of ionic and non-ionic adsorption and the region where the EDL affects the electrode kinetics [7,8]. It should be noted here that the definition of PZC in electrochemistry is different from that in colloidal chemistry. The PZC in colloidal chemistry stands for point of zero charge and it is usually the pH (or concentration of the potential determining ions) at which the surface charge (or Zeta-potential) is zero. In this manuscript PZC refers to the potential of zero charge.

Apart from the fundamental significance of the PZC in EDL studies, it is also a very useful parameter in the evaluation of colloidal particles–solid surface interactions (e.g., electrophoretic deposition

and sensors for particulate fouling detection) [9]. When submicron solid particles are placed in a solution, a variety of forces such as fluid drag, particle boundary hydrodynamic interaction, colloidal interaction and external applied body forces (gravity) act on the particles [10,11]. When a particle reaches the electrode surface, at distances less than 100 nm, colloidal forces control the particle–wall interaction [12]. Colloidal interactions can be explained by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloid stability and these include the van der Waals (VDW) attractive force and the electrical double layer (EDL) force, which can be repulsive or attractive depending on the surface charge of the interactive solids [13–15]. Consequently, one can evaluate whether particles are attached to/or suspended on the surface if one knows the particle charge and the PZC of the electrode.

Extensive studies have dealt with PZC measurement of metallic and non-metallic (conductive) electrodes and thus a large number of methods have been proposed. For more details, readers are referred to an excellent review of theory, methods and experimental results for a wide range of metallic electrodes done by Trasatti and Lust [6]. It is known that the capacitance measurement method is suitable for PZC determination. A number of researchers have used this method to measure the PZC of GC electrodes. For instance, Shao et al., reported the PZC of 270  $\pm$  5 mV vs. SHE for a GC electrode in a 0.05 M NaF solution by differential capacitance measurement at different frequencies (100 mHz–6 Hz) [16]. They also found that the frequency variation does not alter the PZC. Lockett et al. investigated the PZC of a GC electrode/imidazolium-based ionic liquid interface at various temperatures [3]. They used a non-aqueous reference electrode and observed a negative

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shift in the PZC values with temperature increase. In another work, Randin and Yeager evaluated the differential capacitance of a GC electrode in 0.9 M NaF, 0.5 M H<sub>2</sub>SO<sub>4</sub> and 1 M NaOH to understand the effect of pH on its PZC and capacitive behavior [17]. They found that the capacity–potential curves were pH dependent and the PZC changes vs. pH showed a slope of –30 mV per pH unit over the entire pH range from 0 to 14.

The aim of the present work is to evaluate the PZC of a GC electrode at temperatures up to 473 K using differential capacitance measurements, and by employing an External Pressure Balanced Reference Electrode (EPBRE). This work is part of a larger program aimed at the development of an electrochemical sensor for the detection of particulate fouling at elevated temperatures and pressures.

## 2. Experimental procedure

### 2.1. Electrodes

It is well known that the electrochemical properties of GC electrodes are greatly affected by surface preparation and activation methods. Much has been published on the techniques and procedures used to produce an active and reproducible GC surface [1,18–20]. The most common method consists of polishing the GC surface with micro-sized abrasives to activate the surface. In this study, a GC disc (7 mm diameter, 5 mm thickness, Alfa Aesar) was polished to a mirror-like finish with 600 grit, 1.0 μm, 0.5 μm, and 0.05 μm alumina slurries (Buehler, Ltd.) with high purity deionized water (18.2 MΩ cm, NANOpure Diamond, Barnstead, USA) on a ground glass plate. Between each successive polishing step, ultrasonication (10 min) and protective glove changes were done to avoid any possible contamination. The degree of activation of the GC disk electrode was evaluated by looking at the difference in the peak potential for the ferri/ferrocyanide redox couple. The cyclic voltammetry results (not shown here) for the freshly polished GC electrode obtained in 1 mM ferrocyanide, 1 M KCl showed an acceptable separation between anodic and cathodic peaks of Δ*E*<sub>p</sub> = 71 mV, which is expected to be close to 60 mV in an ideal case for a reversible electron transfer reaction [18]. The GC electrode then was connected to a copper wire using a high temperature silver epoxy and this assembly was mounted in a high temperature polymer epoxy resin. The last step of the activation process was repeated immediately prior to inserting the electrode in the autoclave. A Pt foil (6 cm<sup>2</sup> surface area) was used as counter electrode and placed parallel to the GC electrode. The Pt was treated with a standard cleaning solution, H<sub>2</sub>O<sub>2</sub>–H<sub>2</sub>SO<sub>4</sub> mixture (1:5) and rinsed completely using high purity deionized water (18.2 MΩ cm) in an ultrasonic bath for 5 min.

A Ag/AgCl External Pressure Balanced Reference Electrode was used for all the electrochemical potential measurements. The design of the commonly used EPBRE was patented by MacDonald and Scott [21]. It has been modified and the calibrations confirmed by the following studies [22–27]. In this design the electrochemically active element was kept at room temperature and was connected to the high temperature zone via a non-isothermal electrolyte bridge. In order to accurately compare the measured potential at different temperatures, the components of the potential need to be corrected to a thermodynamic scale. These components consist of the streaming potential, the isothermal liquid junction potential, the thermal liquid junction potential and the contribution of the ohmic drop. In fact, due to a temperature gradient through the electrolyte bridge, the thermal diffusion component (as expressed by the thermal junction potential) is expected to have the largest effect on the potential measurements, and since this component does not change over time, one can convert the

potential to the standard hydrogen scale. As the streaming potential originates from the pressure gradient it has less influence in this reference electrode design (as it is pressure balanced). The IR drop contribution of the reference electrode was automatically eliminated by the potentiostat used in this work.

In order to convert the experimentally determined potentials (measured by EPBRE) to a thermodynamic scale a correction potential was calculated for a given operating temperature. Although according to convention SHE potential is assumed to be zero at all the temperatures, a definite potential difference does exist between SHE at 298 K and SHE at any elevated temperature. In this work all potentials refer to measured potentials vs. SHE at 298 K as given by Eq. (2-1):

$$E_{\text{SHE}}(\text{at } 298 \text{ K}) = E_{\text{meas}} - E_{\text{correction}} \quad (2-1)$$

where *E*<sub>correction</sub> is the conversion constant calculated between the measured potential (*E*<sub>meas</sub>) and the potential vs. SHE reference (*E*<sub>SHE</sub>) at room temperature. *E*<sub>correction</sub> values have been calculated for temperatures up to 573 K and for various concentrations of KCl reference solution (0.0050–0.505 mol kg<sup>−1</sup>) [23,27]. A 0.100 mol kg<sup>−1</sup> KCl reference solution was used in this work; corresponding *E*<sub>correction</sub> values are reported as 0.288, 0.244, 0.197, 0.153, 0.104, 0.059, 0.012, and –0.036 V for *T* = 298, 323, 348, 373, 398, 423, 448 and 473 K, respectively.

### 2.2. Electrochemical measurements

All the experiments were carried out in a glass lined autoclave at temperatures between 298 K and 473 K at 25 K intervals. EIS was used in this work to measure the differential capacitance (*C*<sub>diff</sub>) vs. electrode potential. In the absence of any specific adsorption, the minimum in the *C*<sub>diff</sub> vs. *E* curve represents the PZC. It will be discussed in the following section that the minimum in the *C*<sub>diff</sub> vs. *E* curve exists only when the diffuse part of the EDL is dominant [28], which occurs in solutions of concentration less than 10<sup>−2</sup> M. As F<sup>−</sup> and ClO<sub>4</sub><sup>−</sup> are known to show little or no tendency for specific adsorption, 10 μM, 1 mM, 5 mM and 10 mM NaF (99.8 %, Fisher Scientific, Canada) and NaClO<sub>4</sub> (99.7%, Fisher Scientific, Canada) electrolytes were used in this work and pH was adjusted to 9 with NaOH [29]. All the solutions were made using 18.2 MΩ deionized water.

A Princeton Applied Research Versastat 3F potentiostat/galvanostat was used to conduct the EIS experiments. Single-sin EIS experiments were carried out with amplitude of 5 mV (peak to peak) in the frequency range of 5 kHz–1 Hz in order to identify suitable frequency ranges for studying the minimum in *C*<sub>diff</sub>. In addition, single-frequency capacitance measurements were carried out at 10, 20, 30, 100 and 1000 Hz, while the potential sweep rate used was 10 mV s<sup>−1</sup>. It is to be noted that these are the typical frequencies for PZC measurement [28]. In all the experiments and calculations of differential capacitance in this work, the effect of ohmic resistance (*R*<sub>s</sub>) was taken into account. This was done by compensating *R*<sub>s</sub> during differential capacitance measurements using the IR compensation technique available in the potentiostat software (Versa Studio software, Princeton Applied Research, USA).

## 3. Results and discussion

### 3.1. Differential capacitance of glassy carbon

EIS was used to measure the PZC of the GC electrode in supporting electrolytes of NaF and NaClO<sub>4</sub> and in the double-layer region of the GC electrode, that is, the potential range at which faradaic processes do not occur. Fig. 1 shows a cyclic voltammogram of the GC electrode in 5 mM NaClO<sub>4</sub> at 298 K, which shows the

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