



## Electrochemical corrosion of a glassy carbon electrode

Youngmi Yi<sup>a</sup>, Gisela Weinberg<sup>b</sup>, Marina Prenzel<sup>a</sup>, Mark Greiner<sup>a,b</sup>, Saskia Heumann<sup>a,\*</sup>,  
Sylvia Becker<sup>a</sup>, Robert Schlögl<sup>a,b</sup>

<sup>a</sup> Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36, 45470 Mülheim an der Ruhr, Germany

<sup>b</sup> Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany

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### ABSTRACT

Glassy carbon is widely used in electrochemistry due to its properties of high temperature resistance, hardness, low density and low electrical resistance. The present study focuses on the chemical resistance under electrochemical oxidative conditions, which occur under oxygen-involving reactions like oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The electrochemical performance of glassy carbon investigated in alkaline, neutral and acidic media reveal the same chemical processes during the OER but showing different degradation mechanism.

The electrochemical signature of the corrosion in different media could be directly associated with the formation of oxygen functional groups determined by spectroscopic methods like Raman, infrared (IR) and x-ray photoelectron spectroscopy (XPS). The morphology change of the carbon surface caused by carbon oxidation was investigated by microscopy. A rough surface was obtained in the acidic case, whereas dents were seen in alkaline media.

It is assumed that the glassy carbon electrode in acidic media degrades by forming surface oxides by acid catalyzed process leading to ring opening in the graphitic structure and therefore oxidation in the bulk. In alkaline media OH radicals preferentially react with alkyl site chains, leading to oxidation of the edges of carbon layers until they become hydrophilic and dissolve.

### 1. Introduction

A variety of nanostructured carbon materials, such as carbon nanotube, mesoporous carbon and graphene, have been utilized in heterogeneous catalyst and electrocatalysis for a catalyst support to improve the catalytic efficiency due to the better catalyst utilization and reduction of the catalyst loadings. At a point of booming interest in metal-free catalysts for electrochemical reactions, carbon materials have been applied itself as electrocatalyst. One of the well-known approaches is oxygen reduction reaction (ORR) on nanostructured carbon materials. Extensive studies have reported that nitrogen-containing carbon materials possess similar catalytic activity for ORR in alkaline media as a commercial carbon supported Pt catalyst [1–4]. Very recently, carbon materials were used as electrocatalysts for water oxidation, which is the oxygen evolution reaction (OER), in spite of carbon corrosion at oxidative conditions. The selected literatures about OER on carbon electrodes are listed in Table S1. Carbon doped with heteroatoms [5], [6,7] or surface-oxidized carbon [8,9] show good electrochemical performance for OER that is even comparable to metal(oxide) catalysts. Furthermore, many efforts are under way to identify the

catalytic sites for ORR and OER on carbon materials by analyzing the surface change of carbon electrodes before and after the reaction [5,10]. Although the electrocatalytic activity of carbon materials could be used potentially as metal-free catalysts, the instability of carbon materials at its condition are rarely considered. Because the standard potential of carbon oxidation reactions is 0.207 V vs. RHE [11], carbon corrosion is inevitable at high anodic potential. At the cathode of fuel cells, where ORR takes place, the potential goes up to 1.4 V in abnormal conditions due to fuel starvation [12,13]. At the anode of electrolyzers, where OER occurs, the operating potential for the OER is practically above 1.5 V [14–16]. Under these anodic conditions, the oxidation of carbon to CO<sub>2</sub> and/or CO leads to the destruction of the carbon electrode.

Beyond many studies on ORR and OER activity of carbon-based catalysts, we intend to investigate the change of carbon electrodes due to its instability at oxidative conditions. In our previous study [17], we investigated the electrochemical degradation of multiwall carbon nanotubes (MWCNTs) in acidic media. MWCNTs at high anodic potential for OER in acidic media undergo first electrochemical activation by forming functional groups, followed by a passivation due to a fully

\* Corresponding author.

E-mail address: [saskia.heumann@cec.mpg.de](mailto:saskia.heumann@cec.mpg.de) (S. Heumann).

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covering oxide layer. In the present work, we chose glassy carbon as the investigating material, and compare the corrosion behavior of a carbon depending on the pH of electrolyte.

Glassy carbon (GC) is a type of non-graphitic carbon formed by pyrolysis of certain polymeric precursor. The microstructure of GC is composed of discrete fragments of curved carbon planes, like imperfect fullerene-related nanoparticles. GC synthesized at high temperatures above 2000 °C exhibits a network of stacked graphite-like ribbon molecules. Entities of polyhedral graphite crystals were also detected in commercial glassy carbon as used in our studies [18]. The network of randomly and tangled carbon planes forms a dense carbon structure. Due to low reactivity, high hardness, impermeability and good electrical conductivity of GC, it is commonly employed as an electrode material for electroanalysis [19,20]. Due to the assumed chemical inertness, it is also often used as a substrate to cast powder catalysts in order to evaluate their catalytic performance in electrochemical reactions. However, at high anodic potentials carbon oxidation can occur, giving rise to deterioration of the electrode and potentially affecting the evaluation of the electrochemical performance of catalysts. Nevertheless electrochemical oxidation of carbon can be advantageous for electrochemical sensors, as it is generally agreed that the electrochemical oxidation of GC activates the electrode surface, leading to faster electron transfer kinetics [21–24].

The results demonstrated in the present study are important for interpreting electroanalytical and electrocatalytic data from studies using GC electrodes. We investigated the morphology and surface change of carbon electrodes caused by prolonged oxidation at high anodic potentials. To consider the wide variety of environments experienced in electrocatalytic reactions, the electrochemical degradation of carbon electrodes was characterized depending on the pH, especially acidic, neutral and alkaline media. The different degradation behavior of the carbon electrodes, and its dependence on the pH of electrolyte, is documented in this study. Since carbon is commonly used as an electrode material for electroanalytical and catalytic applications, the understanding of the electrochemical stability of carbon electrodes is of crucial importance for the electrochemical community.

## 2. Experimental

Glassy carbon (GC) disks (SIGRADUR G discs, 1 mm thick and 10 mm diameter, polished with diamond  $R_a > 50$  nm) were purchased from HTW (Hochtemperatur-Werkstoffe GmbH, Germany).

The electrochemical experiments were performed using a standard three-electrode cell consisting of a Pt wire as a counter electrode, a standard calomel electrode (SCE) and a mercury/mercury oxide (Hg/HgO) reference electrode. All values of the potential were corrected to reversible hydrogen electrode (RHE) [25]. The electrochemical oxidation of GC was performed in 0.5 M  $H_2SO_4$ , 0.5 M  $K_2SO_4$ , or 0.1 M KOH at the applied potential of 1.8 V vs. RHE for 24 h under Ar bubbling. In order to analyze the electrochemical change of the GC electrode, cyclic voltammetry was carried out in a range of potentials between the oxygen and hydrogen evolution reactions.

The GC before and after the prolonged electrochemical oxidation were characterized with several techniques to examine the change in morphological and physicochemical properties upon oxidation. The morphological changes of GC were determined by scanning electron microscopy (SEM, Hitachi) and atomic force microscopy (AFM). Energy-dispersive X-ray spectroscopy (EDX) was conducted, in conjunction with the SEM analysis, to analyze the elemental composition of the carbon surface. Raman spectroscopy was performed on a Thermo Scientific DXR Raman Microscope with a  $50\times$  magnification and 532 nm laser. Infrared spectroscopy was carried out in the attenuated total reflection (ATR) mode (Thermo Scientific<sup>®</sup> Nicolet iS50) using a DTGS detector and a diamond crystal. X-ray photoelectron spectroscopy (XPS) was measured using a Versaprobe spectrometer from Physical Electronics (PHI 5000 VersaProbe) employing monochromatic Al K $\alpha$

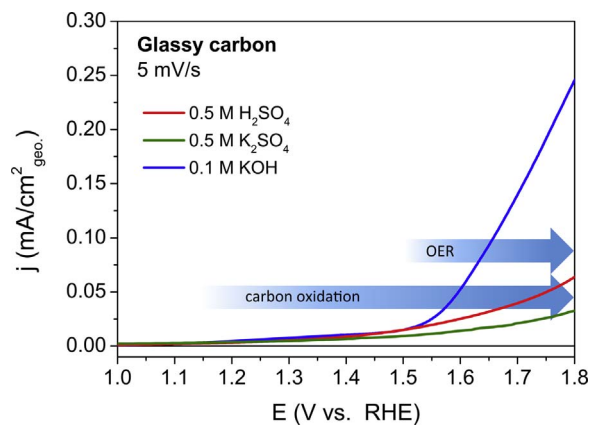


Fig. 1. Linear sweep voltammetry of GC disc at high anodic potential in 0.5 M  $H_2SO_4$  (acidic), 0.5 M  $K_2SO_4$  (neutral) and 0.1 M KOH (alkaline). Scan rate: 5 mV/s.

(1486.6 eV) radiation with a spectral resolution of 0.35 eV at pass energy of 23.5 eV. All measurements were performed with a spot size of 200  $\mu$ m diameter and with a take-off angle for 45°. The binding energy scale of the system was calibrated using clean gold surface with Au4f $_{7/2}$  at 83.98 eV, and correction using the C1s peak and valence band spectrum resulted in a constant position of the C1s core level at 284.5 eV  $\pm$  0.2 eV.

## 3. Results and discussion

Linear sweep voltammograms (LSV) of GC are shown in Fig. 1, scanned at anodic potentials between 1.0 and 1.8 V in acidic, neutral and alkaline media. The thermodynamic potential for carbon and water oxidation is at 0.207 V and 1.23 V vs. RHE, respectively. Because of slow reaction kinetics and intrinsic properties of the electrode materials, these reactions generally start above the thermodynamic potential. The oxidation current of GC gradually rises with sweeping of the anodic potential, where two notable points can be observed. At around 1.2 V a slight increase of the current is observable which can be mainly attributed to carbon oxidation. Above 1.5 V vs. RHE a significant increase of current is detected due to the anodic oxidation of water (OER) and ongoing carbon oxidation.

The electrochemical oxidation process on a carbon electrode is influenced by the water oxidation and can be confirmed by chronoamperometric measurements of GC applied at oxidative potentials in acidic media. The transient anodic current on a GC electrode at a fixed potential of 1.2 and 1.5 V gradually declines to a steady-state value (Fig. S1). Once oxygen evolution caused by water oxidation is involved in the oxidation process on the carbon electrode, at an applied potential of 1.8 V, the initial current increases with time, assuming that the surface of the carbon electrode undergoes vigorous change due to the oxidation. In order to investigate the surface change of GC caused by carbon oxidation, it was subjected to prolonged electrolysis at an anodic potential of 1.8 V vs. RHE where both, water and carbon oxidation, occurs simultaneously. Fig. 2 shows the chronoamperometry of GC at the anodic potential in 0.5 M  $H_2SO_4$  (acidic), 0.5 M  $K_2SO_4$  (neutral) and 0.1 M KOH (alkaline) solution. Significant current peaks are observed in the different media, which can be related to the formation of oxygen species on the GC electrode. The oxidation process is most rapidly in alkaline media, followed by the oxidation in acidic media. A steady state and therefore steady current is reached after one hour in both cases. The transition of oxidation current in neutral media is much lower and slower than in the other media, indicative of slow kinetics of the oxidation. A close look at Fig. 1 (Fig. S2) supports these observations also on the short time scale as the current increase assigned to the oxidation process begins at 1.2 V in alkaline media, at slightly higher potential in acidic media and convoluted to determine

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