Recent progress in the electrochemistry of planar and reticulated vitreous carbon: Fundamentals and applications

M. I. Awad1,2,*, M. M. Saleh1,2,# and T. Ohsaka1,$

1Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8502, Japan.
2Chemistry Department, Faculty of Science, Cairo University, Cairo, Egypt

ABSTRACT
This review outlines the recent published works on the fundamental studies and electrochemical applications of glassy carbon in both forms, i.e., planar glassy carbon (GC) and reticulated vitreous carbon (RVC) electrodes. Special attention is placed on our recent works for using glassy carbon electrode in hydrogen evolution reaction (HER), oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), and the relevant literature on these are also reviewed. This includes the use of electrochemically pretreated GC and modified GC electrodes. The effects of surface modification via oxidation of the GC were outlined.

KEYWORDS: reticulated vitreous carbon, glassy carbon, oxygen evolution, oxygen reduction, ozone electrogeneration

1. INTRODUCTION
Glassy carbon electrodes (GCEs) represent a main class of important electrode materials from both fundamental and application points of view. Many papers, review articles and several chapters in several books have been published in this area [1-5]. Glassy carbons have two forms; planar glassy carbon (GC) and reticulated vitreous carbon (RVC) electrodes. Advantages of carbon electrodes include wide potential window, low cost, relatively inert electrochemistry, and electrocatalytic activity for a variety of redox reactions. Both of them have common characteristics albeit RVC has more advantages from practical point of view since it has high surface to volume ratio which reduces the volume of the reactor of interest. Planar GC electrode, on the other hand, acquires its importance as an electrode for intensive fundamental studies in designing chemical and biochemical sensors and testing of electrocatalytic properties. In most of these applications GC with its ordinary properties cannot be used without modification. Surface of GC has high potential for chemical and electrochemical modifications, loading of precious metals and grafting [6-10]. One of the most important characteristics is the oxidation and reduction of organic and biological molecules in both aqueous and non-aqueous media [11-14]. Important applications also include batteries, supercapacitors and metals electrowining, and applications required ideal substrate for loading many catalysts [15-20].

The present review focuses on the properties of the GCE, its modification by electrochemical oxidation and its applications in hydrogen evolution reaction (HER), production of hydrogen peroxide (H₂O₂) and oxygen evolution reaction (OER).

2. Manufacture and properties of GC materials
Glassy carbon (GC) is made by heating different types of polymers. Polycrylo-nitrile is a common
Reticulated vitreous carbon (RVC) is different than planar GC with its porous foam-like structure. The structure of RVC is achieved by polymerization of a resin combined with foaming agents, followed by carbonization [5]. A low volume disordered glassy porous carbon was obtained with some crystallographic order and a continuous skeletal structure. Classically, polyurethane and phenolic resins are used although furfuryl and epoxy resins can also be used; these have 3% and 50% carbon yield, respectively. The foam resin is, typically, dried and cured at 120°C then carbonised at 700-1100°C. The starting polymer and the temperature of the carbonization have a great influence on the physicochemical properties of glassy carbons [5]. Controlling parameters of the process include the solution viscosity, the concentration of resin, the type of solvent, the concentration of curing agents, the precursor foam pore size and the firing temperature. Glassy porous carbon can also be obtained from high molar mass thermoplastic carbons (pitch) [5, 27]. During the production of RVC, a linear shrinkage of approximately 30% occurs. The porosity (void fraction) of RVC range is between 0.90 and 0.97 depending on the ppi grade, and briefly speaking, a surface area of approximately 65 cm² cm⁻³, for the 100 ppi grade is obtained [28]. The honeycomb structure of the RVC is given in Fig. 1 A, B at different magnifications. The structure is formed by strands of carbon, also called struts that form a so-called trigonal strut, which appears like a triangle from above but is in fact more like a tetrahedron, with one of the strands hidden out of view under the others. Replication of this arrangement gives rigid structure to the RVC [5]. RVC does not combust after heating (less than 350°C) to bright incandescence in air followed by removal of the heat source. It is highly resistant to
in 0.1 M H$_2$SO$_4$ was performed potentiostatically at potential of 2 V (SCE). Figures 3A-C show current transient of the oxidation process of the three electrodes for specific time periods. For the flow-through porous electrode the flow rate was 0.08 cm s$^{-1}$. The $i$-$t$ relations are similar for all the electrodes. The only difference is the maximum shown for the planar GC electrode after about 30 s. The curves for the planar GC electrode are similar to that obtained in literature for GC [33]. The obtained high current at the beginning was attributed to the charging of the double layer. The current decreases to a minimum value at about ten seconds and begins to increase again to reach a constant value. The current increase in Fig. 3 corresponds to the activation of the electrode process towards water oxidation [33]. The increase in current reaches its saturation limit once the water oxidation process is catalyzed to its possible maximum extent. The assignment of the increase in the current reaching its saturation value to electrolytic oxidation of water was previously proved by in situ measuring of the dissolved oxygen concentration where the oxygen concentration was found to increase immediately after applying the anodization potential [33]. Note that the initial high currents in curves b are larger.

### 3. Modifications of GC surface

Modifications of GC electrodes include chemical and electrochemical oxidation, loading with precious metals (e.g., Ni, Pb Pt and Au) or grafting by loading organic molecules of specific fictionalization [29-40]. In this part we will focus on the electrochemical treatment by anodic oxidation of the GC electrodes. While the literature for the characterization and applications of chemically and electrochemically oxidized planar GC electrode are vast, only few papers have been reported in regard to the chemical or electrochemical oxidation of reticulated vitreous carbon (RVC) [41]. The electrochemical pretreatment procedures of planar GC electrode can be anodic oxidation [42-44] or cathodic reduction [44, 45]. The anodic activation may be in some cases followed by reduction or potential cycling [46-49]. The electrocatalytic activity of the pretreated GC depends not only on the pretreatment procedure but also on the electrochemical active species participating in the electrochemical reaction [32]. In other words, the pretreatment process may activate a specific electrochemical reaction. The oxidation has always been aimed to be applied in electroanalysis of biochemical species [50-52], electrochemical capacitors [15, 16] and important electrocatalytic reactions such as oxygen reduction reaction (ORR). Carbon electrodes have long been known for its selectivity for oxygen reduction to H$_2$O$_2$ [53]. It has been reported in literature that anodically oxidized glassy carbon electrode imparts better electrocatalytic activity and stability behavior towards oxygen reduction both in acid and alkaline solutions [29, 54, 55].

#### 3.1. Characterization of electrochemically oxidized GC

The oxidation of three types of electrodes was conducted in order to compare their behaviors during the course of the oxidation in acid solution. These are planar GC and RVC electrodes (as flooded (stationary solution) and flow-through porous electrodes). The flow system and the arrangement of the flow-through porous electrode is given in Fig. 2. Oxidation of the three electrodes in 0.1 M H$_2$SO$_4$ was performed potentiostatically at potential of 2 V (SCE). Figures 3A-C show current transient of the oxidation process of the three electrodes for specific time periods. For the flow-through porous electrode the flow rate was 0.08 cm s$^{-1}$. The $i$-$t$ relations are similar for all the electrodes. The only difference is the maximum shown for the planar GC electrode after about 30 s. The curves for the planar GC electrode are similar to that obtained in literature for GC [33]. The obtained high current at the beginning was attributed to the charging of the double layer. The current decreases to a minimum value at about ten seconds and begins to increase again to reach a constant value. The current increase in Fig. 3 corresponds to the activation of the electrode process towards water oxidation [33]. The increase in current reaches its saturation limit once the water oxidation process is catalyzed to its possible maximum extent. The assignment of the increase in the current reaching its saturation value to electrolytic oxidation of water was previously proved by in situ measuring of the dissolved oxygen concentration where the oxygen concentration was found to increase immediately after applying the anodization potential [33]. Note that the initial high currents in curves b are larger.
than the initial currents of the fresh electrodes due to increase of the surface area and hence increase of the charging current. It can be concluded that the electrolyte flow does not affect the general features of the i-t curve as evident from Fig. 3B and C.

Shown in Figure 4 are SEM images of different sections (slices) of RVC flow-through porous electrode obtained after oxidation for 20 min at 2 V. The electrolyte was 0.1 M H₂SO₄ flowing at 0.08 cm s⁻¹. We used the 20 min oxidation here in order to obtain a considerable penetration depth of the current to the interior of the porous electrode. The roughness is taken as a measure of the oxidation extent [6]. As shown from the figure the roughness decreases as going down from the front of the electrode at x = 0 to the back at x = 2 cm for an electrode with 3 cm thickness. The image at 2 cm is completely smooth indicating lower extent of oxidation. The images reveal that only about one half of the porous electrode was subjected to stronger oxidation. The non-uniform distributions of the oxidation extent are attributed to the non-uniform distributions of the potential and current within the bed [56, 57]. At the present case the mixed ohmic and kinetic charge transfer resistances may affect the present current distributions within the porous electrode. In principle, optimum conditions e.g., higher electrolyte conductivity and thinner electrodes could be chosen to obtain a more uniform distribution of the oxidation extent within the RVC matrix.

X-ray photoelectron spectroscopy (XPS) is a strong surface analytical technique. It is widely used for probing the surface oxygen concentration and the surface functional groups on carbon electrodes [58, 59]. It has been utilized as an efficient tool for the characterization of carbon electrode pretreatment. A wide range of survey spectrum of plain (untreated) RVC sample was taken (data are not shown) and as expected the spectrum shows only two peaks at binding energies of 284.1 and 532.0 eV corresponding to carbon and oxygen, respectively, in agreement with the literature [60]. Only short range spectra for oxygen and carbon are shown in Fig. 5. The curve fitting of both peaks was performed using the “Asymmetric Gaussian-Lorentzian Formula”. The values of the peak intensity of both peaks (for O1s and C1s) were obtained and the oxygen-to-carbon ratio (Φ) was calculated from the following expression [61]:

\[
\Phi = \frac{(I_o / S_o)}{\sum (I_i / S_i)}
\]

Fig. 3. Current-time relations for the anodic oxidation of different electrodes obtained by applying constant potential of 2.0 V for 5 min.; A) GC, B) flooded RVC and C) flow-through porous RVC electrode (in 0.1 M H₂SO₄ flowing at 0.08 cm s⁻¹).
Recent progress on electrochemistry of vitreous carbon

The survey spectrum of the oxidized RVC was similar to the untreated sample and the two peaks corresponding to oxygen and carbon are also revealed at same binding energies mentioned above for the untreated electrode. However, the morphology of oxygen peak does not significantly change while that of carbon is accompanied by two shoulders and one peak at high binding energies, typically at 285.2, 286.2 and 289 eV (see Fig. 6). As reported, where $I_0$ and $S_0$ are the peak intensity and the sensitivity factor for oxygen, respectively and $I_j$ and $S_j$ are the peak intensity and the sensitivity factor for an element j, respectively, where j is carbon and oxygen. The oxygen to carbon ratio in this case equals 0.2. This value is comparable with the reported values for untreated glassy carbon electrode [62, 63].

The distribution of the O/C ratio within the porous bed was estimated using XPS measurements for the same samples (sections) of Fig. 4. The survey spectrum of the oxidized RVC was similar to the untreated sample and the two peaks corresponding to oxygen and carbon are also revealed at same binding energies mentioned above for the untreated electrode. However, the morphology of oxygen peak does not significantly change while that of carbon is accompanied by two shoulders and one peak at high binding energies, typically at 285.2, 286.2 and 289 eV (see Fig. 6). As reported,

![Fig. 4. SEM micrographs obtained for oxidized RVC (3.0 cm thickness) at different depth, $x$ inside the electrode; 1) $x = 0$, 2) 0.5, 3) 1.0, 4) 1.5 and 5) 2.0 cm. RVC was oxidized using flow-through assembly by holding the potential at 2.0 V (Ag/AgCl) for 20 min in 0.1 M H$_2$SO$_4$ flowing at 0.08 cm s$^{-1}$.](image-url)
Fig. 5. C1s and O1s XPS spectra of plain (untreated) RVC.

Fig. 6. C1s (A) and O1s (B) XPS spectra of oxidized RVC. (C) Curve fitting spectra of C1s of oxidized RVC.
the formed two shoulders in addition to the new peak at 289 eV correspond to the functional groups generated on electro-oxidation of the electrode [48, 64]. The peak corresponding to carbon was deconvoluted into different surface functional groups as shown in Fig. 6C. The peak at 284.2 eV is ascribed to the graphitic carbon and that at 285.2 is ascribed to a type of carbon in phenol. The peak at 286.2 eV is ascribed to carbon in carbonyl functional group and finally that at 289 eV corresponds to carbon in the carboxylic group [48]. The oxygen/carbon ratio in this case was found to increase to 0.38 as compared to the untreated RVC sample (Fig. 5). In this case oxygen to carbon ratio was calculated using the following equation:

\[
\frac{O}{C} = A_{C-OH} + 2 \times A_{COOH}
\]  

where \( A_{C-OH} \), \( A_{C-O} \) and \( A_{COOH} \) are the intensity ratios of the different functional groups in the C\(_{1s}\) spectrum.

Fig. 7 shows the XPS spectra corresponding to oxygen taken at different depth inside the RVC electrode. The distance notation, \( x \) is the same as in Fig. 4 for the same samples (sections). The oxygen to carbon ratios were calculated based on Eq. 2 and its change with the depth inside the RVC electrode is given in Fig. 8. The O/C ratio decreases with the depth inside the electrode down to a value of 0.21, which is very close to the value (0.2) of the plain (untreated) electrode. This indicates the non-uniform distribution of the potential within the porous electrode. It can be concluded that around one half of the electrode is utilized in the oxidation process. These results confirm the conclusion extracted from the SEM results shown above. It is noteworthy to mention that we can obtain different distributions of the O/C ratios within the porous electrode by proper control of the anodic oxidation conditions.

4. Electrochemical hydrogen evolution reaction (HER)

Hydrogen and hydrogen energy are important issues for the current scientific literatures both for its technological and academic importance. Storage of energy in a form of hydrogen and using of hydrogen gas for direct energy conversion devices such as fuels cells represents a core for the energy future. The advantage of hydrogen energy is the
high power output, high efficiency and zero emission of pollutants. Those factors drove the world attention to the hydrogen energy as a strong candidate for replacing ordinary power sources. The electrochemical production of H₂ represents an important and main source for H₂ gas of a high purity. Hydrogen is important both for industry and energy storage applications. The development of reliable and cost effective technologies for the production of pure hydrogen is a challenging issue from electrochemical engineering point of view. For instance, for the H₂/O₂ PEM fuel, ultra pure hydrogen gas (as a fuel) is a pre-requisite. Most important conditions to fulfill good catalyst conditions are; high electrocatalysis, high stability and chemical availability of the electrocatalyst. Pure hydrogen represents a main product which is consumed in many industries. It is a key reactant needed to produce commonplace chemicals such as ammonia. The petrochemical industry uses hydrogen gas to process common fossil fuels, upgrading them to purer forms. Many electrode materials have been used for the electrochemical production of hydrogen. Those include metal, bimetallic and conducting polymer-metals composites electrocatalysts. Carbon electrode is not good candidate for HER and yet needs modifications with metals such as Ni, Ag, Au or Cu to increase its electrocatalytic properties towards HER.

In our previous works [65, 66], the hydrogen evolution reaction was studied at different type of metal loadings onto RVC matrix in alkaline medium. Copper and nickel were used and the results of HER were compared to the planar GC electrode. A mathematical model was developed to simulate the HER on GCE and the system was optimized and important kinetic parameters such as exchange current densities of HER on Cu/RVC or Ni/RVC were determined. Both planar glassy carbon and RVC were used in the measurements for comparison. The RVC was used in a flow-through porous electrode design where the electrolyte (alkaline) was forced to flow through the electrode (see Fig. 2). This is an advantage since the evolving gas bubbles are swept out of the pores resulting in a lower polarization and hence lower power consumption. Nickel metal is currently used as a cathode for water electrolyzers, and different procedures were introduced to prepare nickel electrodes with high specific surface areas. These include sintering micro porous nickel [67] production of nanoporous Raney-Nickel [68] and incorporation of Ni into PolyHIPE (high internal phase emulsions) polymer (PHP) matrix [69]. Three-phase (solid-liquid-gas) porous electrodes could be a special category of porous electrodes in which several operating parameters inherently control the overall performance of electrodes.

Fig. 8. The relation between oxygen to carbon (O/C) ratio and the dimensionless distance, y inside the electrode.
Of particular importance, the gas bubbles that are evolved accumulate inside the porous matrix resulting in non-uniform distributions of potential and current and, hence, in a lower effectiveness factor of the porous electrode [70]. Optimizing the electrolyte flow rate by other structural and transport parameters plays an important role in maximizing the performance of three-phase porous electrodes. Mathematical modeling can help to simulate the effects of different operating parameters on such systems.

Reticulated vitreous carbon (RVC) electrodes have been used as possible porous cathodes, operating in flow-through mode for the purpose of the electrolytic generation of hydrogen gas from flowing alkaline solutions. The electrocatalytic performance of the RVC cathode was tested under different operating conditions, such as electrolyte flow regimes and temperature. Also, the effect of electroplating the RVC with copper metal or Watts nickel in flowing electrolytes has been assessed. Potentiodynamic and galvanostatic techniques along with SEM images were used to investigate the performance of the different cathodes: bare (uncoated) RVC, copper-coated RVC (RVC/Cu), and Ni-coated RVC (RVC/Ni). Fig. 9 shows SEM images for the RVC, RVC/Ni and RVC/Cu.

The hydrogen evolution reaction (HER) was found to be enhanced by coating RVC either with Cu or Ni. Polarization behavior had higher rates for HER using RVC/Ni than using RVC/Cu or bare RVC. Fig. 10 reveals these results. This trend was confirmed by using a planar glassy carbon electrode (GC) coated with Cu and Ni under the same conditions. The activation energies for HER using RVC and RVC/Ni were estimated to be 32 and 14 kJ mol⁻¹, respectively. Current transient and SEM micrographs showed good electrocatalytic and mechanical stability of the metal loadings. There was no indication of loss of the catalytic properties after operation for 30 h. Model calculations helped to extract kinetic parameters for the HER using different electrodes.

5. ORR and H₂O₂ production

While electrochemical reduction of oxygen via 4e⁻ path is an ultimate goal for fuel cell electrochemistry, it is not so for electrochemical production of H₂O₂. The latter needs ORR via 2e⁻ to produce H₂O₂ rather than H₂O. Hydrogen peroxide is an important chemical for many applications and uses. Here carbon electrodes can offer such conditions and yet can be used as a cathode for ORR yielding H₂O₂.

The oxidation of reticulated vitreous carbon (RVC) and its impact on the oxygen reduction reaction (ORR) in H₂SO₄ solutions has been studied. The results are compared with that of a planar glassy carbon (GC) electrode. The oxidation process was characterized by using different electrode configurations, GC (planar) and RVC electrodes both with flooded (batch process) and flow-through assembly. Cyclic voltammetry and potentiodynamic were used for the characterization of the ORR. Anodically oxidized GC and flooded RVC are similar in that the ORR on both electrodes gave a more defined limiting current plateau. Oxidation of RVC led to an enhancement of its electrocatalytic
properties towards ORR. H₂O₂ production was tested at the oxidized RVC from flowing acid solutions. The oxidation of RVC resulted in higher current efficiencies and higher outlet concentrations of the H₂O₂ acid solutions.

The oxidation procedure was applied to RVC electrode at stationary conditions i.e., flooded assembly in 0.1 M H₂SO₄ for 1 and 5 min. Fig. 11 shows CVs for the ORR at the potential range from 0.3 to -0.7 V at the untreated and the above oxidized RVC electrodes in 0.1 M H₂SO₄. The background current at the oxidized RVC electrode is larger than that at the untreated electrode. At the oxidized RVC the oxygen reduction occurs at
that in Fig. 12B) of the quinone redox couple at the RVC electrodes; plain and oxidized for 1 and 5 min. These were found to be 0.0, 0.05 and 0.15 C for these electrodes, respectively. The zero charge of the plain RVC is evident from the CV of the plain RVC in Fig. 12B. Note that the charging current of the double layer (base current) was subtracted in each CV of the 1 and 5 min. oxidation. The number of surface quinone units \( S \) was estimated using the following equation:

\[
S = \frac{NQ}{nF}
\]  

(3)

where \( N \) is the Avogadro number, \( n \) is the number of electrons involved in the quinone-hydroquinone redox reaction represented by Eq. 4:

\[
Q + 2 H^+ + 2e = QH_2
\]  

(4)

and \( F \) is the Faraday constant. The number of active sites equals \( 1.4 \times 10^{16} \) and \( 5.2 \times 10^{17} \) quinone units for the oxidized RVC for 1 and 5 min, respectively. The increase of the peak current and positive shift of peak potential in Fig. 11 may be attributed to the increase of the quinone active sites.

6. Electrogeneration of H\textsubscript{2}O\textsubscript{2} on oxidized RVC

H\textsubscript{2}O\textsubscript{2} is an important chemical in the current technological, environmental and academic research fields [72, 73]. One of the most common materials used as a porous cathode for H\textsubscript{2}O\textsubscript{2} generation is the RVC electrode [74, 75]. In most cases the electrode was used as it is or with little treatment. The activation of RVC electrodes in all of the above applications was either not mentioned at all or only reported briefly as a repetitive potential scan of the RVC electrode to obtain reproducible electrochemical measurements. Strong et al., [76] have recently found that the oxidation of the RVC material with a mixture of H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3} significantly increased the number of carboxylic acid groups on the surface. This enabled a covalent attachment of functional groups capable of metal ion exchange. The electrochemical pretreatment effects on the electrochemical generation of H\textsubscript{2}O\textsubscript{2} at flow-
H₂O₂ is electrochemically produced via 2e reduction of oxygen as follows:

O₂ + 2H⁺ + 2e⁻ = H₂O₂  \( E^0 = 0.682 \text{ V vs. NHE} \)  \( (5) \)

In acidic media, there are two possible competitive reactions during this reduction, i.e., further reduction of H₂O₂ to H₂O and hydrogen evolution reaction (HER):

H₂O₂ + 2H⁺ + 2e⁻ = 2H₂O  \( E^0 = 1.776 \text{ V vs. NHE} \)  \( (6) \)

through porous electrode made of reticulated vitreous carbon are tested in comparison with those of GC electrode [40]. Do and Chen [77] studied the effects of the anodic treatment of graphite planar electrode on the electrocatalysed H₂O₂ electrogeneration. To the best of our knowledge, there is no systematic study on the anodic oxidation of RVC electrode and its effects on the electrocatalytic properties towards ORR albeit RVC electrodes have been used for many applications.

Fig. 12. CVs obtained at electro-pretreated GC (A) and RVC (B) electrodes at different scan rates in N₂-saturated 0.1 M H₂SO₄. Scan rates: (1) 50, (2) 100, (3) 200, (4) 300 and (5) 500 mVs⁻¹.
The main reaction in this case is the HER since further reduction of H₂O₂ to H₂O occurs at a relatively higher negative potential [78, 79]. Figure 13 shows polarization curves for the RVC and oxidized RVC electrodes in 0.1 M H₂SO₄ flowing at 0.08 cm s⁻¹. Both ORR and HER are enhanced at the oxidized RVC electrode (see Fig. 11). No limiting current plateau was observed at both electrodes due to ohmic drop within the electrode bed [80]. H₂O₂ was electrochemically produced at the plain RVC and compared with that obtained at the oxidized RVC (RVC was oxidized by applying a constant potential of 2.0 V in 0.1 M H₂SO₄ for 5 min). The electrogeneration of H₂O₂ was conducted using accumulation set up, i.e., a given volume of O₂-saturated H₂SO₄ was circulated over the RVC bed electrode at a suitable flow rate. The flow rate of 0.28 cm s⁻¹ was used to enable an efficient recirculation of the electrolyte. The outlet stream was recirculated for a period of 10 min. The absence of further reduction of H₂O₂ to H₂O in the present condition may enable the production of H₂O₂ of high concentration on accumulation. It has been reported that under similar conditions H₂O₂ is not reduced at more positive potential than -1.0 V [78, 79]. The current efficiency of H₂O₂ electrogeneration after accumulation, CE% can be given as:

\[
CE\% = \left[ \frac{2 F C_{H_2O_2} V}{i_{cell} t} \right] 100
\]

where \(C_{H_2O_2}\) is the H₂O₂ concentration in the outlet stream in mol cm⁻³, \(V\) is the volume (cm³) of the electrolyzed solution, \(i_{cell}\) is the observed current in ampere and \(t\) is the time of operation in s. Fig. 14 shows the effect of applied potential on the current efficiency of H₂O₂ obtained at the plain RVC (curve a), and oxidized RVC (curve b) electrodes. At the oxidized RVC electrode, the current efficiency of 100% was obtained at a potential as positive as -0.2 V and decreased as the applied potential was increased negatively. At higher negative potentials the HER becomes a
competing reaction with the ORR and the CE% decreases with the potential.

The effect of applied potential on the concentration of the produced H₂O₂ is shown in Table 1. As the potential increases negatively, the concentration of H₂O₂ increases in the examined potential range. That is to say, the higher rates of the ORR (higher currents) obtained at more negative potential are outweighing the decrease in CE%. The increase in current is more pronounced than loss in current efficiency. The increase in concentration of the produced H₂O₂ with the applied potential indicates an insignificant reduction of H₂O₂ to H₂O at this potential range.

The anodic oxidation of RVC resulted in the electrocatalysis of the oxygen reduction and consequently the generation of H₂O₂ at lower negative potentials than at the untreated electrode. This was reflected on the higher current efficiency obtained at the oxidized RVC. This point can be formulated suitably by calculating the energy saving, $\Delta \xi$ (at a certain electrode potential $E$) by the following equation;

$$\Delta \xi = \xi_{\text{bare}} - \xi_{\text{ox}}$$  \hspace{1cm} (9)

where $\xi_{\text{plain}}$ and $\xi_{\text{ox}}$ are the specific energy consumption in kWh per kg of H₂O₂ at the plain and the oxidized RVC, respectively. The specific energy consumption, $\xi$ can be generally given by;

$$\xi = \frac{i_{\text{cell}}E_{\text{cell}}t}{3600 m}$$  \hspace{1cm} (10)

where $E_{\text{cell}}$ is the measured cell voltage in volt and $m$ is the mass of H₂O₂ in g produced in time, $t$ (second). Eqs. 9 and 10 were applied to estimate the energy saving, $\Delta \xi$ at different electrode potentials. Table 1 shows the energy saving obtained at different potentials. In general, the energy saving increases with the electrode potential until it reaches a constant value. The difference in the cell currents at the plain and the oxidized RVC electrodes increases with the electrode potential (see Fig. 14). As the cell current increases, the rate of the electrochemical reaction (current) increases and also the amount of the produced H₂O₂ increases. A combination of the above effects results in the obtainable energy saving. At highly negative electrode potentials, however, the rate of the hydrogen evolution reaction becomes significant and no further energy saving is obtained beyond potentials more negative than -0.6 V. It is obvious that an energy saving is gained as a result of the anodic oxidation process, which should be considered for applications of RVC.

7. Oxygen evolution at modified GCE

In this section the recent applications of manganese oxide (MnOₓ) modified GCE in oxygen evolution will be summarized. MnOₓ is characterized by its natural abundance and low cost and its environmental compatibility in addition to its unique electrocatalytic properties, and thus it has made it one of the most promising electrode materials for many applications. Mn oxides are commonly prepared by co-precipitation [80, 81], thermal decomposition [82], physical vapor deposition [83], sol-gel processes [84, 85], hydrothermal synthesis [86], and electrochemical methods [87-95].

<table>
<thead>
<tr>
<th>Applied potential / V</th>
<th>$C_{H_2O_2}$ / µM</th>
<th>$\Delta \xi$ / (kWh per kg H₂O₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare RVC</td>
<td>Oxidized RVC</td>
<td></td>
</tr>
<tr>
<td>-0.3</td>
<td>27.5</td>
<td>52.5</td>
</tr>
<tr>
<td>-0.4</td>
<td>22.5</td>
<td>57.5</td>
</tr>
<tr>
<td>-0.5</td>
<td>47.5</td>
<td>72.5</td>
</tr>
<tr>
<td>-0.6</td>
<td>62.5</td>
<td>102.5</td>
</tr>
<tr>
<td>-0.7</td>
<td>62.5</td>
<td>102.5</td>
</tr>
</tbody>
</table>
Developing of non-noble metal catalysts for oxygen evolution and reduction is of interest for fuel cells that use alkaline electrolyte solutions. Among these electrocatalysts MnOx is one of the most promising catalyst for this purpose [95-99]. Oxygen evolution reaction (OER) plays a prominent role in electrochemical science and technology as it is inherently involved in many vital applications, e.g., energy conversion and energy storage devices [100]. It couples many of the cathodic processes occurring in aqueous solutions such as water electrolysis. It is considered as the main source of overpotential in the industrial water electrolysis processes. Thus, a great interest is directed to the catalyst of this reaction for developing of a low-overpotential oxygen evolution anode which has a prime importance in electrochemical technology. Water electrolysis is traditionally carried out in alkaline media for the production of highly pure hydrogen gas [101-105]. Alkaline media are preferred because of the less susceptibility of the anode to corrosion problems and thus cheaper materials with long life time can be used as efficient anodes [106, 107]. Some metal oxide-based electrodes have been reported to catalyze the OER. Among them Ni and Co oxides have been extensively studied [108-115]. Various Mn oxides have been also reported to catalyze the OER; the extent of catalysis is based on the synthesis method of the electrode as well as on the nature of the dopant such as Mo or W [116-119].

7.1. Preparation and characterization

MnOx nanoparticles (nano-MnOx) were electrodeposited onto GCE from a solution containing 0.1 M Na2SO4 + 0.1 M Mn(CH3COO)2 via cycling the potential between 0.0 and 0.4 V vs. Ag/AgCl/KCl(sat) at 20 mV s-1 [99]. The SEM of the thus prepared nano-MnOx/GC is shown in Fig. 15. The MnOx was electrodeposited homogeneously on the entire surface of the GC electrode in a porous texture, which enables the accessibility of the solution species to the underlying substrate through nano channels across the MnOx nanotexture. The electrodeposited nano-MnOx/GC has been characterized using XRD and XPS [92, 93]. X-ray photoelectron spectroscopy (XPS) results proved the effective deposition of nano-MnOx on GC [93]. The X-ray diffraction (XRD) pattern of the MnOx modified electrode revealed characteristic peaks of the manganite (manganese oxide hydroxide, γ-MnOOH) phase appeared at 2θ = 26.58°, i.e, indicating the electrodeposition of MnOx in a single crystalline phase [92, 93].

![Fig. 15. SEM images of the nano-MnOx modified GC electrode. The nano-MnOx was electrochemically deposited from an aqueous solution of 0.1 M Na2SO4 containing 0.1 M Mn(CH3COO)2 by applying 50 potential cycles between 0 and 0.4 V vs. Ag/AgCl/KCl (sat.) at potential scan rate of 20 mV s⁻¹.](image)

7.2. Electrochemical measurements

Figure 16 shows the CV response measured in N2-saturated 0.5 M H2SO4 at (a) bare and (b) modified GC electrode. The MnOx possesses some sort of electrochemical activity as revealed from the broad (rather small) reduction peak located at ca. 1.1-1.2 V [89]. The following redox reaction may account for the observed redox response [120-122]:

\[
\text{MnO}_2 + \text{H}^+ + e^- \rightarrow \text{MnOOH}
\]  

This reaction involves a reversible proton insertion process in acidic media concurrently with a reversible change of the oxidation state from Mn(IV) to Mn(III) [123].

Fig. 17 shows linear scan voltammograms (LSV) for the oxygen evolution reaction (OER) measured in N2-staurated 0.5 M KOH solution at (a) bare and (b) nano-MnOx modified GC electrodes. This figure shows a significant enhancement of the polarization behavior of the GC upon modification with nano-MnOx; around
γ-MnOOH phase has been proposed to be involved in one (or more) of the above steps according to:

\[ 2 \gamma\text{-MnOOH} + (O^-)_{\text{ads}} \rightarrow 2 \text{MnO}_2 + H_2O + e^- \] (16)

\[ \text{MnO}_2 + (OH)_{\text{ads}} \rightarrow \gamma\text{-MnOOH} + (O)_{\text{ads}} \] (17)

where the subscript term “ads” refers to surface adsorbed species.

7.3. Origin of the electrocatalytic enhancement

The OER is an anodic process which takes place at most of the metal electrode surfaces at potentials sufficiently anodic to allow for the formation of various kinds of oxides. Some of these oxides are known to enhance the OER, e.g., nickel oxide in the β-phase (i.e., NiOOH) [124, 125]. This oxide is thought to participate in the reaction mechanism in such a way that facilitates the charge transfer. In the current study the electrodeposited manganese oxide (γ-MnOOH) is of an isomorphous structure to NiOOH and thus is likely to function similarly towards the OER in alkaline media. Thus, the following mechanism was suggested for the observed enhancement of the OER [91, 124].

\[ \text{OH}^- \rightarrow (OH)_{\text{ads}} + e^- \] (12)

\[ (OH)_{\text{ads}} + OH^- \rightarrow (O^-)_{\text{ads}} + H_2O \] (13)

\[ (O^-)_{\text{ads}} \rightarrow (O)_{\text{ads}} + e^- \] (14)

And finally

\[ 2 (O)_{\text{ads}} \rightarrow O_2(\text{gas}) \] (15)

Fig. 16. CVs response obtained at (a) bare and (b) nano-MnOx modified GC electrode in N\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) at potential scan rate of 100 mV s\(^{-1}\). The nano-MnO\(_x\) modified electrodes were prepared as mentioned in the caption of Fig. 15.

Fig. 17. LSV for the OER in N\(_2\)-saturated 0.5 M KOH at (a) bare and (b) nano-MnOx/GC electrode at potential scan rate of 20 mV s\(^{-1}\). The nano-MnO\(_x\) modified electrodes were prepared as mentioned in the caption of Fig. 15.

300 mV negative shift in the onset potential of the oxygen evolution is observed.

8. Ozone electrogeneration

In this part the ozone electrogeneration at carbon electrodes will be reviewed with special attention to our recent work in this area. In the previous section the oxygen evolution catalysis is mentioned. In fact for an electrode to be suitable for ozone electrogeneration it should be not active for oxygen evolution. Ozone (O\(_3\)) is the candidate for the application of advanced oxidation technology which involves the hybrid use of several oxidants at the same time. It is the first choice for better oxidation performance both from environmental and technological points of view [126, 127], and for achieving a high purification standard of drinking water [128-132].
Generally, there are two methods for the generation of O₃, the electrochemical and the corona methods. The former leads the latter one as it generates O₂ at higher current efficiencies and it enables on-site applications of O₃ which is a remedial for the instability of O₃ [133-137].

The electrogeneration of O₃ at high current efficiency is of prime importance [133, 138-162] for forcing the application of O₃ in many fields such as water drinking, silicon wafer cleaning in semiconductor device manufacturing, wood pulp bleaching, combustion of resistant organic pollutants, and clean-up of effluents pushing the development of a chlorine-free technology [163-169]. The selection of a suitable anode for electrogeneration of O₃ is the main challenge. Several electrodes such as the costly Pt [155, 170], glassy carbon [71], boron-doped diamond [159] and lead oxide [146, 171-177] have been used for O₃ electrogeneration. An efficient electrode for the electro-generation of O₃ is the one that fulfills the most important requirements; that is impeding the oxygen evolution, which is thermodynamically favorable over O₃ evolution (see Eqs. 18 and 19) and achieving the stability terms.

\[
\begin{align*}
O_2 + 4H^+ + 4e^- &= 2 H_2O \quad E^o = 1.23 \text{ V} \quad (18) \\
O_3 + 6H^+ + 6e^- &= 3 H_2O \quad E^o = 1.51 \text{ V} \quad (19)
\end{align*}
\]

Carbon electrodes have been reported to be inactive for O₃ evolution under common experimental conditions due to its instability for the severe environment formed in the anode compartment. The latter includes the formation of strong oxidant, applying a high anodic potential for generation of O₃, and operating at low pH in the anodic compartment [146]. Under special conditions of very low temperature and in the presence of fluoride-containing electrolytes, glassy carbon electrode (GCE) has been proved to be an efficient O₃ generator with a high current efficiency of 62% at -5°C [133]. The modification of the adsorbability of the O₂ intermediate in presence of fluoride anion increases the O₃ yield [146]. Using low temperature is also important in increasing the yield as decreasing temperature generally increases O₃ yield via inhibiting O₂ electrochemical evolution and decreasing the continuous decomposition of O₃ which is significant at room temperature [158, 163].

However, using such drastic conditions is not facile for practical applications. Among noble metals, a platinum electrode is considered to be the candidate favorable for retarding O₂-evolution [178, 179], and it has been also reported to produce high current efficiency for the generation of O₃ at low temperatures, e.g., -63.5°C [146, 180]. This efficiency significantly decreases upon increasing temperature to room temperature [146, 180].

Electrogeneration of O₃ has been also studied at porous electrodes, especially flow-through porous electrode [181, 182]. Flowing electrolyte or continuous process has advantages over batch process as it gives a continuous feed of the dissolved products. Three-dimensional electrodes made of RVC have diverse applications especially when they operate as flow reactors [5, 183]. They have been suggested for waste water treatments [184, 185] and removal of heavy metal ions from dilute streams [56, 185, 186]. The combination of the properties of Pt and RVC resulted in a suitable arrangement for O₃ generation using stationary and flowing H₂SO₄ solutions has been reported [182]. Kraft et al. [187] used diamond planer electrode for the electrogeneration of O₃ from flowing solutions. Operating porous electrode in a flow regime offers many merits such as sweeping out the gas bubbles. Accumulation of gas bubbles deteriorates the overall performance of the porous electrode and affects the polarization and current distributions within the porous electrode [66, 188, 189]. In addition, using continuous feeding of O₃ aqueous solutions could solve the problem of continuous decomposition of O₃.

8.1. Electrogeneration of ozone at flooded RVC

The electrogeneration of O₃ at RVC/Pt electrode both in flooded and flow regimes has been reported [181]. In case of flooded electrode the electrogeneration of O₃ at a constant potential of 4.0 V applied for 5 min was increased from 0.2% at bare RVC to 1.6% at RVC/Pt electrode. This value is more than twice the reported value at the planar platinum electrode [136].

8.2. Electrogeneration of ozone at flow-through RVC

8.2.1. Effect of potential

The electrogeneration of O₃ using a flow-through regime arrangement produces a continuous feeding
of O₃-containing streams. Several parameters have been studied including the effect of acid concentration, flow rate and potential. The current efficiency and power saving for O₃ electrogeneration at different applied anodic potential in the potential range from 2 to 4 V are shown in Table 2. The lower limit of this potential range (2.0 V) was selected to be higher than the thermodynamic potential of the O₃ evolution and the upper limit (4.0 V) to test the performance of the electrode at a relatively high potential. The current efficiency (CE%) per single pass was determined from Eq. 8. Specific electrical energy consumption (SE) in kWh per kg of O₃ was determined by Eq. 10. The data in Table 2 reveals that the highest current efficiency is obtained at potential around 3.0 V. The concentration obtained at 3.0 V was also comparable to that obtained at higher potentials. At the same time, a much lower specific energy consumption compared to that at higher potentials was obtained.

8.2.2. Effect of acid concentration

The effect of acid concentration on the electrogeneration efficiency of O₃ and the specific energy consumption at different acid concentrations at a specific electrode potential holding the potential for 5 min and at a specific flow rate is shown in Fig. 18. The current efficiency is shown in the inset at the same conditions. The current efficiency was not significantly changed with increasing the acid concentration (inset). As the acid concentration increases the Cₒ₃ increases and the specific energy decreases. However, using a high concentration of acid may result in a new competition reaction (persulfate formation) with O₃-evolution in addition to the unavoidable oxygen evolution. The decrease in SE is due to the decrease in the cell voltage upon increasing the electrolyte concentration. Minimum specific electrical energy consumption at a Cₐₐcid 1.0 M was obtained.

8.2.3. Effect of flow rate

Figure 19 shows the relationship between the O₃ concentration in the outlet solution and the flow rate obtained at an applied potential of 3.0 and 4.0 V in 0.1 M H₂SO₄. The outlet concentration of O₃ increased with the decrease in flow rate. As the flow rate decreases, the residence time increases leading to the increase in the concentration of O₃ in the outlet effluent solution. At a certain flow rate, the Cₒ₃ obtained at 4.0 V is higher than that obtained at 3.0 V even though the current efficiency at 3.0 V is higher than that at 4.0 V. This could be understood from the high current sustained, i.e., higher electrochemical rate of O₃ generation at 4.0 V in comparison with that at 3.0 V. This may outweigh the higher current efficiency obtained at 3.0 V. A desired O₃ concentration may be obtained at a specific flow rate using a flow-through porous electrode, because not only the electrochemical parameters but also the hydrodynamic parameters affect the product concentration.

8.2.4. Stability of the electrode

The stability of RVC/Pt electrodes has been tested by recording the current-time relation at a specific electrode potential. When the electrolysis was carried out in 0.1 M H₂SO₄ at 4.0 V, for the flooded RVC/Pt electrode the current decreased from 73 to 60 mA cm⁻² for an operation period of 2 h. The current efficiency decreased from 1.6 to 1.2% during this period. On the other hand, for the flow-through porous electrode a constant current of 80 mA cm⁻² was obtained for about 20 h in 0.1 M H₂SO₄ at 3.0 V. The current efficiency

<table>
<thead>
<tr>
<th>Applied potential /V</th>
<th>% CE</th>
<th>[O₃] / µM</th>
<th>SE (kWh kg⁻¹ O₃ x 10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.6</td>
<td>5</td>
<td>0.75</td>
</tr>
<tr>
<td>2.5</td>
<td>1.9</td>
<td>10</td>
<td>1.06</td>
</tr>
<tr>
<td>3.0</td>
<td>2.2</td>
<td>24</td>
<td>1.37</td>
</tr>
<tr>
<td>3.5</td>
<td>1.8</td>
<td>23</td>
<td>2.18</td>
</tr>
<tr>
<td>4.0</td>
<td>1.5</td>
<td>25</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Table 2. Current efficiency, ozone concentration, and specific energy consumption obtained at different applied potentials.
Fig. 18. Effect of $C_{\text{acid}}$ and electrode potential on the concentration of the generated O$_3$ and specific energy at RVC/Pt electrode using flow rate of 0.08 cm s$^{-1}$. Inset shows the current efficiency of O$_3$ generation at different acid concentrations. Applied electrode potentials: (- - -) 3.0 and (—) 4.0 V.

Fig. 19. Effect of flow rate on $C_{\text{O}_3}$ at flow-through porous RVC/Pt electrode using applied potential of (a) 3 and (b) 4 V in 0.1 M H$_2$SO$_4$ and at 25°C.
remained constant during this period ($CE = 2.2\%$). However, the $CE\%$ decreased to a lower value after this period. The faster loss of the current efficiency at the flooded electrode may be attributed to the electroplating procedure of Pt. At the flooded electrode, a stationary electrolyte containing $H_2PtCl_6$ was used, while a flowing-electrolyte was used at flow-through porous electrode. In the latter case, a more uniform and effective deposition of Pt onto the RVC matrix may be guaranteed while in the former case the deposition takes place only on the external surface of the RVC matrix. At the flooded electrode the Pt was easy to be flaked off from the matrix. This point can be confirmed by studying the SEM in Fig. 20 in which the SEMs of the RVC/Pt were taken before (image a) and after (image b) being used for the electrolysis of 2 h. A considerable fraction of the surface Pt flaked off as shown in image b. This may help to understand the significant decrease in the current efficiency after the electrolysis at the flooded electrode. A similar conclusion can be driven to rationalize the loss of the efficiency of the flow-through porous electrode.

![Fig. 20. SEMs for RVC/Pt (a) before and (b) after being used for electrolysis of 2 h at flooded RVC electrode at 25°C. Pt was deposited from stationary 0.1 M $H_2SO_4$ solution containing 5 mM platinate by applying a constant potential of 0.0 V vs Ag/AgCl for 1 h.](image)

### Table 3. Some literature values for the electrogeneration efficiency of $O_3$ at different electrodes and experimental conditions.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Temp. ($°C$)</th>
<th>Electrolyte</th>
<th>Current density (A/cm$^2$)</th>
<th>Efficiency (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-PbO$_2$</td>
<td>RT</td>
<td>1 M $Na_2SO_4$</td>
<td>0.4</td>
<td>5.1</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3 M $H_2SO_4$ + KPF$_6$</td>
<td>0.8</td>
<td>&lt; 6</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>phosphate buffer (pH 7.5)</td>
<td>0.2</td>
<td>6.1</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>0.0</td>
<td>5 M $H_2SO_4$</td>
<td>0.6</td>
<td>&lt; 8</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>-63.5</td>
<td>3.25 M $H_2SO_4$</td>
<td>0.75</td>
<td>32.4</td>
<td>192</td>
</tr>
<tr>
<td>Pt</td>
<td>0.0</td>
<td>3.25 M $H_2SO_4$</td>
<td>0.75</td>
<td>1.2</td>
<td>193</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>11 M $HClO_4$</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti/RuO$_2$</td>
<td>0</td>
<td>5 M $H_2SO_4$</td>
<td>0.4 -1.4</td>
<td>0</td>
<td>147</td>
</tr>
<tr>
<td>Au, Pd</td>
<td>0</td>
<td>5 M $H_2SO_4$</td>
<td>0.4 -1.4</td>
<td>0</td>
<td>146</td>
</tr>
<tr>
<td>Sb-Ni doped SnO$_2$</td>
<td>0</td>
<td>0.1 M $H_2SO_4$</td>
<td>$E = 2.2$ V</td>
<td>36.3</td>
<td>194</td>
</tr>
<tr>
<td>Ti/IrO$_2$-Nb$_2$O$_3$</td>
<td>RT</td>
<td>3 M $H_2SO_4$ + 30 mM KPF$_6$</td>
<td>0.2 -1.4</td>
<td>12</td>
<td>193</td>
</tr>
</tbody>
</table>
Table 3 summarizes some of the reported values for the current efficiencies of O₃-electrogeneration obtained at different electrodes under various experimental conditions with that obtained at the RVC/Pt electrode. Usually, the generation of O₃ is carried out at very low temperature (0°C or lower) and in the presence of very high concentrated acidic medium as it is reported that the oxygen overvoltage increases with decreasing temperature and pH [162, 163]. Supporting electrolyte-containing F⁻ has been reported to give the high current efficiency as compared with those not containing F⁻. This has been attributed also to the increase of the oxygen overvoltage in the presence of F⁻ [146]. Foller and Tobias reported that on adding F⁻ to 3.5 M H₂SO₄, the anode potential of β-PbO₂ electrode shifted to high positive potential and this was reflected in the doubling of the ozone current efficiency [146]. However, electrogeneration of O₃ under drastic conditions of high acidity and in the presence of F⁻ limits the applications of O₃ as it decreases the endurance of the electrode and contaminates the O₃ solution with the corrosive F⁻. In addition, the generation of O₃ at very low temperature is another economical limitation.

**ACKNOWLEDGEMENTS**

The present work was financially supported by Grant-in-Aid for Scientific Research (A) (No.19206079) to T. Ohsaka, from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

**REFERENCES**