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Singlet oxygen and the origin of oxygen functionalities on the surface of carbon electrodes

Korbua Chaisiwamongkhol^[a], Christopher Batchelor-McAuley^[a], Robert G. Palgrave^[b], Richard G. Compton^{[a]*}

Abstract: The generation of oxygen-containing functionalities on pristine carbon surfaces is investigated and shown to be light sensitive, specifically to infra-red radiation. A mechanistic route involving singlet oxygen, $^1\text{O}_2$, is proposed and evidenced.

Carbon-based materials find extensive use as heterogeneous catalysts and catalyst supports. Challengingly, significant variation in the apparent activity of these materials is found to be reported in the literature. Certainly, the presence and diversity – both in terms of identity and concentration – of trace metallic impurities is one important aspect where low amounts heavily influence the electrochemical behaviour of these materials.^[1] Further, the surfaces of carbonaceous materials are reactive and “aging” effects leading to differing surface functionalities are documented. A variety of surface oxo groups, most notably quinonyl, hydroxyl, and carboxyl groups decorated on carbon electrode surface especially on the edge-plane defects have been characterised and reported.^[2] The presence of these oxygen functionalities alter the behaviour of the material both for electron transfer^[3] and provide active sites for catalysing various reactions.^[4]

Due to the diverse range of possible surface oxygen containing functionalities a number of mechanistic routes may contribute to their creation. Previous literature has focused theoretically on the interaction of oxygen-containing gas with model graphite structures^[5] and in some cases reporting experimental studies at high temperatures.^[6]

The route by which surface quinone and hydroxyl groups are formed is of distinct interest. Specifically triplet oxygen ($^3\text{O}_2$) is unable to directly participate in Diels-Alder cycloadditions and “ene” type reactions toward singlet state organic molecules.^[7] In contrast, singlet oxygen ($^1\text{O}_2$) has long been reported to be active. In the 1960s, Foote and Wexler revealed the utility of $^1\text{O}_2$ for generating oxygenated hydrocarbons including oxygenation of cyclic dienes and polycyclic aromatic compounds to give 1,4-endoperoxides, in a reaction analogous to the Diels-Alder [4+2] cycloaddition.^[8] For olefins containing allylic hydrogen atoms, $^1\text{O}_2$ reacts to give allylic hydroperoxides in which the double bond has shifted position a reaction which is analogous to the “ene” reaction.^[9]

In this study, the mechanistic pathway and the photosensitivity of making oxygen functionality on carbon electrode surfaces under atmospheric temperature and pressure are investigated.

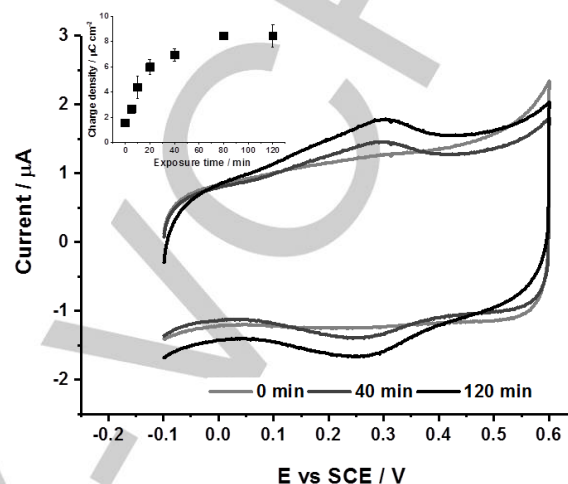


Figure 1 Cyclic voltammograms of oxygen functionalities on EPPG electrode after expose to the air for 0, 40, and 120 minutes tested in 0.01 M HNO_3 + 0.1 M KCl supporting electrolyte (pH 2) at a scan rate of 0.1 V s^{-1} . Inlay shows the plot of charge per unit area of the oxidative peaks as a function of exposure time (0, 5, 10, 20, 40, 80, 120 minutes).

Functionality on aged^[10] edge plane pyrolytic graphite (EPPG) surface was characterised electrochemically. Figure 1 shows a typical cyclic voltammogram (CV) in 0.01 M HNO_3 + 0.1 M KCl supporting electrolyte, with peak potentials at 0.293 V and 0.273 V vs. SCE for the oxidative and reductive processes. The presence and magnitude of the voltammetric wave for the redox active species on EPPG electrode surface increases with the exposure time in the air (Inlay Figure 1), but with a decreasing rate over time. The process leading to the formation of the surface redox species is inhibited in water. Immersion of the EPPG surface immediately after renewal into a solution of 0.01M HNO_3 (pH 2) + 0.1 M KCl supporting electrolyte did not lead to an increase in the magnitude of the redox wave (data in SI, Figure S3). Figure S4 depicts the variation of the voltammetric wave as a function of pH demonstrating the process to be reversible and to involve the transfer of an equal number of electrons and protons, most likely indicating the feature to be due to the presence of quinonyl surface species (or possibly phenolic). X-ray photoelectron spectroscopy (XPS) was performed on the electrode surfaces. XPS detected oxygen at >5 atomic% on all EPPG surfaces, even those measured immediately after polishing. Ar ion depth profiles showed that the oxygen was confined to the electrode surface and was not present in the bulk. In contrast, highly ordered pyrolytic graphite (HOPG) electrodes show undetectable levels of surface oxygen in XPS immediately after polishing,^[11] this difference is likely due to exposure of the edge planes in EPPG. On our EPPG electrodes, the oxygen signal from the XPS was an order of magnitude greater than that found by electrochemistry; this demonstrates that the redox active species identified

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electrochemically only corresponds to a small fraction (<10%) of the oxygen present on the EPPG surface (calculation data in SI section 5). Assignment of O1s XPS peaks to oxygen functionalities is challenging due to the small chemical shift that exists between different functional groups.^[12] As found by others^[13], we were not able to unambiguously assign the O1s environments to specific chemical environments.

The photosensitivity of the surface modification process was investigated. After surface renewal the EPPG electrode was exposed to differing light conditions. Figure S9 (A-D) show the cyclic voltammetric profiles of oxygen functionalities on EPPG surface after exposure to infrared, UV, a no light control, and infrared under a nitrogen atmosphere respectively. The electrochemical redox responses show qualitatively similar CV for all cases; however the magnitude of responses with time is different. Note that in this study EPPG electrode is chosen due to its high reactivity. The results of other types of graphite electrodes are included in the SI section 7.

The effect of different lighting conditions was analysed in terms of the voltammetric charge densities as a function of the exposure time. Figure 2 presents these data as a function of exposure time.

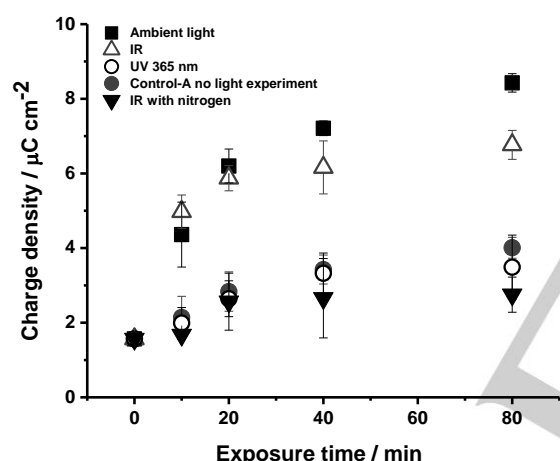


Figure 2 Comparison of plots of charge densities as a function of exposure time of different conditions including the exposure to normal light (■), IR (△), UV (○), control in dark conditions (●), and control IR under a nitrogen atmosphere (▼).

Note that in the absence of exposure to light the surface coverage of the formed surface redox activity moiety is significantly depleted. Moreover, the charge densities for an electrode exposed to an IR light source were comparable to the electrode being left under ambient conditions. In contrast UV light did not demonstrate an effect on the build-up of oxo groups on the electrode surface; the charge densities were comparable to that of the no light control experiments. This result strongly indicates the involvement of a photochemical process in the aging of the electrode surface and that the photo-sensitivity is predominantly associated with IR wavelengths. A further control experiment was performed where an electrode was exposed to IR light under a nitrogen atmosphere. The results were comparable to those of the no light control experiment. Such a result is consistent with the aging of the carbon surface being at least partially due to reaction with $^1\text{O}_2$.^[14] The transition

wavelengths from $^3\text{O}_2$ to $^1\text{O}_2$ are ca. 1270 nm and 1070 nm for its vibrational excited states $v=0$ and $v=1$ respectively.^[15] The home-fabricated IR coils employed as a broadband IR-generator irradiate a short-wave or near infrared (NIR) with the range from 780 nm to 1400 nm.^[16] This range of irradiated wavelengths is a close match to the molecular oxygen transition [$^1\Delta_g (v=1)$] \leftarrow [$^3\Sigma_g^- (v=0)$] and [$^1\Delta_g (v=0)$] \leftarrow [$^3\Sigma_g^- (v=0)$] absorption band. Note that the charge densities of an electrode exposed to ambient conditions show a slightly higher value than under IR conditions, indicating the surface modification likely occurs via multiple parallel pathways under ambient conditions.

To further evidence the involvement of $^1\text{O}_2$ in the aging process experiments to generate and expose $^1\text{O}_2$ to the electrode surface were made. In this study, the reaction of hydrogen peroxide with in-situ generated hypochlorite was employed to produce $^1\text{O}_2$ (experimental detail in SI section 8). The generation of $^1\text{O}_2$ was clearly evidenced by a red chemiluminescence from the reaction.^[17] This emission results from an excimer emission formed from two activated oxygen molecules. For the excited oxygen optical transitions $^1\Sigma_g^+ \leftrightarrow ^3\Sigma_g^-$ and $^1\Delta_g \leftrightarrow ^3\Sigma_g^-$ radiative half-life in the gas phase is estimated to be 7 sec and 45 min respectively.^[18] The generated $^1\text{O}_2$ gas was directly blown on to the electrode surface.

Figure S11 in SI presents the cyclic voltammetry profiles of redox species on EPPG electrode after exposure to $^1\text{O}_2$ gas for different times. The analysed charge densities plotted as a function of exposure time is depicted in Figure 3. Relatively larger and steadily increasing charge densities are obtained for EPPG electrodes that have been exposed to a flow of $^1\text{O}_2$. This result further evidences the likely involvement of $^1\text{O}_2$ in generating oxygen functionalities on the graphitic surface.

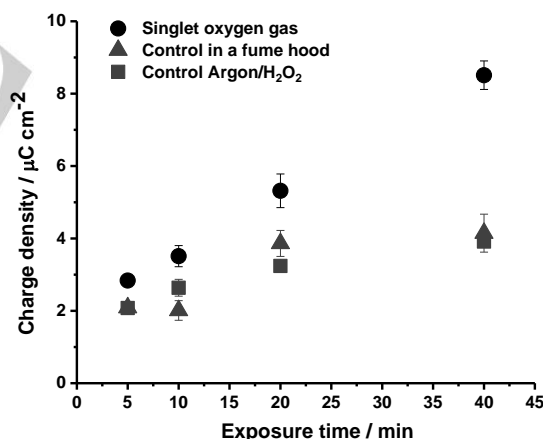


Figure 3 Charge densities of oxygen functionalities on electrode surface as a function of exposure time at various exposure conditions.

In view of organic synthesis, typical reaction modes often encountered with $^1\text{O}_2$ include Diels-Alder [2+2] and [4+2] cycloadditions and “ene” reactions.^[19] This pattern of reactivity is suggestive of the electrophilic character of the $^1\text{O}_2$. Accordingly, $^1\text{O}_2$ reacts favourably with electron-rich compounds or π -electrons on a carbon framework.^[20] Much literature has reported that $^1\text{O}_2$ undergoes oxygenation reactions with naphthalene, anthracene and higher members of the acene series resulting in endoperoxides and/or anthraquinone.^[8-9, 21]

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Considering basic structural units of graphitic materials, edge planes of graphite might be considered as electron-rich zones which preferentially react with $^1\text{O}_2$. Specifically, graphitic surface after fresh polishing cannot be perfect idealised structures: there must be “dangling bonds” at the edge. Mechanical renewal surface must lead to bond breaking and the generation of dangling bonds or radicals on the graphitic surface. Accordingly, one plausible process for generating oxygen-containing functionalities may arise from a Diels-Alder [2+2] and [4+2] of $^1\text{O}_2$ with electron-rich aromatic zones on graphite structures. The proposed mechanism of $^1\text{O}_2$ with graphitic surface is shown in Figure 4.

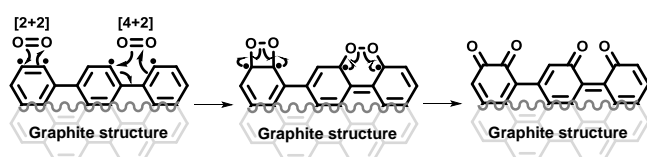


Figure 4 Proposed mechanism of singlet oxygen with graphitic structures

How might $^1\text{O}_2$ be formed under ambient aerial conditions at the electrode surface? Due to the spin forbidden nature of the transition^[14] it is most likely that the graphitic surface is itself acting as a sensitizer. Single-walled carbon nanotubes and fullerenes have been previously reported to be a very effective oxygen sensitizer.^[22] However, the plausible importance and role of metallic impurities in the graphite material should not be ignored. Metallic or other heavy atom centres may play an important role in the formation of $^1\text{O}_2$ due to spin orbit coupling.^[23]

In conclusion, singlet oxygen reacts with graphite surfaces to create quinone features evident in the electrochemistry and the catalytic properties of such surfaces.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry • singlet oxygen • surface chemistry • surface functionality

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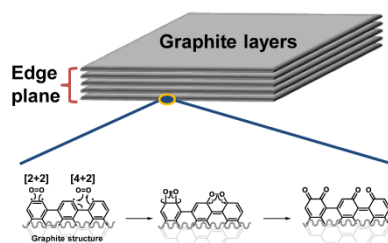
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Entry for the Table of Contents (Please choose one layout)

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The mechanistic pathway and the photosensitivity of generating oxygen functionality on pristine carbon surfaces are studied under atmospheric temperature and pressure conditions. A reaction route of singlet oxygen ($^1\text{O}_2$) with electron-rich aromatic zones on graphite surface is proposed.



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