Pseudocapacitance of Zeolite-Templated Carbon in Organic Electrolytes

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Abstract

Carbon materials and graphene-based materials, including reduced graphene oxides, can be used for supercapacitors and batteries, and they often show some amount of pseudocapacitance, which are owing to their oxygen functional groups. However, such pseudocapacitance is generally negligible in organic electrolytes and it has not attracted much attention thus far. In this work, we report a large pseudocapacitance derived from oxygen functional groups in a unique carbon material, zeolite-templated carbon (ZTC) which has significant amount of active edge sites. ZTC can be easily electrochemically oxidized in 1 M tetraethylammonium tetrafluoroborate dissolved in propylene carbonate ($\text{Et}_4\text{NBF}_4/\text{PC}$), and a large amount of oxygen functional groups are introduced into ZTC as a result. The electro-oxidized ZTC shows a high specific capacitance (330 F g^{-1}) mainly due to a large pseudocapacitive contribution from the oxygen functional groups in the organic electrolyte. Based on the experimental results, possible redox reactions in ZTC are proposed to be the formation of anion and cation radicals of quinones and ethers, respectively. Moreover, ZTC shows a similar pseudocapacitance also in 1 M lithium hexafluorophosphate dissolved with a mixture of ethylene carbonate and diethyl carbonate ($\text{LiPF}_6/\text{EC}+\text{DEC}$) which is used for lithium-ion batteries and lithium-ion capacitors.

Keywords

Electrochemical reaction, Fran, Pseudocapacitors, Graphene oxides

1. Introduction

Towards the development of high-energy pseudocapacitors and hybrid capacitors, various types of redox-based active materials have been investigated, e.g. conductive polymer [1,2], organic compounds [3,4,5,6,7], and metal oxides [8,9]. The conductivities of these active materials are generally not sufficient for capacitor application, and therefore, they are usually mixed with carbon materials to achieve sufficiently low inner resistance. However, this results in low mass-fraction of the redox-active materials. In addition, the redox active materials are generally not durable for long-term use, and most of them are redox-active only in aqueous electrolytes, which further limits their applications. It would be ideal if conductive carbon materials themselves could exhibit a large pseudocapacitance, especially in organic electrolytes having a wide potential window (ca. 3 V).

We have recently reported that zeolite-templated carbon (ZTC), an ordered microporous carbon prepared by using zeolite as a hard template [10,11], has a very large amount of active edge sites, namely ca. 10 times larger than the amount of ordinary activated

carbons. Moreover, such edge sites can be easily functionalized by a large amount of quinone groups in H_2SO_4 electrolyte [12,13]. The quinone groups give rise to high pseudocapacitance (ca. 500 F g^{-1}) with reasonably high rate capability and good cyclability [13]. In this work, we report the introduction of redox-active oxygen functional groups to ZTC in tetraethylammonium tetrafluoroborate dissolved in propylene carbonate ($\text{Et}_4\text{NBF}_4/\text{PC}$). The edge sites of ZTC are so active that the functional groups are easily introduced even within a potential range which is too narrow for general carbon materials to be electrochemically-reacted. The oxygen functional groups thus introduced in ZTC show a large pseudocapacitance at two different potentials in the organic electrolyte. We then try to understand the origin of the pseudocapacitance. Moreover, we examine the behavior of ZTC in lithium hexafluorophosphate dissolved with a mixture of ethylene carbonate and diethyl carbonate ($\text{LiPF}_6/\text{EC}+\text{DEC}$) to see if ZTC exhibits a similar pseudocapacitive behavior in the different type of organic electrolyte.

2. Experimental

ZTC was prepared using the method reported elsewhere [14]. ZTC is characterized by a very large BET surface area of $3600 \text{ m}^2 \text{ g}^{-1}$ as well as by ordered micropores with a

uniform size of 1.2 nm. A three-electrode cell was constructed inside a glove box (Ar atmosphere). An electrode sheet for a working electrode was prepared by mixing ZTC, PTFE, and carbon black with the weight ratio of 90:5:5. About 10 mg of the electrode sheet was sandwiched by a Pt mesh to form the working electrode. Using the same manner, a counter electrode was also prepared, but an activated carbon fiber (Unitika, A20) was used instead of ZTC. The working electrode was isolated from a counter electrode by a cellulose separator. A reference electrode consisted of Ag/AgClO₄. The electrochemical characterization was carried out using the three-electrode cell with 1 M Et₄NBF₄/PC electrolyte at 25 °C, in a fixed potential range from –1.5 to 1.0 V to clarify the mechanisms of electrochemical oxidation of ZTC and the appearance of the resulting pseudocapacitance. For comparison, two types of commercial activated carbons (Kansai Coke and Chemicals Co., Ltd., MSC30; Kuraray Chemical Co., Ltd., YP-50F) were used as reference. MSC30 is a KOH-activated carbon having a large BET surface area of 2680 m² g^{–1}. YP-50F is a steam-activated carbon which is indeed used as an electrode material of commercial electric double-layer capacitors. YP-50F has a moderate BET surface area of 1700 m² g^{–1}, and is highly durable for long-term use.

By the electrochemical oxidation [13], quinone-functionalized ZTC was also prepared. In this case, a working electrode was prepared in the same manner as described above,

and ZTC was electrochemically oxidized in 1M H₂SO₄ electrolyte through four scans of CV in a potential range of -0.1 to 0.8 V (vs. Ag/AgCl/Cl⁻(sat.)). Then, the working electrode was thoroughly rinsed with ultrapure water and allowed to stay in ultrapure water for 48 h. The working electrode was then rinsed again with ethanol and dried at 150 °C under reduced pressure for 24 h to completely remove water and ethanol in the modified ZTC. Finally, the working electrode was characterized in 1 M Et₄NBF₄/PC.

In order to understand the effect of the electrochemical oxidation on the carbon surface chemistry, some of electrode sheets before and after the electrochemical characterizations were subjected to the temperature-programmed desorption (TPD) analysis equipped with a mass spectrometer [15]. Besides, the oxygen functional groups before and after the electrochemical oxidation were analyzed with a FT-IR spectrometer (Shimadzu, FTIR-8900) [13]. For the TPD and FT-IR analyses, the electrode sheet taken out from the current collector was washed by acetone with sonication for 30 min. Then, the washed sample was separated from the acetone by filtration. The sonication and filtration were repeated twice and the sample was finally dried at 80 °C under reduced pressure for 6 h.

The stable potential range of ZTC, in which ZTC shows stable charge/discharge cycles, was also examined by the following method. First, cyclic voltammetry (CV) was

performed for 4 cycles in a narrow potential range of $-1.5 \sim 0.5$ V (vs Ag/AgClO₄). Then, galvanostatic charge/discharge cycling (GC) was conducted at several different current densities. Next, the upper limit potential was increased stepwise from 0.5 to 1.3 V, and the set of CV and GC was repeated at each of the potential ranges. Similar potential expansion towards negative potential region was done in the same manner but the upper limit potential was fixed at 0.5 V and the lower limit potential was expanded stepwise from -1.5 to -2.3 V. The stable potential range of ZTC was determined from the change of the specific capacitance or color change of the electrolyte. Then, the electrochemical performance of ZTC was examined in the potential range (-2.0 to 1.0 V) determined by the above experiment.

A set of electrochemical measurements was made also in 1 M LiPF₆/EC+DEC. In this case, stainless mesh was used instead of Pt mesh, and Li foil was used as both reference and counter electrodes.

3. Results and Discussion

3.1. Pseudocapacitance of ZTC in 1 M Et₄NBF₄/PC

Figure 1a shows cyclic voltammograms of ZTC in 1 M Et₄NBF₄/PC. The black and red lines corresponds to the 1st and the 4th scans measured in -1.5 to 1.0 V, respectively.

For comparison, the data of two activated carbons (MSC30 and YP-50F) are also shown in Figure 1b and c, respectively. In Figure 1a, a large anodic current is observed above 0.5 V at the initial positive-direction scan up to 1.0 V (black line). Then, at the subsequent negative-direction scan, a redox peak is observed around 0.4 V, and this redox peak appears at the following cycles, as can be seen in the red line. We have recently reported very similar results of ZTC in an aqueous electrolyte (1M H₂SO₄) [13]. In the previous work, we have proved that ZTC is intensively oxidized at the first positive-direction scan and a large amount of quinone-type groups are introduced, which give rise to a large pseudocapacitance. From the quite similar electrochemical response mentioned above, it is possible to expect the similar electro-oxidation of ZTC also in the present organic electrolyte as well. For reference, the 1st scan (blue line) measured in -1.5 V to 0.5 V is also shown in Figure 1a, as a datum in which ZTC is not subjected to a severe anodic condition yet. It is noteworthy that the blue line doesn't show the redox peak around 0.4 V. Figure 1a thus indicates that the redox active species is generated during the initial positive-direction scan above 0.5 V. Additionally, another broad and weak redox peak can be observed at a negative potential around -0.6 V. Unlike the case of the peak at 0.4 V, this peak is very weak at the 1st negative-direction scan (black line), and becomes more intense in the 4th scan (red line). Thus, the redox

active species corresponding to this pseudocapacitance seems to be different from the origin of the pseudocapacitance around 0.4 V, and is gradually introduced into ZTC during the four CV cycles.

The aforementioned behavior of ZTC is totally different from those of the commercial activated carbons (Figure 1b and c), whose voltammograms exhibit a typical rectangular shape based on pure electric double layer capacitive behavior regardless of the number of cycle. Since the activated carbons do not show such intense anodic current as in the case of ZTC, the anodic process seen in ZTC would be due to the unique property of this carbon, and not due to the electrochemical cell. However, it is well known that Pt, the present current collector, can catalyze the anodic decomposition of PC solvent [16]. To clarify the effect of the Pt mesh (current collector), a similar electrochemical measurement to Figure 1a was carried out by using a stainless mesh (Supporting Information Figure S1). The results are almost the same as in Figure 1a, and therefore, the introduction of the redox-active species by the anodic process is due to the nature of ZTC itself.

To investigate the origin of the pseudocapacitance, ZTC after the polarization was subjected to the TPD analysis. During the heating in a TPD run, the oxygen functional groups are decomposed to CO and CO₂ gases at different temperatures, depending on

their types. It is generally accepted that the decomposition of ethers, phenols, and quinone-type carbonyls results in the desorption of CO, carboxylic groups and lactones give CO₂, and acid anhydrides produce both CO and CO₂ (molar ratio 1:1) [17,18,19]. The amount and the type of oxygen functional groups can therefore be estimated from the TPD patterns. The resulting CO and CO₂ desorption profiles are shown in Figure 2, and the corresponding amount of oxygen is summarized in Table 1. It is found that the amounts of CO and CO₂ desorption from ZTC increase upon the positive polarization up to 1.0 V, indicating that oxygen functional groups are indeed introduced into ZTC by the electrochemical oxidation in 1 M Et₄NBF₄/PC. In Figure 2, major enhancement can be seen in the CO evolution around 400-1000 °C. Since CO₂ evolution is not similarly increased, the large CO evolution in the oxidized ZTC would be mainly derived from ethers, phenols, and/or quinone groups [17,18,19]. Consequently, one or some of these groups may contribute to the pseudocapacitance.

In the present system, there are the following two possibilities for oxygen source: the solvent (PC) or a trace amount of H₂O (< 30 ppm) in the electrolyte solution. To check the latter possibility, we carried out a separate electrochemical measurement by using a limited amount of electrolyte solution (0.7 ml). In this case, the total H₂O impurity possibly contained in the electrolyte solution is less than 1.2 μmol. The resulting CV

pattern is shown in Figure 3, where ZTC shows a large oxidation peak as well as a large pseudocapacitance peak. Their electric charges are 2.5 and 1.4 C, corresponding to 26 and 14 μmol of electrons, respectively. Since both values are much larger than the total H_2O amount ($<1.2 \mu\text{mol}$) in the solution, the oxygen source of the electrochemically introduced functional groups in ZTC should not be H_2O , but PC. It has been reported that the present solvent (PC) reacts with many compounds, such as phenol and thiophenol, to form CO_2 and hydroxyalkyl derivatives including oxygen derived from PC [16,20] at a high potential. This reaction occurs also on the edge site of carbon especially on the oxygen-functional groups [20]. Therefore, it can be reasonably understood that the active edge sites of ZTC easily react with PC and new functional groups containing oxygen are introduced as a result. Since the edge sites of ZTC are electrochemically more active than those of conventional porous carbons [12,13], only ZTC can react with PC in Figure 1.

3.2. Redox reaction in the negative potential range

As discussed above, ZTC reacts with PC during the electrochemical oxidation, and a large amount of ethers, phenols, and/or quinone groups are introduced into ZTC. Since the present electrolyte includes not only oxygen but also nitrogen and boron, it is

necessary to consider the possibility of the introduction of other functional groups including these heteroatoms which also exhibit pseudocapacitance[21,22,23]. However, we have confirmed that functional groups containing nitrogen or boron are not introduced into ZTC by the present polarization condition (see the Supporting Information, S2). Thus, the next question is which type of oxygen functional group may be responsible for the observed pseudocapacitance. We have recently reported that ZTC can be easily electro-oxidized in H_2SO_4 , and a large amount of quinone groups can be introduced into ZTC with a high selectivity. In addition, the quinone groups are electrochemically active and exhibit a large pseudocapacitance based on the quinone/hydroquinone redox reaction in the acidic aqueous electrolyte [13]. Thus, we prepared the quinone-functionalized ZTC, and examined its electrochemical response in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$. Figure 4 shows CV patterns of the pristine ZTC and the quinone-functionalized ZTC in two potential regions. First, these samples were characterized in the range of -1.5 to 0.5 V (solid lines in Figure 4). The quinone-functionalized ZTC exhibits a couple of broad peaks in a negative potential range, and the peaks are more intense than those of the pristine ZTC. Quinone groups would therefore correspond to the pseudocapacitance in the negative potential range. Quinones are generally known as redox-active functional groups, which can exhibit

pseudocapacitance in organic electrolytes [24,25]. The redox potential of quinones in organic molecules varies with the molecular structure and/or with the adjacent functional groups, both of which affect the electron affinity of quinones [25,26]. But, most of the observed potentials stay within the range of the broad peak in Figure 4.

3.3. Redox reaction in the positive potential range

Figure 4 shows the appearance of pseudocapacitance around 0.4 V in the pristine ZTC, after it is subjected to the electrochemical oxidation up to 1.0 V. As discussed above, the most probable origin of this pseudocapacitance is the oxygen functional groups which are introduced into the active edge sites of ZTC. On the other hand, the quinone-functionalized ZTC does not show such pseudocapacitance in the positive potential range (Figure 4). Note that this sample was fully oxidized in H_2SO_4 beforehand and most of edge sites must be already occupied by quinone groups. Therefore the quinone-functionalized ZTC was not severely oxidized in the initial positive-direction scan, compared with the pristine ZTC (Supporting Information, Figure S3) and the oxygen functional groups responsible for the positive potential pseudocapacitance were not formed as a result. Consequently, the origin of the pseudocapacitance cannot be ascribed to quinones, but it may be ethers and/or phenols.

Figure 5 shows FT-IR spectra of ZTC before and after the polarization up to 0.7 V. Ethers, phenols, and quinones generally give IR absorption bands at 1000-1300, 3200-3400 and 1600-1900 cm^{-1} due to C-O, O-H and C=O stretching modes, respectively [27,28]. By the polarization up to 0.7 V, a new peak appears in the region of the C-O stretching, suggesting that the redox peak at 0.4 V (Figure 1a, 3, and 4) corresponds to ethers. It has been indeed reported that PC reacts with edge sites of carbons to produce functional groups including an ether chain [20].

To our best knowledge, a furan ring is the only ether-type group which shows reversible redox reaction in this positive potential range [29]. We have previously elucidated that ZTC framework has a significant amount of carbon-pentagons, considering its curved structure [30]. It is therefore very likely that furan rings (5-membered hetero-ring) were introduced into ZTC framework by the electrochemical oxidation. We thus propose a possible redox reaction scheme of ZTC in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$, as shown in Figure 6. ZTC is first electrochemically oxidized above 0.4 V (Figure 1a) with PC, and furan-type ethers are introduced as a result. By the following cycles, in addition to the ethers, redox-active quinones are slowly introduced in ZTC. The former is reversibly oxidized/reduced by the formation of its cation radical [29], and thus shows pseudocapacitance around 0.4 V. The latter is also reversibly oxidized/reduced by the

formation of its anion radical [31], and shows pseudocapacitance around -0.6 V.

3.4. Stable potential range of ZTC in 1 M Et₄NBF₄/PC

Figure 7 shows the change of capacitance of ZTC and MSC30, when the upper (Figure 7a) or lower (Figure 7b) limit potential is expanded to a positive or negative direction, respectively. Electric double-layer capacitance is generally independent of an operating potential. Therefore, in Figure 7a, MSC30 keeps a constant capacitance (ca. 180 F g^{-1}) up to 1.6 V. At a very high potential of 1.8 V, the capacitance is decreased probably due to the decomposition of electrolyte and the subsequent formation of polymer-like solids which cause the pore blocking [20]. This is a typical result in general porous carbons. By contrast, ZTC shows capacitance enhancement with increasing the upper limit potential up to 1.0 V. A similar extraordinary behavior of ZTC was previously observed also in an aqueous electrolyte [13] due to the development of pseudocapacitance. However, the capacitance declines above 1.1 V, much lower potential than the case of MSC30 (1.8 V). Probably, the active edge sites of ZTC enhance also the decomposition reaction of the electrolyte. In our previous work, it was indeed confirmed that the decomposition of electrolyte is affected by the state of the edge sites of carbon [20]. Thus, we concluded that the upper limit of the stable potential range of ZTC in 1 M

Et₄NBF₄/PC is 1.0 V.

In the negative potential region (Figure 7b), the capacitance of MSC30 is stable (ca. 200 F g⁻¹) down to -2.4 V. On the other hand, ZTC shows capacitance increase down to -2.2 V, followed by a decline at -2.3 V. It should be noted that the color of the electrolyte was however turned into light brown at -2.2 V, indicating the degradation of the electrolyte already at this potential. Therefore, we concluded that the lower limit of the stable potential range of ZTC is -2.0 V.

3.5. Rate capability and cycle stability

The rate capability and cycle stability of ZTC are then examined in its stable potential range (-2.0 to 1.0 V). By the contribution of pseudocapacitance, ZTC indeed has a higher specific capacitance (330 F g⁻¹) than those of YP-50F (120 F g⁻¹) and MSC30 (250 F g⁻¹) in GC measurement at 50 mA g⁻¹. Figure 8a shows capacitance dependence on current density for ZTC and MSC30. Despite the contribution of pseudocapacitance, ZTC retains a high specific capacitance (224 F g⁻¹) at a large current density of 2280 mA g⁻¹, and its rate performance is good to that of MSC30. In addition, the ZTC retains 94% of its initial capacitance even after 2000 cycles of charge/discharge measurements (Figure 8b), indicating its excellent cyclability. These results prove that the redox-active

functional groups introduced into ZTC are very stable in the conclusive potential range (−2.0 to 1.0 V) and can repeat the fast redox reactions reversibly thousands of times.

3.6. Pseudocapacitance of ZTC in 1 M LiPF₆/EC+DEC

Redox-active organic materials (e.g. molecules and polymers) are expected as a positive electrode of rechargeable batteries [25,32,33,34,35], and a high redox potential is desired to achieve a high voltage operation of the batteries. Accordingly, the pseudocapacitance of ZTC at a positive potential range by furan-type ether is of interest. Since the proposed redox mechanism (Figure 6) is based on the reversible conversion of furan into its cation radical, the pseudocapacitance can be expected regardless of the type of anion. We thus examined the electrochemical behavior of ZTC in LiPF₆/EC+DEC, which is a common organic electrolyte for lithium-ion batteries (LIBs) and lithium-ion capacitors (LICs), and it is compared with those of MSC30 and YP-50F. For each of these carbons, four CV scans were measured at first in the range of 3.0 to 4.1 V (vs. Li/Li⁺). Then, the upper limit potential was expanded stepwise by 0.2 V up to 4.7 V with repeating four CV measurements at each of the potential ranges. Figure 9 shows the fourth CV patterns at each potential range. Like in the case shown in Figure 1a, the capacitance of ZTC is increased upon expanding the upper limit potential, and

ZTC finally shows broad peaks in a potential range around 3.4 to 4.4 V. Thus, the pseudocapacitance of ZTC appears in the potential range required for positive electrodes of LIBs and LICs. On the other hand, the activated carbons (MSC30 and YP-50F) never show such a pseudocapacitance in this potential range (Figure 9b and c), and they show almost constant capacitance regardless of the potential range, like the cases in 1 M Et₄NBF₄/PC (Figure 1b and c). The results shown in Figure 9 again demonstrate the highly reactive nature of ZTC which is quite unique compared to general activated carbons, and suggest the introduction of redox-active functional groups in a variety of electrolyte solutions.

4. Conclusion

ZTC contains a lot of highly reactive edge sites, so it can be electrochemically oxidized very easily in organic electrolytes unlike activated carbons. By the electrochemical oxidation in 1 M Et₄NBF₄/PC, a large amount of oxygen functional groups are introduced into ZTC. The oxidized ZTC shows two different types of redox reactions in positive and negative potential regions, respectively. The former reaction could be the formation of the cation radicals of furan-type ethers, while the latter one is assigned to the anion radicals of quinone-type functional groups. Due to the significant contribution

of pseudocapacitance, ZTC shows a high specific capacitance of 330 F/g. Moreover, despite the large pseudocapacitive contribution, its rate capability is as good as that of activated carbons, and the cycle stability is sufficiently high. Also in 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$, which is a common electrolyte for LIBs and LICs, the experimental results suggested that ZTC is electrochemically oxidized and shows a large pseudocapacitance in a positive potential range. Thus, ZTC is expected as a redox-active material for electrochemical capacitors and for LIBs and LICs as well.

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Captions for Figures

Figure 1. CV patterns of (a) ZTC, (b) MSC30, and (c) YP-50F, measured in 1 M Et₄NBF₄/PC at 25 °C. A scan rate is 1 mV s⁻¹. The 1st and the 4th CV patterns measured in a potential range from -1.5 to 1.0 V are expressed by black and red lines, respectively, while the 1st CV pattern measured in a potential range from -1.5 to 0.5 V is expressed by a blue line.

Figure 2. CO and CO₂ TPD patterns of electrode sheets including ZTC, (a) before and (b) after polarization between -1.5 to 1.0 V.

Figure 3. The initial voltammogram of ZTC in 0.7 ml of 1 M Et₄NBF₄/PC between -1.5 to 1.0 V at 25 °C. A scan rate is 1 mV s⁻¹.

Figure 4. Cyclic voltammograms (fourth scan) of the pristine ZTC (black lines) and the quinone-functionalized ZTC (red lines), measured in 1 M Et₄NBF₄/PC up to 0.5 V (solid lines), and 1.0 V (dotted lines). A scan rate is 1 mV s⁻¹.

Figure 5. FT-IR spectra of ZTC before and after polarization up to 0.7 V.

Figure 6. A possible redox-reaction scheme of oxygen-functionalized ZTC in 1 M Et₄NBF₄/PC.

Figure 7. Capacitance versus (a) lower or (b) upper potential range of GC measurement (0.1 A g⁻¹) in 1 M Et₄NBF₄/PC for ZTC and MSC30. The potential range was expanded

stepwise from 0.5 V to more positive range in the case of (a), and from -1.5 V to more negative range in the case of (b).

Figure 8. (a) Capacitance versus current density for ZTC and MSC30, measured between -2.0 to 1.0 V in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$. (b) Durability test of ZTC upon 2000 charge/discharge cycles, measured at 1 A g^{-1} in 1 M $\text{Et}_4\text{NBF}_4/\text{PC}$.

Figure 9. CV patterns (fourth cycle) of (a) ZTC, (b) MSC30, and (c) YP-50F, measured in 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$. Scan rate is 1 mV s^{-1} .

Captions for Table

Table 1. Amounts of CO, CO₂, and H₂O evolutions and total oxygen content of the pristine ZTC electrode and the one polarized in –1.5 to 1.0 V.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Table 1.

Polarization potential (V)	Amount of gas evolution ($\mu\text{mol g}^{-1}$)			Total oxygen content (wt%)
	CO	CO ₂	H ₂ O	
Pristine	1624	173	1095	4.9
-1.5 to 1.0	3939	1039	3007	14.4

Graphical abstract