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Onion-like carbon as dopant/modification-free electrocatalyst for \([\text{VO}]^2+/[\text{VO}_2]^+\) redox reaction: Performance-control mechanism

Young-Jin Ko\(^a,1\), Keunsu Choi\(^b,1\), Jun-Yong Kim\(^a, d\), Inho Kim\(^a\), Doo Seok Jeong\(^a\), Heon-Jin Choi\(^c\), Hiroshi Mizuseki\(^b, **\), Wook-Seong Lee\(^a, *\)

\(^a\) Center for Electronic Materials, Korea Institute of Science and Technology, Seongbuk-gu, Seoul, 02792, Republic of Korea
\(^b\) Computational Science Research Center, Korea Institute of Science and Technology, Seongbuk-gu, Seoul, 02792, Republic of Korea
\(^c\) Advanced Materials Science and Engineering, Yonsei University, Seodaemun-gu, Seoul, 03722, Republic of Korea
\(^d\) Department of Materials Science and Engineering, Korea University, Seoul, 02841, Republic of Korea

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**Abstract**

We investigate the application of the onion-like carbon (OLC) as an electrocatalyst for \([\text{VO}]^2+/[\text{VO}_2]^+\) redox flow reaction: its performance (electrocatalytic activity and reversibility) strongly increases with the synthesis to peak at 1800 °C in 1000–2000 °C range. The dopant/modification-free, optimized redox performances of the OLC is comparable to some of the best data in the literature of various types of carbon materials with post-synthesis modifications or doping. Mechanism behind such performance optimization is investigated employing various physical/electrochemical analyses as well as the first-principles calculations. We demonstrate that the carbon dangling bonds or the crystalline defects, generated by an inherent mechanism unique to the OLC, played a pivotal role in determining the electrocatalytic performances.

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1. Introduction

Vanadium redox-flow battery (VRFB) is the next-generation large-scale electrochemical energy-storage system [1,2], which benefits from low cross-over (owing to using identical electrolytes i.e. vanadium ions and vanadium oxide ions, on both electrodes) [3], low electrode damage (owing to the electrode-surface-confined redox reaction of the electrolytes) and consequently high cycling stability [4]. Nevertheless, the activity and the reversibility of the most commonly adopted electrocatalyst material, i.e. the carbon felt or carbon papers [5], are poor due to the multi-step \([\text{VO}]^2+ /[\text{VO}_2]^+\) coupled reaction at the cathode [6]. The usual approach to this issue is the catalytic agent dispersion or the direct surface modification. The relevant catalytic agents include 1) the noble metal nanoparticles [7–9], 2) oxygen-functionalized nanocarbon [10–16], 3) graphene modified by heteroatom (mostly nitrogen) doping [6,17,18]. The direct modification of the carbon electrode is carried by the heteroatom doping or by the oxygen-functionalization [6,14]. However, such approaches suffer the risk of hazardous chemicals (heteroatom doping or oxidation) [19–21], and inconvenience of complex processing, or high-cost (noble metal nanoparticles). Alternative approach has been in strong demand, but relevant studies were rare.

Recently, Park et al. reported an approach that resolved such issue, based upon the electrochemically-active intrinsic defect sites on the carbon nanofiber (CNF), hybridized with CNT of good electrical conductivity, co-grown by CVD on the carbon felt [22]. On the other hand, we recently reported a unique intrinsic defect generation mechanism in nanodiamond (ND)-derived onion-like carbon (OLC), based upon the phase transformation in its diamond-graphite core-shell structure, in the course of its synthesis; it enabled a strong intrinsic-defect-induced enhancement in density of states (DOS) and in the DOS-dependent electron transfer kinetics, with consequent electrochemical activation in dopamine sensing [23]; the performance was equivalent to those enabled by the extrinsic means such as doping and post-synthesis treatments on other carbon-based catalysts [23]. The strong point of such OLC-based approach was that the synthesis was a simple vacuum annealing of the raw powder at the optimized temperature, free from additional catalytic agents or post-synthesis treatments; the
temperature provided a facile control over the types and densities of the generated intrinsic defects, which determined the electrochemical sensing performance [23], or the surface chemistry for the chromate adsorption [24]. It suggested a possible application of the same OLC as an electrocatalyst for \([\text{VO}_2^+/\text{VO}_2^+]\) redox reaction [12], where the electron/mass transfer to the OLC surface active sites and hence the redox performance might be strongly affected by the intrinsic defects of the OLC. In such case, the simple OLC synthesis temperature control, rather than the inconvenient post-synthesis treatments or doping, might serve as a facile optimization route of the redox performances. So far such intriguing point was not clarified yet, even for the cases of the previously reported electrocatalytic agents [6,12], let alone those concerning the OLC. Here we investigated this issue, by studying the temperature-dependent intrinsic defect evolution in the ND-derived OLC and the consequent electrocatalytic activity evolution in \([\text{VO}_2^+/\text{VO}_2^+]\) redox reaction.

2. Experimental

2.1. Materials

All materials were purchased from Sigma Aldrich Co. All aqueous solutions were prepared with deionized water (DI water, ionic resistivity = 18.2 MΩ/cm). The \([\text{VO}_2^+]\) solutions were prepared in 3 M sulfuric acid solution.

2.2. Synthesis of OLCs

The OLC powders were synthesized by vacuum annealing of the nanodiamond powder in the tube furnace. The furnace was evacuated with rotary pump to 10⁻³ torr with the annealing time fixed at 1 h. The annealing temperatures were varied as 1000 °C, 1200 °C, 1400 °C, 1600 °C, 1800 °C and 2000 °C; the samples were accordingly denoted as OLC-1000, OLC-1200, OLC-1400, OLC-1600, OLC-1800 and OLC-2000. The annealed samples were furnace-cooled after the annealing process.

2.3. Preparation of working electrodes

The glassy carbon electrode (GCE) of 0.247 cm² area was polished with alumina abrasive powders prior to drop coating. It was subsequently rinsed with aqueous solution of Isopropyl alcohol (IPA) and was dried at room temperature. Five milligrams of synthesized OLC powder were ultrasonically blended with IPA (0.5 mL), DI water (1.5 mL) and 5 wt% nafion solution (50 μL). Twenty microliters of catalyst ink was loaded onto the pre-treated GCE and was dried at room temperature. The mass loading was 0.1975 mg/cm². Prior to half-cell test of Carbon felt (CF, PAN CF-20-3, Nippon carbon), catalyst inks were prepared by mixing 10 mg of synthesized OLC powder in mixture of IPA (0.9 mL) and Nafion solution (5 wt%, 100 μL). The 5 mg/cm² of suspension was dropped onto the CF and dried at 60 °C for 12 hr.

2.4. Electrochemical measurement

A conventional three-electrode system was used throughout all the electrochemical measurements. A platinum wire and the Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The electrochemical impedance spectroscopy was carried out at open circuit voltage (OCV) from 10⁵ Hz down to 10⁻² Hz with 10 mV AC amplitude.

2.5. Structural and physical characterization of OLC

The microstructure of OLCs was analyzed by high-resolution transmission electron microscopy (HR-TEM, FEI Co., Titan 300 kV). The defect density and strain of OLCs was characterized by visible-Raman spectroscopy (Renishaw Co., inVia Raman spectroscopy, Beam Source: 532 nm Nd:YAG laser). Since the visible-Raman is 50–230 times more sensitive to sp²-carbon than sp³-carbon, the sp²-carbon signal was negligible. Curve fitting for the measured spectra was carried out according to the previous report [25]. The density of state (DOS) was analyzed by ultraviolet photo-emission spectroscopy (UPS, Ulvac Co., PHI 5000 VersaProbe). A He(I) emission lamp (photon energy: 21.2 eV, penetration depth: few Å) was used as beam source. The spectral resolution was 0.01 eV and the electron take-off angle was 90°. Gold was used as the reference sample. The oxygen ratio of OLCs was characterized by X-ray photoemission spectroscopy (XPS, Ulvac Co., PHI 5000 VersaProbe).

The sp²-sp³ ratio of OLCs were analyzed by near edge x-ray absorption fine structure spectroscopy (NEXAFS, resolution: 0.1 eV, total electron yield mode, at the 10D KIST beam line of the Pohang Accelerator Laboratory in Republic of Korea). The sp²-sp³ ratio was calculated from the obtained NEXAFS spectra employing the technique of the previous report [26].

The dangling bond densities of OLCs were measured by electron-spin resonance (ESR, JEOL Co., JES-FA100). Samples of 5–10 mg were put in the quartz tube and were placed in the cavity. The copper sulphate pentahydrate was used as reference sample (1 spin/molecule).

Dispersion of OLCs in water was carried out in order to visually confirm their hydrophobicity. Two milligrams of OLCs were wetted with 5 mL DI water and dispersed in sonication bath. After the sonication, the mixtures were manually agitated and put to rest for 24 h; subsequently they were visually inspected.

2.6. Computational methods

We carried out first-principles calculation based on density functional theory (DFT) by using Vienna ab initio Simulation Package (VASP) [27,28]. The exchange correlation functional is described by generalized gradient approximation (GGA) and pseudo-potential is parameterized by Perdew, Burke and Ehrnhorst (PBE) under projector augmented wave (PAW) method [29–31]. The Monkhorst-Pack scheme is used for k-point sampling in the Brillouin zone with \(2 \times 2 \times 1\) mesh [32]. The adsorbent is obtained based on the 6 × 6 super cell, of which size is 14.85 × 14.85 × 15.00 Å. The energy cutoff for planewave basis is 500 eV and criteria force for optimization is 0.01 eV/Å. All configurations in the figures were drawn by using VESTA [33].

3. Results and discussion

Fig. 1 shows the HR-TEM images of the OLCs derived from detonation nanodiamond, annealed at various temperatures. The number of the graphitic shells increased with temperature at the expense of the diamond core, which agreed with previous report [34]. At 1600 °C, the diamond core was completely consumed in the majority of the particles. While the graphitic shell was quasi-spherical up to 1600 °C, the shell polygonization (or polyhedralization in 3-dimensions) prevailed at 2000 °C (Fig. 1f). Fig. 5 shows the particle size distributions at various annealing temperatures; the obtained averaged particles sizes were plotted versus the synthesis temperature in Fig. 5: it rapidly increased upto 1200 °C and the slop was reduced thereafter. The initial steep increase was attributed to the volume expansion arising from the
diamond-to-graphite phase transformation [23], while the slope reduction beyond 1200 °C was attributed to the eventual consumption of the diamond core [23]. The electrochemical activities were analyzed for [VO]^{2+}/[VO_2]^+ redox reaction on the electrodes, which were drop-coated with the aforementioned OLCs (rotating ring disk electrode: Fig. 2, carbon felt electrode: Fig. 3). The peak currents vs annealing temperature profile for both types of electrode peaked at 1800 °C. The parameters from the CV (peak potential difference: ΔE_p, oxidation peak current: I_p^ox, peak current ratio: I_pA/I_pC) were summarized in Table S1 (rotating disk electrode) and Table S2 (carbon felt). Since the drop-coated OLC masses differed greatly in the two electrodes (Experimental), the redox probe concentrations were adjusted accordingly: 1 M for the glassy carbon electrode and 0.1 M for the carbon felt electrode. Table S3 compares the redox performance of the OLC-1800 with some of the best data in the literature. It was remarkable that the peak current densities (J_p) of the OLC-1800, which was neither oxygen-functionalized nor post-treated, were comparable to those of the various nitrogen-doped or oxygen-functionalized nanocarbons, as well as those of the best non-doped sample (CFN/CNT-700) [22].

Another important property, i.e. the reversibility is represented by two equivalent parameters: peak potential separation (ΔE_p) and the redox peak currents ratio (I_pA/I_pC ratio, see Table S2 and Fig. S3). The reversibility is inversely proportional to ΔE_p; it is also proportional to the proximity of the I_pA/I_pC ratio to unity [12]. Both of the reversibility parameters profiles (vs temperature) again peaked at 1800 °C. The I_pA/I_pC ratio was among the best, i.e. the closest to unity (Table S3).

While it was remarkable that such post-treatment/dopant-free
redox performances of the OLC were comparable to the best of the post-treated/doped performances in the literature, the origin of such temperature-dependent evolutions of the performance, which unanimously peaked at 1800 °C, was intriguing. In the following analyses, we start by analysing the rate-determining steps of the redox reaction, from the CV. We found that the present redox reaction was mixed-controlled, with concurrent steps of electron transfer and the mass transfer (Statement S1, Figs. S4-S7 and Table S4-S5).

Since the electrocatalytic activity in the redox reaction was frequently reported to be strongly enhanced by oxygen [10–16], we first tested this possibility, employing the XPS (Fig. S8): the oxygen content monotonically dropped with temperature. It was in contrast to the CV responses (anodic peak currents) which peaked at 1800 °C (Figs. 2 and 3). It clearly pointed the irrelevance of the oxygen contents and demanded further analyses.

Fig. 4a and b shows the Raman spectra of the OLC samples, which give bulk-originating information concerning the lattice defect density [35]. The peaks were deconvoluted into five individual bands, i.e. I, D, A, G, and D’ [25]. The I_D/I_G ratio derived from Fig. 4a and b was summarized in Table S6 and was plotted in Fig. 4c. The defect density represented by the I_D/I_G ratio increased with temperature, again to peak at 1800 °C [35], in accord with the aforementioned temperature dependences (Figs. 2b and 3b). Fig. 4d shows the temperature dependence of the I_D/I_G ratio, which was reported to reflect the evolution of the defect type in the graphene [36]. It gradually increased with temperature from 3 to 7 and eventually past 14, which corresponded to the various defect types: grain boundaries (3.6), vacancies (7.06) and sp³-type defects (13.9) [36]. Hence the type of the defects dominant in the OLC-1800, where a number of properties shown so far peaked at, seemed to be the vacancies rather than grain boundaries or the sp³-carbon type defects. Such vacancy formation should accompany the dangling bond formation, which was actually confirmed by ESR analyses as will be shown later below.

Fig. S9 shows the corresponding Raman spectra in the 2D band region; they were blue-shifted with respect to that of the graphene, which indicated that the OLC shells were subjected to the tensile rather than compressive strain [37,38], in accord with our previous work [23]. Fig. S9c, d shows the 2D peak shift and the corresponding tensile strain calculated from the shift [23], respectively; it peaked at 1400 °C (Fig. S9d) instead of 1800 °C.

Fig. 5a shows the electron-spin resonance (ESR) spectra of the OLC samples; it gives information concerning the carbon dangling bonds [39], probably generated in the course of the vacancy formation in the nanodiamond-derived OLC shells [40,41]. The resonance peak became broader with temperature; deconvolution of the spectra gave two isolated peaks (the peaks widths were plotted in Fig. 5b, as narrow and broad peak, respectively) of which the simultaneous existence agreed with earlier report [42]. Both peaks were attributed to the non-bonding π-electrons [42]. The narrow peak was attributed to the localized dangling bond (hence interference-free) spins associated with the structural defects in the OLC shells [43]. By contrast, the broad peak was attributed to the delocalized π-electrons shared in the molecular orbitals in the non-defective portions of the OLC shells [43]. Therefore, the spin densities, which might be regarded as the dangling bond density [43], was calculated from the narrow peak intensity (Fig. 5c); it initially dropped with temperature from that of raw material (detonation nanodiamond) until 1400 °C, probably due to temperature-dependent consumption of the diamond core in the OLC shells, and hence the corresponding removal of the initial dangling bonds therein [39]. Then it increased again to peak at 1800 °C, which was obviously attributed to the continued increase in the dangling bonds density, probably due to the bond ruptures caused by the vacancy generation, as indicated by the aforementioned I_D/I_G ratio, i.e. the lattice defect density evolution (Fig. 4), which also peaked at 1800 °C. The spin density dropped again at 2000 °C, of which the origin will be explained later, in the discussion concerning the polyhedralization of the shell.

Fig. 6a shows the UPS spectra of the OLC samples, which gives surface-specific information concerning the mid-gap DOS which controls the electron transfer kinetics in graphene [44] as well as in OLC [23]. Fig. 6b shows the temperature-dependence of the DOS as normalized by the Au reference; the profile also peaked at 1800 °C, again in agreement with the aforementioned temperature-dependent defect density evolution (Raman, Fig. 4c) as well as the dangling bond density evolution (ESR, Fig. 5c). Such agreements strongly suggested that the temperature-dependent evolution of the DOS might be attributed to the mid-gap states generated by the crystalline defects [45], relevant to the aforementioned vacancy generation or dangling bond formations.

Fig. S10 shows the spectra obtained by electrochemical impedance spectroscopy (EIS), which provided additional information concerning the electron transfer and the mass-transfer. For the EIS data fitting, the Randle circuit was adopted [46]; results were summarized in Table S7. The semi-circle appearing at the high frequency domain represented the charge transfer resistance and the double layer capacitance [46,47], while the linear slope at the low frequency domain represented the mass transfer factor, i.e. the
Warburg element [46]. The coexistence of these two differing domains indicated the mixed-control of the present Redox reaction, in accordance with the aforementioned conclusion from the CV (Statement S1, Figs. S4-S7 and Table S4-S5) [46]. The inverse of the

Fig. 4. (a, b) Raman spectra of OLCs (from 1000 cm\(^{-1}\) to 1800 cm\(^{-1}\)) synthesized at various annealing temperatures; (c) \(I_D/I_G\) ratio vs annealing temperature and (d) \(I_D/I_{D'}\) ratio vs annealing temperature profile corresponding to Fig. 4a and b. (A colour version of this figure can be viewed online.)

Fig. 5. (a) The ESR spectra of the OLCs, (b) annealing temperature dependence of the ESR line widths (\(\Delta H_{pp}\)) and (c) the spin densities. (A colour version of this figure can be viewed online.)
charge transfer resistance, which translated to the electron transfer kinetics [46], was plotted in Fig. S11. The temperature-dependence of $R_{ct}$ again agreed with that of DOS (Fig. 6) in that they peaked at 1800 °C.

Such repeatedly observed agreements (in 1800 °C peaking) mentioned so far, in the temperature-dependent evolutions of the various properties, i.e., the Redox performances, $I_D/I_G$ ratio, spin densities, DOS, electron transfer kinetics indicated the electron-transfer-relevant origin of the temperature-dependent evolution of the redox performance (Figs. 2 and 3), i.e., the temperature-dependent density evolution of crystalline defects (vacancies plus dangling bonds), of which the generation mechanism was well explained in our previous work on ND-derived OLC [23], in terms of the following steps: 1) the volume expansion associated with the consecutive new-born shells due to the diamond-to-graphite phase transformation in the diamond-graphite core-shell structure of OLC during its thermal synthesis; 2) consequent tensile strain forcibly exerted on the consecutive shells; 3) the strain-induced bond ruptures in the OLC shells and consequent lattice defects (Raman, $I_D/I_G$ ratio) or dangling bonds formation (ESR, spin density); 4) consequent consecutive enhancements in DOS (UPS), electron transfer kinetics (EIS), and Redox performances. In addition, the mass-transfer-relevant issue of the Redox performance, which we have shown above to be mixed-controlled, will be discussed later.

The only discrepancy from the 1800 °C peaking arose for the aforementioned tensile strain in the shell (Fig. S9d). It was attributed to the fact that the observed strain was the residual elastic portion of the tensile strain remaining subsequent to the vacancy-generation-related plastic portion of the strain in the shells, as we reported earlier (see the discussion concerning Fig. 4 in the reference [23]); the discrepancy was not surprising, since the 1800 °C peaking was relevant to the vacancy generation (hence the plastic portion of the strain) rather than to the residual elastic portion of the strain.

On the other hand, the origin of the drop subsequent to the 1800 °C peaking, in the temperature-dependent evolution of the aforementioned properties, was still intriguing; it will be clarified as follows. Fig. S12 shows the $sp^2/sp^3$ carbon masses (contents) as analyzed by the NEXAFS. In our previous report, we showed that such $sp^2/sp^3$ carbon contents ratio represented the extent of the diamond-to-graphite phase transformation, of which the accompanying volume expansion drove the defect-generating, forced tensile strain of the OLC shells in 1000–1400 °C region [23]. In the present report, the $sp^2$-carbon contents initially increased steeply with temperature up to 1200 °C, while it kept increasing mildly up to 2000 °C. It was in contrast to aforementioned properties (peak currents, defect density, DOS and the $R_{ct}$), which unanimously peaked at 1800 °C. It indicated that some new defect-healing mechanism was triggered at 2000 °C to become dominant over the aforementioned defect-generation mechanism. A possibility of defect healing was already suggested by the aforementioned drop in dangling bond density at 2000 °C as shown by ESR analyses (Fig. S5c). A possible origin of such healing might be associated with the shell polyhedralization occurring at 2000 °C (Fig. 1). It should involve the transformation of the quasi-spherical shells to the faceted shells, probably through the recrystallization process, where the atomic rearrangements accompany the defect healing and consequent stress/strain relaxation [48, 49]. Such possibility was also supported by the temperature-dependence of the inter-planar spacing between the outermost shell and the 2nd-shell of the OLC, which were reported to be controlled by the vacancy density in the shells; [30, 31] we determined it from the HR-TEM pictures (Table S8, Fig. S13). The spacing peaked at 1800 °C and thereafter dropped back to the level of the low temperature domain. It indicated the structural change of the OLC shells from turbostratic to graphitic in the course of the recrystallization and consequent defect healing [50]. Such defect healing resuming at 2000 °C was also supported by the report by Okotrub et al. [51]; they reported (using the X-ray Emission Spectroscopy) the temperature-induced holded-structure in OLC at 1900K, which might be regarded as vacancy clusters, and its disappearance at higher temperature [51].

So far we have discussed the factors contributing to one of the rate-determining steps: the electron transfer. Now we discuss the other step, i.e. the mass transfer, in the mixed-controlled reaction. Recall that the present Redox reaction was given as follows.

$$[VO]^{2+} + H_2O \rightleftharpoons [VO_2]^++ 2H^+ + e^-$$  (1)

There are two possible electrode material issues relevant to the mass-transfer rate: the surface structure and the hydrophilicity [6]. The hydrophilicities of the OLC samples were compared by the water-dispersion test (Fig. S14, visual inspection), which was widely adopted for the hydrophilicity test; in visual inspection, no meaningful difference was detected among the samples, except for the OLC-1000. It indicated that the mass transfer was dominated by
the surface structure. Among the various properties of the OLC shown so far, the most probable surface-structure-relevant factor was the dangling bond density obtained by the ESR analyses (or, equivalently, but somewhat less directly, the defect density represented by the $I_D/I_G$ ratio in Raman spectra), for obvious reasons. By contrast, DOS (and hence DOS-dependent properties also) was obviously relevant to the electron-transfer rather than the mass-transfer. The portion of the Redox reaction path, through which such dangling bond evolution could affect the mass transfer at the molecular level, was investigated by the first principle calculations as follows.

The first principles calculation was carried concerning the two important features in the reaction path: adsorption of $[VO]^{2+}$ on the hydroxyl and carboxyl groups, respectively, which were shown to

![Image](image_url)

**Fig. 7.** The O 1s XPS spectra of the OLC-1800 after (a) reduction and (b) oxidation reaction. (A colour version of this figure can be viewed online.)

![Image](image_url)

**Fig. 8.** Three configurations, (a) hydroxyl group around mono-vacancy, (b) adsorption of VO, and (c) attachment of O atom to adsorbed VO, are obtained from full relaxation. (A colour version of this figure can be viewed online.)
be present at the OLC as functional groups (by XPS analysis after reaction; Fig. 7). The calculation was focused on clarifying the impact of an oxygen atom (O_{add}) bonding to the VO, which was adsorbed on the mono-vacancy-containing outermost shell of the OLC (approximated as flat graphene layer). The modelled adsorbent was shown in Figs. 8a and 9a, with the hydroxyl and carboxyl groups set around the mono-vacancy, respectively. Fig. 8b shows the optimized configurations of VO adsorbed to hydroxyl group. When VO approached the OH group, the latter released H to accept VO and form the VO_{2}. On the other hand, when VO approached the carboxyl group, the calculation indicated that its bonding favoured the O site rather than the OH group in the carboxyl group (Fig. 9b). Since the bond length is closely related to the bond strength, we adopted it to predict the reaction subsequent to the O atom (O_{add}) bonding to VO adsorbate in the aforementioned two cases (Figs. 8b and 9b). The relevant changes in bond lengths were summarized in Tables 1 and 2. In both cases, C–O_{1} bond length decreased, while V–O_{1} bond length increased. It indicated that C–O_{1} bond grew stronger while the V–O_{1} bond grew weaker.

Table 1
The bond lengths between atoms in each reaction step between vanadium oxide and hydroxyl group are given.

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Adsorption</th>
<th>None</th>
<th>VO</th>
<th>VO–O_{add}</th>
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<td>1.34 Å</td>
<td>1.32 Å</td>
<td></td>
</tr>
<tr>
<td>V–O_{1}</td>
<td>1.88 Å</td>
<td>1.90 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V–O_{2}</td>
<td>1.62 Å</td>
<td>1.63 Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2
The bond lengths between atoms in each reaction step between vanadium oxide and carboxyl group are given.

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Adsorption</th>
<th>None</th>
<th>VO</th>
<th>VO–O_{add}</th>
</tr>
</thead>
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<tr>
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<td>1.30 Å</td>
<td>1.28 Å</td>
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</tr>
<tr>
<td>V–O_{1}</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>V–O_{2}</td>
<td>1.63 Å</td>
<td>1.64 Å</td>
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</tr>
</tbody>
</table>

Scheme 1.
Redox reaction mechanism for [VO]^2+/[VO_{2}]^+ redox couple with (a) hydroxyl (–OH) and (b) carboxyl (–COOH) functional groups.
suggesting that $Q_{ad}$ atom bonding to VO triggered the $VO_2$ desorption from the adsorbent, in both cases (as summarized in Scheme 1).

It was important that the bond length of $V\cdots O_1$ in carbonyl group was longer than that in hydroxyl group by 0.11 Å. It indicated that the $VO_2$ bonded to the O atom in carbonyl group might desorb more easily, relative to that bonded to hydroxyl group. It suggested that the catalytic kinetics of carbonyl group was faster than that of hydroxyl group, in agreement with previous experimental report [52].

4. Conclusions

ND-derived OLC was successfully applied as an electrocatalyst for $[VO_2]^+/[VO_2]^+$ redox reaction. Electrocatalytic activity and reversibility of the redox reaction were strongly dependent on the synthesis temperature. Both properties peaked at 1800°C where they were comparable to some of the best data in the literature (where the oxygen-functionalization/doping/post-treatment prevailed), although it was neither oxygen-functionalized nor doped/post-treated. The redox reaction was mixed-controlled, i.e. by electron and mass transfer steps. The electron transfer step was controlled by the mid-gap density of states (DOS), induced by the mutually-competing/temperature-controlled defect (vacancy + dangling bond) generation/healing mechanisms unique to ND-derived OLC. The mass transfer step was controlled by the chemical bonding of the vanadium oxide (as $[VO_2]^+/[VO_2]^+$) to the carbon dangling bonds (located at the vacancy sites, of which the density was also controlled by the same vacancy-generation mechanism) of OLC, which were functionalized by hydroxyl or carbonyl groups.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.carbon.2017.10.073.

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