Pt monatomic wire supported on graphene nanoribbon for oxygen reduction reaction

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Among the issues inherent to fuel cells, the high cost of the Pt electrocatalyst restricts its widespread application. Controlling nano- or subnano-material structures could improve the utilization of Pt. Here, the catalytic activity of the oxygen reduction reaction (ORR) on Pt monatomic wire that is supported on the zigzag edges of graphene nanoribbon (Pt–GNR) is studied using density functional theory. It is found that Pt–GNR is inert for ORR, due to the strong binding of OH and H₂O. However, when Pt–GNR is covered by the chain of OH and H₂O (cPt–GNR), it becomes catalytically active for ORR. Through the free energy diagrams on cPt–GNR, we demonstrate that the highest potential U for ORR as an exothermic process is 0.82 eV. When U is larger than 0.82 V, the rate-determined step (RDS) of ORR is located at the reduction of O₂* to OOH* (* denotes adsorbed species) where the energy barrier ΔG is less than 0.41 eV. These results support cPt–GNR as a candidate for ORR.

1. Introduction

Oxygen reduction reaction (ORR) is one of the important electrochemical reactions in energy-conversion devices, such as fuel cells and metal-air batteries, where the four-electron electrochemical reaction is usually catalyzed by Pt to accelerate the process of conversion of chemical energy to electrical energy. However, the scarce resources and high cost of Pt give strong momentum to reduce or replace Pt. Nanostructure engineering is one of the feasible methods to increase the surface/volume ratio and decrease the amount of Pt-based nano-materials. However, to our knowledge, a few studies are focused on Pt subnanomaterials, such as Pt clusters (n = 4–60), single (double) wall nanotubes, and single atom. It is well known that the free monatomic wires cannot exist except Au. Thus no attention has been focused on monatomic wires.

Graphene has attracted widespread scientific and technological interest due to its unique properties, and graphene/metal contacts are inevitable and omnipresent components in graphene-based devices, such as memory devices, plasmonic devices and energy-conversion devices. It has been shown that defects in graphene play a key role in stabilizing metal clusters by providing strong anchoring sites. Thus, it is expected that the edge of graphene can provide active sites for chemical bonding, due to the unsaturated bonds, which has served as a good support for metal monatomic wires. To our knowledge, Pt nanowires can be exclusively formed on the edge of highly oriented pyrolytic graphite by open circuit deposition, or atomic layer deposition technique, due to the strong chemical binding between Pt atoms and the edge C atoms. Thus, if the substrate changes from graphite to graphene, the binding face location of graphite for the above Pt nanowires becomes a line one for forming a Pt monatomic wire, if other experimental conditions remain. In fact, this has been carried out on graphene when the element is Cr, where a monatomic chain of Cr is built on the edge of graphene experimentally. Since the binding energy between Cr and C (4.9 eV) is smaller than that between Pt and C (6.4 eV), Pt atoms can be trapped by the edge of graphene. Recently, the atomic structure of the boundary between a graphene zigzag edge and a Pt(111) step has been unveiled by STM experiments and DFT calculation, which shows the strong bonding between the edge C and Pt atoms. Thus, the synthesis of Pt monatomic wire that is supported on the zigzag edges of graphene nanoribbon (Pt–GNR) is feasible.

Here, we consider Pt–GNR as ORR catalyst by using density functional theory (DFT) calculations. It is found that Pt–GNR is inert as ORR catalyst due to strong adsorption ability. However, when Pt–GNR is covered by a chain consisting of OH and H₂O, defined as cPt–GNR, it is activated. Based on the free energy diagrams, we demonstrate that the highest potential for ORR underway is 0.82 eV, being comparable with 0.75 or 0.78 eV of Pt(111). The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional is employed to describe exchange and correlation...
effects. The DFT semi-core pseudopots (DSPP) core treat method is implemented for relativistic effects, which replaces core electrons by a single effective potential and introduces some degree of relativistic correction into the core. The double numerical atomic orbital augmented by a polarization function (DNP) is chosen as the basis set. A smearing of 0.005 Ha (1 Ha = 27.21 ev) to the orbital occupation is applied to achieve accurate electronic convergence. The spin-unrestricted method is used for all optimization calculations. A vacuum larger than 20 Å thick is added to avoid the artificial interactions between Pt–GNR and its images. In all of the structure optimization calculations, all atoms are fully relaxed.

Combining high resolution STM experiments and DFT calculations, Merino et al. have unambiguously unveiled the atomic structure of the boundary between a graphene zigzag edge and a Pt(111) step, and the corrugation of Pt atoms at the graphene–Pt junction has been identified. Thus, the corrugated Pt–GNR is considered in our work. The structure of Pt–GNR that is proposed in ref. 30 is shown in Fig. 1(a). The average bond lengths of Pt–C bonds (l_{Pt–C}) and Pt–Pt bonds (l_{Pt–Pt}) are 1.92 and 2.57 Å, respectively. The monatomic wire is high corrugated with the corrugation angle of θ = 148°. However, another structure is more stable with the energy 0.77 eV per cell lower, as shown in Fig. 1(b) and (d). The average l_{Pt–C} and l_{Pt–Pt} are 1.93 Å and 2.51 Å, respectively, and θ is 158°. Thus, in our study, the latter one is adopted. On the other hand, in order to demonstrate the coadsorption phenomenon, Pt(111) is modeled by a three-layer (2√3 × 2√3)R30° periodic slab where the two bottom layers are fixed (36 atoms per cell). It is worth noting that the convergence testing is performed on four layers of atoms with the bottom two fixed, and the same adsorption structures are given. Thus, we expect the three layer periodic model is enough.

The adsorption energy (E_{ads}) of adsorbates on these substrates are calculated by,

\[ E_{ads}(M) = E_{sys} - E_{M} - E_{substrate} \]  

where \( E_{sys} \), \( E_{M} \) and \( E_{substrate} \) are the total energies of the adsorption systems, an isolated adsorbate species and the substrate, respectively. M denotes \( \text{O}_2 \), \( \text{OOH} \), \( \text{O} \), \( \text{OH} \) and \( \text{H}_2\text{O} \). \( E_{ads} < 0 \) corresponds to an exothermic adsorption process.

Due to the structural deformation during the adsorption process, besides adsorption energy \( E_{ads} \), the interaction energy \( E_{int} \) should give accurate information of the bonding strength between the adsorbates and substrate,

\[ E_{int}(M) = E_{sys} - E_{M-def} - E_{substrate-def} \]  

where \( E_{M-def} \) and \( E_{substrate-def} \) are the energies of M and the substrate with the deformed geometry, respectively. \( E_{int} < 0 \) denotes an exothermic adsorption process.

Free energies of the ORR intermediates in electrochemical reaction pathways are calculated based on a computational hydrogen electrode (CHE) model. The CHE model defines that the chemical potential of proton-electron \((\text{H}^+ + e^-)\) in solution is equal to the half of the chemical potential of a gas-phase \( \text{H}_2 \). Free energy change \( (\Delta G) \) is defined as,

\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S \]  

where \( \Delta E \) is the total energy change directly obtained from DFT calculations, \( \Delta ZPE \) is the change in zero-point energies, \( T \) denotes temperature, and \( \Delta S \) is the change in entropy. The effect of a bias can be applied shifting \( \Delta G \) by \(-eU\), where \( e \) is the elementary positive change and \( U \) is the applied bias. Free energies of adsorbates are calculated by treating 3N degrees of freedom of adsorbates as vibrational frequencies in the harmonic oscillator approximation and fixing the substrate. The zero-point energies and entropies of the ORR intermediates are calculated from the vibrational frequencies according to standard methods. \( \Delta G < 0 \) corresponds to an exothermic adsorption process. The free energy \( G \) of \( \text{O}_2 \) is derived as \( G(\text{O}_2) = 4.92 + 2G(\text{H}_2\text{O}) - 2G(\text{H}_2) \) by utilizing OER equilibrium at the standard conditions.

3. Results and discussion

The ORR process on Pt–GNR

In order to characterize the nature of the interaction between the Pt atoms and the edge C atoms of Pt–GNR, the partial density of states (PDOS) is shown in Fig. 2(a). It is obvious that Pt-5d is highly hybridized with C-2p at the range from \(-6.8 \) to \(-2.7 \) eV while a little contribution comes from s–d hybridization. From the deformation electron density shown in the insert of Fig. 2(a), we can see that electrons accumulate between the Pt atoms and the edge C atoms, indicating the formation of covalent Pt–C bonds. In addition, since the low-temperature polymer electrolyte fuel cells are operated at 253 to 373 K, first-principle molecular dynamics (MD) simulation at a constant temperature of \( T = 400 \) K in the NVT ensemble \( (i.e., \) constant particle number, volume and temperature conditions) has been carried out for 2 ps with the time step of 1 fs. This selection of the temperature, being higher than the working temperature, could confirm the stability of the studied Pt–GNR system at
working temperature. In Fig. 2(b), four structures from MD calculation are present. As shown in the figure, it is found that Pt atoms are fixed at the edge of GNR and the Pt clustering is absent at 400 K.

Before investigating the ORR mechanism, we first study the adsorption of O$_2$ and ORR intermediates on Pt–GNR. The adsorption energies $E_{\text{ads}}$ are listed in Table 1 and the corresponding structures are shown in Fig. 3(a–e). The adsorption and activation of O$_2$ are the first step for ORR. Fig. 3(a) presents the optimized geometry of O$_2$ adsorption on Pt–GNR. O$_2$ is located at the bridge site on Pt–GNR with the $E_{\text{ads}}(\text{O}_2) = -1.39$ eV and the bond length of O–O ($l_{\text{O–O}}$) is elongated to 1.36 Å compared with 1.23 Å of the gas O$_2$. The $E_{\text{ads}}(\text{O}_2)$ on Pt(111) has been determined by experiments and simulations [experimentally $E_{\text{ads}}(\text{O}_2) = 0.3$–0.5 eV on Pt(111) with low-coverage$^{45,46}$ and theoretically $E_{\text{ads}}(\text{O}_2) = 0.41$–0.72 eV when O$_2$ is adsorbed on bridge site of Pt(111)$^{47–49}$. $E_{\text{ads}}(\text{O}_2)$ on Pt–GNR is much stronger than the above results on Pt(111) due to the lower coordination number of Pt in a monatomic wire.\(^\text{xix}\) In order to gain further insight into the origin of the interaction between O$_2$ and Pt–GNR, the corresponding electronic structures are shown in Fig. 4 where the spin-polarized PDOS projected onto the O–O bond has considerable change. Firstly, spin polarization of the adsorbed O$_2$ orbitals is absent, denoting strong interaction between O$_2$ and Pt–GNR. Furthermore, 5$s$, 1$p$ and 2$p^*$ orbitals of O$_2$ are broadening, which dominate the adsorption of O$_2$ while 2$p^*$ orbitals are partially filled. This filling is responsible for the catalytic activation of the adsorbed O$_2$ and the stretching $l_{\text{O–O}}$.\(^\text{xii}\) The charge transfer from Pt–GNR to O$_2$ is 0.29 eV according to Hirshfeld population charge distribution listed in Table 1, which is agreement with the increase of $l_{\text{O–O}}$.

Fig. 3(b) depicts the favorable adsorption structure of OOH on Pt–GNR. OOH is located at the bridge site and binds strongly to Pt–GNR with $E_{\text{ads}}(\text{OOH}) = -2.33$ eV. Therein, the $l_{\text{O–O}}$ of the adsorbed OOH increases to 1.54 Å compared with the unadsorbed one (1.34 Å). The weakening of the O–O bond should promote the dissociation of OOH into O and OH fragments. In accordance with the previous work,\(^\text{xiii}\) $E_{\text{ads}}(\text{OOH})$ is $-1.06$ eV on Pt(111), being weaker than that of Pt–GNR. For O adsorption on Pt–GNR, as shown in Fig. 3(c), O prefers to locate at the bridge site and $E_{\text{ads}}(\text{O})$ is $-3.72$ eV, which is weaker than $-4.21$ eV of Pt(111).\(^\text{xiv}\) In Fig. 3(d), the OH adsorption is more stable at the bridge site with $E_{\text{ads}}(\text{OH}) = -3.14$ eV, which is stronger than that of Pt(111) $(-2.24, -2.31$ eV$)^{49,55}$, H$_2$O is the final product of the ORR. As shown in Fig. 3(e), H$_2$O is located at atop site with $E_{\text{ads}}(\text{H}_2\text{O}) = -0.77$ eV. This value is stronger than the solvation stabilization energy ($-0.40$ eV) of bulk H$_2$O.\(^\text{xv}\) Thus, H$_2$O could not be readily released into the bulk solution, hampering the next ORR cycle.

It has been demonstrated that the best $E_{\text{ads}}(\text{O})$ and $E_{\text{ads}}(\text{OH})$ of the ORR catalysts should be 0.0–0.4 eV and 0.0–0.2 eV weaker than that of Pt(111),\(^\text{xvi–xviii}\) respectively, where there exist a scaling relationship between $E_{\text{ads}}(\text{O})$ and $E_{\text{ads}}(\text{OH})$.\(^\text{xix}\) However, this scaling relationship is invalid for Pt–GNR where there are a
weaker $E_{\text{ads}}(\text{O})$ but a stronger $E_{\text{ads}}(\text{OH})$, compared with Pt(111).
Thus, the ORR reaction under a potential $U$ should be studied in details.

A standard ORR mechanism involves four proton and electron transfers at the cathode, which mainly include three mechanisms: $\text{O}_2$ dissociation, OOH dissociation and $\text{H}_2\text{O}_2$ dissociation. To study the activity of Pt–GNR, the OOH associative mechanism of ORR is taken as an example and considered by the following steps (* denotes adsorbed species and g l$^{-1}$ shows gas/liquid state),

$$\begin{align*}
\text{O}_2(\text{g}) + * & \rightarrow \text{O}_2^*, \\
\text{O}_2^* + (\text{H}^+ + e^-) & \rightarrow \text{OOH}^*, \\
\text{OOH}^* + (\text{H}^+ + e^-) & \rightarrow 2\text{OH}^*, \\
2\text{OH}^* + (\text{H}^+ + e^-) & \rightarrow \text{H}_2\text{O}^* + \text{OH}^*, \\
\text{H}_2\text{O}^* + \text{OH}^* + (\text{H}^+ + e^-) & \rightarrow 2\text{H}_2\text{O}^*, \\
2\text{H}_2\text{O}^* & \rightarrow 2\text{H}_2\text{O(l)} + \text{O}^*. 
\end{align*}$$

According to this mechanism, (R4) is a process of the molecular adsorption and activation of $\text{O}_2$. (R5) shows the reduction of $\text{O}_2^*$ to OOH*, which occurs through coupled proton–electron transfer (CPET), as suggested by Damjanovic and Brusic. (R6) should be the reduction of OOH* to $\text{O}^*$ and $\text{H}_2\text{O}^*$ through a CPET. However, since $\text{O}^*$ and $\text{H}_2\text{O}^*$ are spontaneously transferred to 2OH* after the relaxation, OOH* is reduced to 2OH*. In order to further confirm the stability of 2OH*, we perform geometry optimization with five different initial configurations of O*/H$_2$O* shown in Fig. 5. For the
configurations I and II, the $O^*$ and $H_2O^*$ locate at the adjacent atop sites with different $H_2O^*$ orientations. After relaxation, $O^*$ and $H_2O^*$ are transferred to $2OH^*$ with the same structure. On the other hand, another three configurations are considered where the location of $H_2O^*$ is kept and $O^*$ is moved away in order to increase the distance between $O^*$ and $H_2O^*$. For the configurations III and IV, $O^*$ absorption is located on bridge site while for the configuration V, $O^*$ is at atop site. The above three configurations converge to the same coadsorption structure of $O^*$ and $H_2O^*$ after relaxation where the total energy of these states are 0.45 eV higher than the case of $2OH^*$ pair. Thus, compared with $O^*$ and $H_2O^*$ on Pt–GNR, $2OH^*$ is more stable and we take it as the product of (R3). (R4) and (R5) indicate the recovery of Pt–GNR. The first step (R6) is the desorption of $H_2O^*$ and recovery of Pt–GNR.

Firstly, in order to analyze the stability of ORR intermediates thermodynamically, the \textit{ab initio} phase diagram is established on Pt–GNR, as shown in Fig. 6(a). Here, the stability of the ORR intermediates is characterized as a function of the electrode bias $U$. Obviously, as the potential $U$ changes from 0 to 1.23 V, the coadsorption system of $H_2O^*$ and $OH^*$ is stable and identified as the thermodynamic ground state, where its free energy $G$ is even lower than the system of $H_2O(l)$ and Pt–GNR. This suggests that Pt–GNR should be covered by $H_2O^*$ and $OH^*$ and lose its activity.

To further understand the ORR activity of Pt–GNR, the $G$ under two limiting potentials $U$ of 0 V and 1.23 V are shown in Fig. 7(a) and the free energy change $\Delta G$ of the endothermic steps as a function of $U$ are shown in Fig. 7(b). At $U = 0$ V, (R3) and (R4) are endothermic with $\Delta G_{R3} = 0.12$ eV and $\Delta G_{R4} = 0.53$ eV while other steps are strong exothermic. At the equilibrium bias of $U = 1.23$ V, corresponding to the situation where the fuel cell has the maximum potential allowed by thermodynamics, (R3) changes from exothermic to endothermic process with $\Delta G_{R3} = 0.69$ eV. (R5) becomes more endothermic and $\Delta G_{R5}$ reaches 1.35 eV. $\Delta G_{R6}$ is 0.53 eV, which is independent on $U$. As shown in Fig. 7(b), when $U$ is less than 0.42 V, the rate-determined step (RDS) is located at (R6). On the other hand, when $U$ locates at the range from 0.42 to 1.23 V, RDS changes to (R3), which is consistent with that of the graphene-supported Pt13 cluster. Thus, the endothermic steps are always present for Pt–GNR. Due to the strong endothermic process of (R3) and the thermodynamic stability of $H_2O^*$ and $OH^*$ coadsorption system shown in Fig. 6(a), it is confirmed that the Pt–GNR would be covered by a chain combined with $H_2O^*$ and $OH^*$ (cPt–GNR) whose structure is shown in Fig. 1(c) and (e). Thus, in the following text, we test the ORR activity on cPt–GNR.

The ORR process on cPt–GNR

Compared with Pt–GNR, the average $I_{Pt–Pt}$, $I_{Pt–C}$ and $\theta$ of cPt–GNR are nearly unchanged with the values of 2.51 Å, 1.97 Å and 159°, respectively. The bonding energy between Pt monatomic...
 elongated to 1.35 $H_2O$

Therein, the electronic structure of the adsorbed $O_2$ is in contradiction with the positive orbital is partial.

The spin polarization disappears and 2 positive ability of $O_2$ on Pt adsorption of $O_2$. The GNR is shown in Fig. 3(f). However, the adsorption is absent. The corresponding adsorption structure from the insert in Fig. 2(a), the covalent nature of Pt–C bonds is confirmed by the deformation electron density.

$E_{\text{ads}}(O_2)$ is 0.09 eV as $O_2$ adsorbs at bridge site of cPt–GNR or the adsorption is absent. The corresponding adsorption structure is shown in Fig. 3(f). However, the $I_{\text{ads}}$ of the adsorbed $O_2$ is elongated to 1.35 Å and $O_2$ indeed gets activated. From the PDOS of the adsorbed $O_2$ shown in Fig. 4, it is obvious that the $\pi r$, $1\pi$ and $2\pi^*$ orbitals of $O_2$ are broadened, which dominates the adsorption of $O_2$. The spin polarization disappears and $2\pi^*$ orbital is partial filled. In light of Hirshfeld charge analysis listed in Table 1, 0.18 charge transfers from cPt–GNR to the $2\pi^*$ orbital, further supporting the adsorption and activation of $O_2$.

Therein, the electronic structure of the adsorbed $O_2$ is in contradiction with the positive $E_{\text{ads}}$. Since $E_{\text{ads}}$ can be divided into the deformation energy and the interaction energy $E_{\text{int}}$ the positive $E_{\text{ads}}$ could be originated from the deformation energy [$E_{\text{int}}(O_2) = -0.48$ eV on cPt–GNR, which is in accord with the electronic structure shown in Fig. 4]. Compared with Pt–GNR [$E_{\text{ads}}(O_2) = -1.39$ eV and $E_{\text{int}}(O_2) = -2.01$ eV], the adsorption ability of $O_2$ on cPt–GNR is substantially weakened due to the preferential adsorption of OH* and H$_2$O*. It should be noted that if Pt atoms in Pt monatomic wires are covered by the OH* and H$_2$O*, which could exist in the ORR reaction, the $O_3$ adsorption and activation remain due to the low-coordination number and more open structure, which makes the ORR in proceed. However, this cannot be realized at the case of Pt(111). As shown in Fig. 3(h), $O_2$ cannot be bonded with Pt atoms covered by the OH* and H$_2$O* on Pt(111). For the end-on configuration, $O_2$ locates at the atop site of the adjacent Pt atom to form hydrogen bonding with OH* (OH–H–O) while for side-on configuration, $O_2$ is on the bridge site to form hydrogen bonding with another OH* (OH–H–O–H–O). Further increasing the coverage of the OH* and H$_2$O*, $O_2$ still locates at the uncovered Pt atom (OH–H–O–H–O). Thus, the covered Pt atom on Pt(111) is inert due to the presence of OH* and H$_2$O*, which prevent the adsorption of the reactant $O_3$ and the ORR reaction is terminated.

The stable adsorption structures of ORR intermediates are shown in Fig. 3(g–j) and the $E_{\text{ads}}$ are summarized in Table 1. $E_{\text{ads}}$(OOH) is $-0.99$ eV at atop site and $I_{\text{ads}}$ is 1.40 Å. Compared with 1.34 Å of the gas one, the weakening of the O–O bond appears and should promote the dissociation of OOH into O and OH fragments. $E_{\text{ads}}$(O) is $-3.40$ eV at bridge site. For OH adsorption, atop site is slightly preferred compared with bridge site [$E_{\text{ads}}$(OH) is $-2.08$ eV at atop site and $E_{\text{ads}}$(OH) is $-1.92$ eV at bridge site]. Note that H$_2$O cannot locate at Pt monatomic wire and promote forming two hydrogen bonds with the chain of H$_2$O* and OH*, which benefits for recovery of the catalyst for the next ORR cycle. Obviously, the existence of chain of H$_2$O* and OH* on Pt–GNR weakens the adsorption ability of $O_2$ and ORR intermediates where the electron number transferred from cPt–GNR is smaller than that from Pt–GNR as listed in Table 1.

To provide a physical picture for the potential catalytic activity of cPt–GNR, the deformation density is shown in Fig. 8.

**Fig. 7** The ORR processes on Pt–GNR [(a) and (b)] and cPt–GNR [(c) and (d)]. Zero on the free energy axis corresponds to Pt–GNR or cPt–GNR and two $H_2O$ molecules.
Fig. 8(a) shows the electron accumulation of original cPt–GNR is located on O atoms of the OH*/H2O* chain. In Fig. 8(b)–(e), even the adsorbates are different after the adsorption, electron is still accumulated on O atoms of both adsorbates and OH*/H2O* chain. Thus, the weakening of adsorption ability of cPt–GNR should originate from the electrostatic repulsion between the OH*/H2O* chain and the adsorbates (O2 and ORR intermediates). This conclusion has been found in other systems, such as the adsorption of O or OH on Ru(0001), where the electrostatic repulsion occurs due to the presence of Se.53

Therefore, we expect that the adsorbed species on cPt–GNR could be easily removed and cPt–GNR possesses ORR activity.

Now, the energetics of the ORR on cPt–GNR is analyzed by the simple potential-dependent model,

\[
\begin{align*}
O_2(g) + * &\rightarrow O_2^*, \\
O_2^* + (H^+ + e^-) &\rightarrow OO^*, \\
OO^* + (H^+ + e^-) &\rightarrow O^* + H_2O(l), \\
O^* + (H^+ + e^-) &\rightarrow OH^*, \\
OH^* + (H^+ + e^-) &\rightarrow H_2O(l).
\end{align*}
\]

Since H2O cannot be adsorbed on cPt–GNR, reduction of OO* to O* and H2O(l) through continuous CPET, defined as (R7). (R8) and (R9) indicate the reduction processes from O to OH* and from OH* to H2O(l).

In Fig. 6(b), the phase diagram of ORR intermediates on cPt–GNR is shown. Differing from Pt–GNR, when 0 ≤ U ≤ 1.11 V, the system of H2O(l) and cPt–GNR is thermodynamic ground state. When U > 1.11 V, the adsorption system of O* on cPt–GNR is the stable phase. The G function at the limiting condition (U = 0 V and U = 1.23 V) are shown in Fig. 7(c). At U = 0 V, all steps are exothermic. On the other hand, when U is 1.23 V, (R8) and (R9) become endothermic with ΔG_{R8} = 0.41 eV and ΔG_{R9} = 0.36 eV, respectively. From the ΔG shown in Fig. 7(d), when U is less than 0.82 V, all ORR steps are exothermic, which means that the reactions are thermodynamically favorable. (R2) and (R5) become endothermic at the values of U = 0.82 and 0.87 V, respectively. Furthermore, ΔG_{R2} is always larger than ΔG_{R5}. Thus, the RDS is located at (R2) with the maximum of ΔG_{R2} = 0.41 eV, which is much smaller than the case of Pt–GNR (1.35 eV). The maximal U value corresponding to the exothermic steps of ORR is 0.82 V, which is comparable with Pt(111) (0.75 or 0.78 V).1,17

Since the presence of the overpotential would reduce the thermal efficiency well below the thermodynamic limit, the thermal efficiency ε of this system is considered here. It is well known ε is calculated by,

\[
\varepsilon = \frac{\Delta g}{\Delta h_{\text{HHV}}}
\]

where Δg = −nFU is the useful work, n is the number of transfer electron (n = 2 for 1 mol hydrogen), F is the Faraday constant (F = 96485 C mol⁻¹) and U denotes the maximal U for the exothermic ORR (in our case, U = 0.82 V), Δh_{\text{HHV}} is the ideal energy released by 1 mol hydrogen combustion (Δh_{\text{HHV}} = −286 kJ mol⁻¹). In light of eqn (4), ε value of cPt–GNR reaches 55% [the theoretical limit ε value is 83% at 1.23 V (ref. 64)]. When we calculate the case of Pt(111),1,17 this value is 51–53%. To simplify, the effect of the fuel utilization is neglected.

From the aspect of the free energy barriers, the activity of cPt–GNR could be compared with that of Pt–GNR. Usually, the activity of the ORR catalysts is generally characterized under U = 0.9 V.7,13,14 Thus, the ΔG values of cPt–GNR under this potential are given in Fig. 7(c), which are 0.08 eV and 0.03 eV for (R2) and (R5), respectively. Since the activation barrier for the rate-limiting proton-transfer step is equal to the maximal ΔG value, the thermodynamic barrier associated with over ORR process is 0.08 eV. Compared with the barrier of Pt–GNR (1.02 eV) in Fig. 7(a), the cPt–GNR is more active than Pt–GNR (this value for Pt(111) is 0.07 eV,45 being comparable with cPt–GNR). Thus, it is expected that cPt–GNR would be viewed as a good candidate of ORR electrocatalyst.

4. Conclusions

In summary, we have reported cPt–GNR as a suitable ORR electrocatalyst. It is found that the rate-determined step is located at the reduction of O2* to OO* with maximal barrier of 0.41 eV as U is 1.23 V. Thus, cPt–GNR could be a candidate of ORR electrocatalyst.

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