Ultra-low overpotential and high rate capability in Li–O₂ batteries through surface atom arrangement of PdCu nanocatalysts†

Ran Choi,†a Jaypeong Jung,†b Gyubong Kim,c Kyeongse Song, Yong-II Kim, d Sung Chul Jung, b Young-Kyu Han, b Kyunjoong Song,b and Yong-Mook Kang b

PdCu bimetallic nanoparticles (NPs) having mixed disordered face-centered cubic (fcc) and ordered body-centered cubic (B2-type) phases enhance the kinetics of oxygen reduction/evolution reaction by significant reduction of overpotentials, which leads to the superb round-trip efficiency of ~80%. In addition, the PdCu catalyst demonstrates a remarkable cyclic enhancement in stability and an outstanding rate capability even at a high current density of 5000 mA g⁻¹. Our first-principles calculations demonstrate that the low overpotentials of the PdCu catalyst are strongly correlated with the weak LiO₂ adsorption strength, caused by electron transfer from Cu to the top-layer Pd atoms on the surface.

Recently, Li–O₂ batteries have emerged as promising technology for electric vehicles and energy storage systems due to their high theoretical energy density (gravimetric energy density). The energy density of Li-ion batteries is between 100 and 200 W h kg⁻¹, which is far from the target of matching the practical energy density of gasoline (1700 W h kg⁻¹). However, Li–O₂ batteries are predicted to be an alternative fuel because their theoretical energy density is as high as 11 680 W h kg⁻¹.1,2 At present, there are many obstacles limiting practical applications of Li–O₂ batteries, including poor power capability,3 short cycle life,4 and low energy efficiency5 mainly caused by their sluggish kinetics. Apparently, to improve these kinetics, a rational design of electrocatalysts toward improving oxygen reduction reaction (ORR, during discharge) or oxygen evolution reaction (OER, during charging) must be devised. Numerous researchers have investigated various materials, including porous carbons, metal oxides, and metals, for use as the ORR and/or OER catalysts.5 Among them, noble metal-based catalysts are known to have higher discharge voltages than those of metal oxides.6 In particular, bimetallic catalysts that consist of two distinct noble metals exhibit enhanced catalytic reactivity due to their ensemble, ligand, and geometric effects.6 Shao-Horn et al.6 reported that bifunctional catalysts containing Au, which is highly active in the ORR, and Pt, which is highly active in the OER, demonstrated an enhanced round-trip efficiency. We note, however, that other electrochemical properties important for practical applications, such as discharge rate capability and cycle performance, still remain to be improved. Moreover, the studies on catalysts which can simultaneously improve cycle life and high rate capability, as well as round-trip efficiency, have been seldom reported.

The atomic arrangement of such bimetallic catalysts exerts a significant influence on reaction activity. Sun et al.7 found that the catalytic activity of FePt nanoparticles (NPs) depends on

Broader context

Improving the round-trip efficiency, cycle life and power capability of Li–O₂ batteries through the development of catalysts is essential for their employment in electric vehicles. In particular, bimetallic catalysts that consist of two distinct noble metals exhibit enhanced catalytic reactivity and their atomic arrangement exerts a significant influence on reaction activity. In this communication, we report on bimetallic nanoparticles (NPs) having mixed atomically disordered face-centered-cubic and ordered B2-type phases, and their enhanced electrochemical performance in Li–O₂ cells. Furthermore, our first-principles calculations prove how atomic arrangement of the catalyst surface influences catalytic performance. From the study on the performance of Li–O₂ batteries at the atomic level, we expect that multimetallic nanocatalysts optimized by effective surface engineering can increase the possibilities for the practical application of Li–O₂ batteries in automobiles by enhancing the ORR and OER kinetics, resulting in long cycle life and high rate capability, as well as high round-trip efficiency.

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their structure. Face-centered tetragonal (fct) FePt with a chemically ordered structure exhibited improved catalytic activity and durability toward the ORR compared to face-centered cubic (fcc) FePt with disordered arrangement, indicating the importance of the stable intermetallic Fe and Pt arrangement. It was reported that the homogeneous phase of PdCu catalysts also demonstrated an improved activity toward ORR.\(^8\)

On the basis of these observations, bimetallic catalysts with an atomically ordered structure are expected to be potential cathode catalysts in Li–O\(_2\) batteries. Pd NPs are known to be one of the best catalysts for demonstrating outstanding activity of ORR among noble metal catalysts with the highest discharge potential.\(^6\) To further adjust catalytic performance based on a concept of a bifunctional catalyst, we wanted to combine Pd with another transition metal, i.e., Cu, and precisely control their crystallinity and electronic band structure. PdCu alloy NPs commonly have a random face-centered cubic (fcc) structure with a Cu-rich surface, reflecting the interplay of surface energy, heteroatom-philic bonding, and reduction potential.\(^13\)–\(^14\) Recently, it was reported that PdCu NPs with an ordered body-centered cubic (B2-type) structure had been synthesized either by a chemical reduction method or heat treatment.\(^15\)–\(^18\) In order to figure out the most catalytically active structure, we synthesized PdCu NPs with mixed phases of fcc and B2-type in the presence of benzyl amine.

In this study, we compared the catalytic activity and stability of Pd and PdCu NPs in Li–O\(_2\) batteries, and proved how atomic arrangement of the catalyst surface influences catalytic performance using theoretical calculations. In Li–O\(_2\) cells, the overpotentials of the PdCu NPs toward ORR and OER were significantly reduced to produce the superb round-trip efficiency of ~80% at a current density of 200 mA g\(_{\text{carbon}}\)\(^{-1}\). Moreover, the PdCu catalysts exhibited not only a better cycle performance but also the highest discharge rate capability among various catalysts ever reported to date.\(^7\) The PdCu NPs maintained a significant discharge capacity as high as 1689 mA h g\(_{\text{carbon}}\)\(^{-1}\), even under the harsh condition of 5000 mA g\(_{\text{carbon}}\)\(^{-1}\). We have successfully demonstrated that the LiO\(_2\) adsorption strength on the catalyst surface is strongly correlated with the ORR and OER overpotentials, and that the PdCu in the PdCu catalyst was crucial to the enhanced catalytic activity. Electron transfer from Cu to the top-layer Pd atoms weakened the adsorption strength of lithium oxides on the PdCu surface, which eventually provided low overpotentials for both ORR and OER processes.

The PdCu NPs were synthesized by a polyol method in the presence of benzyl amine. To balance the reaction kinetics of the two metallic precursors, the Pd precursor was mixed with poly(vinyl pyrrolidone) (PVP) in ethylene glycol (EG), and the Cu precursor was separately dissolved in benzyl amine. The solutions were mixed and heated at 200 °C for 1 h under an inert atmosphere (see in the ESI†). The resulting particles had a Pd/Cu molar ratio of 46 : 54, as estimated by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The transmission electron microscopy (TEM) image shows that the PdCu NPs are spherical with an average diameter of 7.8 ± 0.8 nm (Fig. 1a and b and S1 in the ESI†). The high resolution power X-ray diffraction (XRD) analysis with Rietveld refinement confirms that the phase of the PdCu NPs is a mixture of fcc and B2-type structures, with a weight fraction of 49 : 51 (Fig. 1c and Table S1 in the ESI†). In addition, the high resolution TEM (HRTEM) images in Fig. 1a and b show that the d-spacings of adjacent lattice fringes are 2.169 Å and 2.098 Å, which correspond to the spacings of the \{111\} planes in fcc PdCu (2.175 Å) and the \{110\} planes in B2-type PdCu (2.114 Å), calculated from the Rietveld refinement analysis, respectively.

Although the B2-type phase is stable in the bulk state,\(^5\) the PdCu alloy is commonly obtained with a random fcc structure.\(^8\) In this experiment, the precise control of reaction kinetics by benzyl amine allowed the concomitant formation of the B2-type structure, which is relatively unstable, as well as the stable fcc phase in the PdCu NPs. Benzyl amine played a key role in controlling the reduction kinetics of Pd and Cu.\(^6\) Cu is generally considered to be more reactive than Pd; therefore, a Cu precursor with a chelate ligand was chosen to slow down the reaction rate. Without benzyl amine under the present synthetic conditions, the resulting particles were neither uniform nor single-crystalline, and the alloy NPs had only a small fraction (~8%) of Cu (Fig. S2 and Table S2 in the ESI†). By increasing the added amount of benzyl amine in the reaction mixture, the \{110\} peak intensity of the B2-type phase increased in the XRD spectrum (Fig. S3 in ESI†). The benzyl amine could dissolve the Cu species, and accelerate the reduction rate of Cu to be incorporated on the PdCu NPs.

Bimetallic PdCu NPs with mixed phases of fcc and B2-type provide a unique opportunity to investigate the role of surface atomic arrangement in catalytic behavior in the ORR and OER of Li–O\(_2\) batteries. To evaluate the catalytic activity of the PdCu NPs in Li–O\(_2\) batteries, Swagelok-type cells were assembled using a Ketjen black supported PdCu catalyst as a cathode, a Li metal foil as an anode, glass fibers as a spacer and a tetra(ethylene glycol) dimethyl ether (TEGDME)/LiCF\(_3\)SO\(_3\) solution as an electrolyte (see in the ESI†). For the intrinsic comparison of catalytic activity, Pd NPs were synthesized with an average size (7.8 ± 0.7 nm) identical to that of the PdCu NPs (Fig. S4 in...
the ESI†). The cells were purged with O₂ gas (purity: 99.995%) for 10 min and closed after the pressure reached 1.1 atm, and then galvanostatically charged and discharged between 2.0 V and 4.2 V versus Li/Li⁺ (V_Li). To obtain discharge/charge profiles, a constant capacity of 1000 mA h g_carbon⁻¹ was used at the current density of 200 mA g_carbon⁻¹. The first potential profiles of the PdCu and Pd NPs exhibited relatively high OER overpotentials accompanied by undesired side reactions or decomposition of organic moieties on the catalyst surface (Fig. S5a-c in the ESI†). After the first cycle, both PdCu and Pd catalysts showed a gradational decrease of OER potentials up to the third cycle which may be associated with the decomposition of the surfactants (PVP) anchored on the particle surface. The third galvanostatic potential profiles after complete stabilization represent the intrinsic ORR and OER activities of the PdCu and Pd catalysts (Fig. 2a). The discharge/charge voltage profiles normalized by the weight of the electrode and metal catalysts are demonstrated in Fig. S6 in the ESI†. The PdCu and Pd catalysts exhibited average discharge voltage plateaus at 2.73 and 2.72 V_Li, respectively (Fig. 2a inset), while the Ketjen black, commercial Pd–C and Pt–C catalysts had the plateaus at 2.64 V_Li, 2.69 V_Li, and 2.65 V_Li, respectively (Fig. S5c and d in the ESI†). This is because the thermodynamic equilibrium potential of Li₂O₂ formation is within 0.1 eV near the ORR potential plateau of Pd NPs. On the other hand, the PdCu catalyst showed an average charge voltage plateau at 3.40 V_Li, which is remarkably lower than the plateaus of the Pd catalyst (3.75 V_Li), Ketjen black (4.15 V_Li), commercial Pd–C (3.86 V_Li), and Pt–C (3.58 V_Li). The charging voltage of the PdCu catalyst is the lowest value that has ever been reported, i.e., the MnO nanowire (4.0 V_Li at 70 mA g_carbon⁻¹)† and the PtAu–C (3.6 V_Li at 100 mA g_carbon⁻¹)† catalysts.

Such a low OER overpotential of the PdCu catalyst is relevant to the morphology of the discharge products formed during discharge as shown in Fig. 3. Fig. 3b shows that the discharge products in the form of flower-shaped nanosheets are uniformly deposited on the cathodes adopting the PdCu catalyst. In contrast to this, the cathode adopting Pd catalysts displayed the typical toroidal and irregularly dispersed discharge products (Fig. 3e). This observation demonstrates that the OER overpotential can be determined according to the morphology of discharge products, although the discharge products were completely decomposed after 1ˢᵗ charge, regardless of their shape (Fig. 3c and f). A regularly dispersed nanosheet-shaped discharge product on the cathode results in a lower OER overpotential than a toroidal product. The discharge products on the cathode after discharge and charge were also confirmed by X-ray photoelectron spectroscopy (XPS). Fig. S7 in the ESI† demonstrates that a main discharge product is Li₂O₂, and the discharge product is fully decomposed during the OER process. Therefore, it can be concluded that due to regular shape and small size of the discharge product, Li₂O₂, the PdCu catalyst exhibits a low OER overpotential as well as the superb round-trip efficiency of ~80% in Li–O₂ batteries. Fig. 2b presents the change of end discharge potentials during the continuous cycling of Li–O₂ batteries with the PdCu or Pd NPs as the main

Fig. 2 The electrochemical performance of Li–O₂ cells using PdCu and Pd NPs as the cathode catalyst. (a) The third galvanostatic discharge/charge profiles (inset: magnified discharge profiles), (b) The cyclic behaviors of ORR end-potentials measured at the current density of 200 mA g_carbon⁻¹ after ORR is completed at each cycle, and (c) The discharge profiles obtained at various current densities.

Fig. 3 SEM images of (a) pristine, (b) discharged, and (c) charged cathodes commonly adopting PdCu NPs as the cathode catalyst. SEM images of (d) pristine, (e) discharged, and (f) charged cathodes commonly adopting Pd NPs as the cathode catalyst.
catalyst. Previous studies of the cathodes in Li–O2 batteries reported that the ORR potential tended to drastically decrease during cycling although the discharge capacity after ORR seemed to be retained.24–26 This phenomenon was closely related to the high thermodynamic stability of the main ORR products, Li2O or Li2O2, and resulted in the poor round-trip efficiency of Li–air batteries.27–29 However, in the present experiments, the PdCu catalyst displayed an unprecedented stable ORR potential with good discharge capacity retention up to 50 cycles, while it showed a little unstable OER potential (Fig. S8 in the ESI†). In contrast to this, the ORR potential of the Pd catalyst drastically dropped after 20 cycles and the OER potential also rapidly increased to 4.2 V Li a for as-synthesized fcc-rich and B2-type-rich PdCu NPs (Fig. S3 in the ESI†). The discharge/charge curves obtained for every 10 cycles demonstrated a catalytic stability of the PdCu catalyst (Fig. S9 in the ESI†). The galvanostatic potential profiles of PdCu NPs have all plateaus although their average discharge/charge voltage plateaus are a little lower or higher in the later cycles. This unwanted deterioration in the catalytic activities of PdCu NPs can probably result from the decomposition of carbon20 or electrolyte31 as well as the catalysis by O2– ions. In good agreement with this, we confirmed that the decomposed carbon was observed after 50 cycles by scanning electron microscopy (SEM) analysis (Fig. S10 in the ESI†). However, there was no obvious morphological change of the PdCu NPs, as shown in their TEM image obtained after 50 cycles (Fig. S11 in the ESI†). From these data, we could identify that a slight decrease in catalytic activity of PdCu NPs after 50 cycles was just associated with the decay of carbon. Compared with the profiles of the PdCu catalysts, those of the Pd catalysts were more sloped with the repeated potential cycling (Fig. S9 in the ESI†). In addition, the Pd NPs severely agglomerated into clusters larger than 20 nm after 50 cycles, which cannot be reversibly decomposed (Fig. S11 in the ESI†). The high overpotentials of the Pd NPs may be the main cause of the severe dissolution and re-deposition of the catalyst, and the formation of large Pd clusters during repetitive discharge and charge cycles. The decrease of electrochemically active surface area in the large particulates directly drops the catalytic functions. In contrast, the low overpotentials of the PdCu catalyst provide sufficiently high stability to sustain the catalyst morphology and the end discharge potential during the 50 discharge/charge cycles. The well-ordered intermetallic structure of the B2-type with strong spin-orbit coupling also makes the PdCu NPs chemically inert and enhances the catalytic activity toward ORR and OER.32 We performed the galvanostatic discharge/charge measurements for as-synthesized fcc-rich and B2-type-rich PdCu NPs (Fig. S3 in the ESI†) to clarify the catalytic activity depending on the crystalline structure of PdCu NPs in Li–O2 cells. The experimental data demonstrated that B2-type-rich PdCu NPs exhibited about 180 mV lower overpotentials compared to fcc-rich PdCu NPs (Fig. S12 in the ESI†).

The significant overpotential reduction observed during ORR and OER is indicative of the decrease of activation energy necessary to form or decompose reaction products like Li2O2, Li2O, and other lithium oxides. To investigate the effect of the PdCu catalyst on the reaction kinetics of Li–O2 batteries in comparison with that of the Pd catalyst, we measured discharge capacities at the increasing rates from 200 mA gcarbon−1 to 5000 mA gcarbon−1 (Fig. 2c). At the low discharge current density of 200 mA gcarbon−1, the PdCu catalysts demonstrated a discharge voltage increase of 50 mV (2.70 V Li) and more than 2 times improvement of discharge capacity (12 000 mA h gcarbon−1), compared to those of the Pd catalysts (2.65 V Li, 4500 mA h gcarbon−1). Until now, prototype Li–O2 batteries have been able to deliver current densities on the order of 1 mA cm−2 and their improvement has been a major challenge.32 Even though Pd has been known as an excellent catalyst evolving the lowest overpotential among the noble metals, its capacity retention (black line) was negligible when the discharge current density increased up to 5000 mA gcarbon−1, a 25 times higher rate than the initial condition. Surprisingly, the PdCu catalysts maintained a significant discharge capacity (red line) as high as 1689 mA h gcarbon−1 under the harsh condition of 5000 mA gcarbon−1, indicating that the rate capability was improved more than 70% compared to the previous results. At the current density of 2000 mA gcarbon−1, the PdCu catalyst showed a discharge capacity of 8000 mA h gcarbon−1, which is four times larger than the capacity of the Au–C catalyst (2000 mA h gcarbon−1).32

To confirm whether the undesired reaction occurs during the discharge/charge cycle, we calculated a normalized specific capacity based on the ex situ weight measurement of the electrode (see Fig. S13 and S14 in the ESI†). As a result, the specific capacities of 50% and 100% discharged, and 50% and 100% charged states corresponded to 482.46 mA h gLi2O−1, 997.82 mA h gLi2O−1, 504.39 mA h gLi2O−1, and 967.10 mA h gLi2O−1, respectively. The calculated specific capacity from the weight of Li2O looked very similar to the normalized capacity by carbon weight, proving that the main reaction on the cathode including PdCu NPs was Li2O2 formation or decomposition during ORR or OER.

To elucidate the influence of alloying Pd and Cu on the performance of Li–O2 batteries at the atomic level, we examined the adsorption of various lithium oxide intermediates on Pd and Cu single-crystalline surfaces, and PdCu alloy surfaces with low indexes: PdCu(100), PdCu(110), and PdCu(111), in the ordered B2-type structure, by first-principle calculations using the density functional theory (DFT) (see in the ESI†). Fig. 4a shows the energy diagram of ORR and OER on Pd(111), which illustrates the Li2O2 (x = 1, 2, and 4) adsorption/desorption steps representing the ORR and OER pathway.33,34 The energies of O2 and Li+ + e− in these diagrams are referenced to the DFT energies of the isolated O2 molecules and the Li bulk, respectively. Three elementary reaction steps were considered here: (i) Li+ + O2 → LiO2, (ii) LiO2 + Li → Li2O2, and (iii) Li2O2 + 2Li → 2Li2O.35–37 In this procedure, we found that the Li2O adsorption strength strongly correlates with both the calculated overpotentials for ORR (ηORR) and OER (ηERO) for all metal surfaces considered here (vide infra). As the adsorption strength decreases, the catalytic activity of the metal surfaces increases in the order: PdCu(111) > PdCu(100) > Pd(111) > PdCu(110) > Cu(111) (Table 1).

The Pd(111) surface has a lower Li2O adsorption strength, 3.46 eV, than that (4.41 eV) of the Cu(111) surface, leading to the
LiO$_2$ would increase the energy gain in comparison with the electron transfer from the surface Cu atoms to the Pauling electronegativity of Cu (1.90) is lower than that of Pd surfaces for the calculations of Li and thus we used the Pd-terminated PdCu(111) and PdCu(100) pure Pd surface, we evaluated the electron distribution of LiO$_2$ catalytic reactivity of PdCu(100) and PdCu(111) compared to the pure Pd surfaces. The electrostatic energy is proportional to $Q_{\text{surface}}Q_{\text{LiO}_2}/R$, where $R$ is the bonding distance between the surface and LiO$_2$. The $R$ values vary little on the different surfaces considered here (Fig. S17 in the ESI†), and thus enable the strong correlation between LiO$_2$ adsorption strength and $Q_{\text{surface}}Q_{\text{LiO}_2}$. The top-layer Pd atoms in PdCu(100) and PdCu(111) are less positively charged upon LiO$_2$ adsorption due to the electron transfer from Cu (second layer) to Pd (top layer), resulting in the weak electrostatic interactions with LiO$_2$, which eventually provide the better $\eta_{\text{ORR}}$ and $\eta_{\text{OER}}$ values of these surfaces than the values of the pure Pd surface. To investigate the change of electronic structure of PdCu NPs, we analyzed the binding energy of the Pd 3d core level both in PdCu and Pd NPs by XPS (Fig. S18 in the ESI†). Core level XPS analysis has been extensively used to estimate the modification of electronic structures due to the close correlation with valence band XPS. The Pd 3d binding energy of the PdCu NPs is redshifted by 0.86 eV, compared to that of the Pd NPs, directly indicating that the charge flows from the Cu layer to the surface Pd layer.

Fig. 4 Representative calculated energy diagrams for ORR and OER on (a) Pd(111) and (b) PdCu(111) with the optimized geometries of Li$_2$O$_2$ ($x = 1, 2, \text{ and } 4$) adsorption. The gray, yellow and red balls denote the Pd, Li and O atoms, respectively.

Table 1. The calculated overpotentials ($\eta$) of ORR and OER and the LiO$_2$ binding energies ($E_b$) of the employed metal surfaces

<table>
<thead>
<tr>
<th>Material</th>
<th>$\eta_{\text{ORR}}$ (V)</th>
<th>$\eta_{\text{OER}}$ (V)</th>
<th>$\eta_{\text{ORR-OER}}$ (V)</th>
<th>$E_b$ (eV) of LiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(111)</td>
<td>0.56</td>
<td>1.66</td>
<td>2.22</td>
<td>-3.46</td>
</tr>
<tr>
<td>PdCu(111)</td>
<td>0.37</td>
<td>1.08</td>
<td>1.45</td>
<td>-2.88</td>
</tr>
<tr>
<td>PdCu(110)</td>
<td>0.66</td>
<td>1.96</td>
<td>2.62</td>
<td>-3.75</td>
</tr>
<tr>
<td>PdCu(100)</td>
<td>0.43</td>
<td>1.29</td>
<td>1.72</td>
<td>-3.08</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>0.88</td>
<td>2.61</td>
<td>3.49</td>
<td>-4.41</td>
</tr>
</tbody>
</table>

stronger catalytic activity of the pure Pd surface with smaller overpotential values. In contrast to this, the pure Cu surface exhibiting large overpotentials seems inappropriate for both the ORR and OER processes due to the strong LiO$_2$ adsorption. As the Pauling electronegativity of Cu (1.90) is lower than that of Pd (2.20), a large electron transfer from the surface Cu atoms to LiO$_2$ would increase the energy gain in comparison with the case of Pd surfaces. These indicate that the surface Pd atoms in the PdCu alloy are the active sites for the Li$_2$O$_2$ adsorptions, and thus we used the Pd-terminated PdCu(111) and PdCu(100) surfaces for the calculations of Li$_2$O$_2$ ($x = 1, 2, \text{ and } 4$) adsorptions (Fig. 4b and S15 in the ESI†). It is worth noting that the PdCu(111) and PdCu(100) surfaces provide lower $\eta_{\text{ORR}}$ values by 0.1–0.2 V, and lower $\eta_{\text{OER}}$ values by 0.4–0.6 V, than those of the pure Pd surfaces. In contrast, both Pd and Cu elements are exposed on an equal footing in the top layer of the PdCu(110) surface, leading to merely intermediate catalytic activity between pure Pd and pure Cu surfaces (Fig. S16 in ESI†).

To explain the positive role of Cu elements in enhancing the catalytic reactivity of PdCu(100) and PdCu(111) compared to the pure Pd surface, we evaluated the electron distribution of LiO$_2$ ($Q_{\text{LiO}_2}$) and top-layer surface ($Q_{\text{surface}}$) using Bader charge analysis. Note that LiO$_2$ adsorption strength and $Q_{\text{surface}}Q_{\text{LiO}_2}$ are strongly correlated as shown in Fig. 5, which indicates that the electrostatic interaction between LiO$_2$ and the top-layer of the metal surface is a crucial factor for the catalytic activity of Pd, Cu, and PdCu surfaces.

Fig. 5 Correlation between the binding energies ($E_b$) of LiO$_2$ and the charge states of the metal surfaces and LiO$_2$ ($Q_{\text{surface}}Q_{\text{LiO}_2}$). The $Q_{\text{surface}}$ and $Q_{\text{LiO}_2}$ values are tabulated for the employed metal surfaces.

Based on our calculations and experimental results, the strong correlation of LiO$_2$ adsorption strength on the particular PdCu surface can explain the significant enhancement of catalytic activity and rate capability, as well as cycle stability. From the theoretical results, the Pd-skin surface on the PdCu(100) and (111) facets in the well-ordered B2-type phase gives low overpotentials both for ORR and OER. The addition of the Cu elements changes the electronic structure of the Pd-skin surface and weakens the LiO$_2$ adsorption strength, which is strongly correlated with the overpotentials. As a result, the PdCu catalyst exhibited remarkable electrochemical activity superior to that of the Pd catalyst. The strong adsorption of lithium oxides on the active surface delays reaction kinetics during the discharge.
process, and the effect of adsorption strength is more significant at the high current densities. Apparently, the Pd catalyst exhibits such rapid decay of capacity, approaching nearly zero at 5000 mA g\textsubscript{carbon}\textsuperscript{−1}, due to the strong adsorption of lithium oxide species. By contrast, the PdCu catalyst shows remarkable discharge capacities even at high current densities, because of the weak adsorption of lithium oxide intermediates, resulting from the addition of Cu elements.

Conclusions

We have successfully designed PdCu bimetallic NPs as efficient catalysts in both ORR and OER for Li\textsubscript{2}O\textsubscript{2} batteries. Particularly, the PdCu catalyst exhibited a low OER potential of 3.4 V\textsubscript{Li}, providing the superb round trip efficiency of ~80% at a current density of 200 mA g\textsubscript{carbon}\textsuperscript{−1}. In addition, the PdCu catalyst demonstrated a reversible cycle life up to 50 cycles without decay of the discharge potential, and outstanding rate capability even at a high current density of 5000 mA g\textsubscript{carbon}\textsuperscript{−1}. The first-principles calculations indicate that electron transfer from the underlying Cu atoms to the top-layer Pd atoms weakens the adsorption strength of lithium oxides on the PdCu surface, which eventually provides low overpotentials for both the ORR and OER processes.

On the basis of the above-mentioned results, we found that the change of electronic structure due to the surface atomic arrangement of the PdCu NPs has a decisive effect on improving catalytic activity and stability. We expect that multimetallic nanocatalysts optimized by effective surface engineering, as demonstrated in our PdCu catalysts, can increase the possibilities for the practical application of Li\textsubscript{2}O\textsubscript{2} batteries in automobiles by enhancing the ORR and OER kinetics, resulting in long term cycle life and high rate capability, as well as high round-trip efficiency.

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Notes and references