***Ab initio* investigation of the Oxygen Reduction Reaction activity on noble metal (Pt, Au, Pd), Pt₃M (M=Fe, Co, Ni, Cu) and Pd₃M (M=Fe, Co, Ni, Cu) alloy surfaces, for Li-O₂ cells**

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Abstract

First principles, density functional theory (DFT) modeling of the oxygen reduction reaction (ORR) on noble metal (Pt, Au, Pd), Pt₃M (M=Fe, Co, Ni, Cu) and Pd₃M (M=Fe, Co, Ni, Cu) alloy surfaces, was carried out. Periodic models of close-packed (111) surfaces were constructed, their geometry was optimized and the most stable geometric surface configuration was identified. The correlation between the intermediate species binding energy and the favored reaction pathway from amongst 1e⁻, 2e⁻, and 4e⁻ mechanisms were studied by calculating the binding energies of a 1/4 monolayer of O, O₂, LiO, LiO₂, Li₂O₂, and Li₂O on various sites and orientations. The reaction free energies (ΔG_{rxn}) were calculated and used to compute the catalytic activity of the surfaces using molecular kinetics theory. Plots of the catalytic activity vs. Oxygen binding energy ($E_{\text{Binding (O)}}$) showed a typical “volcano” profile. The insights gained from this study can be used to guide the choice of cathode catalysts in Li-O₂ cells.

Keywords: Lithium-oxygen cell, Density Functional Theory, Catalytic activity, Li₂O₂ nucleation, surface passivation.

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1. Introduction

The rechargeable Li-O₂ cell presents great potential as a high energy electrochemical energy storage system due to a high theoretical specific energy of 3505 Wh Kg⁻¹ which is significantly higher than current lithium-ion cells [1]. In the context of transportation, of particular interest is the fact that, with the specific energy of today's automotive Li-ion cells at 105 Wh kg⁻¹ at the pack level, driving range is limited to about 70 miles for a 200 kg pack [2]. On the other hand, the Li-O₂ cells with an estimated practical specific energy in the range of ~500-900 Wh kg⁻¹ can potentially lead to electric vehicles with a driving range approaching ~550 km (340 miles) between charging sessions [1].

To achieve practical application as a replacement for Li-ion cells, current Li-O₂ cells must overcome the problems of (i) poor cycle life, (ii) high charge and discharge overpotentials which result in low coulombic efficiency and low power density [3]. The poor cycle life reported in many studies can be traced to the oxidative instability of the electrolyte [4-6] in conjunction with electrode passivation due to irreversible product deposits and the difficulty in decomposing Li₂O₂. The high overpotentials are also a consequence of the stability of the peroxide product.

The early theoretical picture of the oxygen reduction reaction (ORR) at the cathode envisioned a Li₂O₂ covered surface after the initial cycle, and further ORR as occurring on the deposited Li₂O₂ [7]. Density functional theory (DFT) studies suggesting such mechanisms have predicted large overpotentials in accordance with the experimental observations [8]. However, the issue of electron transfer across the poorly conducting peroxide layer despite low conductivity had to be explained using mechanisms such as d-band bending [7] and polaron hopping [9].

This picture of an electrode surface which does not influence the ORR, was at odds with experimental evidence which suggested that the surface played a crucial role in the ORR. ORR on noble metals [3], metal oxide [12], graphene [13] and metal alloys [14] has been reported to occur with reduced overpotential and longer cycle life. Further, studies of the cathode surface have shown that the Li_2O_2 nucleates in various 3-D morphologies [16, 17] and, even after multiple cycles, a significant portion of the cathode surface was found to be bare [16, 17]. In turn, the pristine surface retention is expected to have a significant role in the ORR kinetics. The use of rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) experiments to study the kinetics and catalytic activity of various surfaces has been a standard in the aqueous ORR literature [18-20]. The application of these techniques to study Li-O_2 ORR is beset with technical challenges, such as surface changes due to the peroxide deposition, previously reported anomalous Tafel behavior [21], and extreme sensitivity to experimental conditions [22]. The use of DFT models to screen potential catalytic surfaces overcomes these challenges and serves as a guide for future experimental studies.

2. The oxygen reduction reaction (ORR) mechanism:

(a)

(b)

Figure 1. (a) The postulated mechanism of Li-O₂ ORR, including the effect of surface binding energies on reaction routes. The dashed line represents the 1-electron mechanism, the solid line represents the 2-electron mechanism and the dashed-dot line represents the 4-electron mechanism, (b) schematic of the possible adsorption orientations considered – (i) Pauling (end-on), (ii) Yeager (bridge), (iii) Griffith (side-on). The adsorbed intermediates are shown on surface sites denoted by "S".

A generalized mechanism for the oxygen reduction reaction on the cathode of a Li-O₂ cell is depicted in **Fig. 1(a)**. The mechanism postulated that oxygen from the electrolyte bulk approaches the surface by diffusive transport. The adsorption of oxygen was followed by electron transfer to produce the superoxide radical which subsequently gained a Li⁺ ion to form LiO₂ on the surface. The possibility of outer sphere electron transfer [40, 41] to form O₂⁻ and subsequent adsorption of the superoxide radical was also considered. This mechanism for forming the superoxide is a possibility in light of the degradation of the electrolyte observed but was not a major factor in screening various potential catalysts surfaces for electrochemical activity. Further, the half-life of O₂⁻ is generally quite short [42] and hence the depiction of the first electron transfer as formation of LiO₂ from O₂ was deemed accurate. Analogous to ORR in aqueous systems, the type of chemisorption on the surface was expected to influence the reaction pathway. The proposed mechanism considered Yeager and Pauling type adsorption while discounting Griffith type adsorption due to the high bond strain involved. These adsorption models are depicted in **Fig. 1(b)**. The Yeager type adoption was found to require a favorable arrangement of proximal sites and hence was thought to be less likely compared to the end-on Pauling adsorption. Further, in the case of formation of the O₂⁻ species by outer sphere electron transfer, the Pauling model of adsorption was considered most likely to occur.

The proposed mechanism envisioned three pathways consisting of 1-electron transfer, 2-electron transfer, and 4-electron transfer respectively. Following the adsorption of oxygen, the first lithiation step was common to all three mechanisms:

Depending on the donor number of the solvent and the consequent stabilization, it was expected that the superoxide radical may have a sufficiently high half-life to allow for the experimental observation of the formation of the superoxide radical on the surface preceding the lithiation. In the case of surfaces with the strong binding of LiO_2 , the mechanism proposed was the 2-electron process (indicated in **Fig. 1(a)** with a solid line) that proceeded electrochemically with a second lithiation step to form Lithium Peroxide:

Desorption of the LiO_2 intermediate was proposed to occur on surfaces with weak binding of the intermediate, which led to the 1-electron process (indicated in **Fig. 1(a)** with a dashed line). The LiO_2 was then postulated to undergo chemical disproportionation to yield Lithium Peroxide as the product:

Electrochemical surface reactions with the O_2 adsorbed in a side-on configuration (Yeager model) may also involve further lithiation following the formation of Li_2O_2 by the 2-electron process. This adsorption configuration could possibly occur in the case of Pt_3M and Pd_3M alloys where creation of sufficiently close adjacent sites on the surface was thought to be possible by controlling the size of the dopant. The highly electropositive Li^+ ions could weaken the O-O bond, which may lead to its cleavage and the formation of adsorbed LiO species. The proposed mechanism envisioned the possible further lithiation of the LiO species to form Li_2O . This constituted the 4-electron process (indicated in **Fig. 1(a)** with a dash-dot line).

3. Density functional theory (DFT) calculations method

Figure 2. (a) Molecular structures used in the calculations (i) O_2 , (ii) LiO_2 , (iii) Li_2O_2 , (iv) Li_2O , (v) LiO ; (b) Structure of various surfaces used for calculation - (i) Pt slab (top view), (ii) Pt slab (side view), (iii) Typical FCC (111) unit cell for noble metals and alloys, (iv) Various adsorption sites and adsorbed species orientation (EO:= End-on, SO:= Side-on).

The FCC (111) skin alloy structure used to model the Pd₃M and Pt₃M alloys for the calculations is shown in **Fig. 2(b)(iii)**. Initially, the unit cell parameters for the noble metals and the alloys were calculated. A Monkhorst-Pack 10x10x10 k-point mesh was chosen for the lattice constant optimization in the bulk unit cell. For the total energy calculations of the (111) planar slabs, a four-layer slab as shown in **Fig. 2(b)(i)** and **2(b)(ii)** was used with six equivalent vacuum layers between each slab. These were periodically repeated. The stable skin4 configuration reported previously by us in Li *et al.* [25] was used for all the binding energy calculations. The unit cell geometry was optimized by performing total energy calculations at various lattice constant values and the lattice constant corresponding to the energy minima was chosen for further study. As a means of evaluating the accuracy of these calculations, the calculated lattice constants for Au and Pt were compared to reported experimental values. The calculated lattice constants for Au and Pt were found to be 4.15Å and 3.95Å respectively in this study. This was in very close agreement with values of 4.08Å and 3.92Å reported experimentally [38] and thus served as an indicator of the ability of these calculations to predict experimental results. The oxygen atom was attached to different binding sites on the geometrically optimized slabs at ¼ ML coverage. This coverage was chosen to be representative of surface coverage in typical Li-O₂ cells with electrolytes that display relatively low oxygen solubility [21]. The DACAPO code, which uses planewave pseudopotential implementation, employing the ultra-soft pseudopotentials [23] of Vanderbilt to represent the ionic cores, was used for all total energy calculations in this study [24]. Adsorption was allowed on only one of the two exposed surfaces of the metal slabs, and the associated electrostatic potential was adjusted accordingly. DFT calculation parameters such as ionic core description, kinetic energy of the plane wave basis and density cutoff are similar to those described elsewhere [25]. The plane wave cutoff was 340 eV,

and the density was treated on a grid corresponding to a plane wave cutoff at 500 eV. The surface Brillouin zone was sampled with an 18(1×1) Chadi-Cohen **k** point grid. In all of the cases, convergence of the total energy with respect to the cutoff energies and the **k** point set was confirmed. The exchange-correlation energy and potential were described by the Revised Perdew-Burke-Ernzerhof generalized gradient approximation (RPBE- GGA) [24].

In the skin4 type FCC (111) slab shown in **Fig. 2(b)(iii)**, the alloying elements were placed at alternate positions compared to the other skin type configurations where the alloying elements are placed in adjacent positions within the second layer. The binding energy of oxygen, for ¼ ML oxygen coverage at the most stable site was calculated using equation (1):

$$E_{\text{Binding}}(^*\text{O}) = \min (TE_{\text{O}^*} - TE^* - E_{\text{O(g)}}) \quad (9)$$

where TE_{O^*} is the total surface energy of the alloy surface including the adsorbed oxygen, TE^* is the total surface energy of the geometrically optimized alloy surface, and $E_{\text{O(g)}}$ is the energy of the oxygen atom in the gaseous phase. Similarly, the binding energy of other ORR intermediates— LiO_2^* , Li_2O_2^* , and Li_2O^* —was also calculated on various types of surfaces.

Earlier publications [26] indicated that the preferred adsorption sites for atomic oxygen on FCC (111) surfaces were generally the octahedral (fcc) and tetrahedral (hcp) hollow sites. In this work, for ¼ ML coverage, oxygen was preferentially adsorbed at fcc and hcp sites. Nomenclature of various adsorption sites are illustrated in **Fig.2(b)(iv)**. The inclination angle of adsorption of intermediates at every site was changed to identify stronger binding energies.

Having obtained the binding energies of O^* , LiO_2^* , Li_2O_2^* , and Li_2O^* above, the ORR free energy was calculated using equation (9). **The structures used to calculate the energies of these molecules in vacuum and later adsorbed on the slab surface are shown in Fig.2(a)(i)-(v).**

After taking into account the zero-point energy correction and the inclusion of entropic contribution, the free energy (ΔG) of any of the above steps can be written, in general, as given in the equation (11):

$$\Delta G = \Delta E - T\Delta S + \Delta(\text{ZPE}) - neU \quad (9)$$

where $\Delta(\text{ZPE})$ is the zero-point energy correction and eU is the free energy corresponding to cell potential. Following the literature [27], the equilibrium potential for the 1-electron and 2-electron processes are taken to be 3.1V while that of the 4-electron process is taken to be 2.9V. **The applied potential is 2.5V.** For each elementary reaction step, ΔE values were evaluated from the energy difference between the products and the reactants for each reaction step, which was calculated from the binding energy of the intermediates involved. For example, $\Delta E_{\text{LiO}_2} = \text{TE}^*_{\text{LiO}_2} - \text{TE}^* - E_{\text{LiO}_2}$. Zero point energy corrections and entropic contributions to the free energies for the radicals and molecules involved in the reaction mechanism are listed in **Table 2**. The detailed calculation of free energy for each corresponding reaction step is given in **Table 3**.

The detailed kinetics of the reactions could not be deduced from the model described above, as the data was essentially thermodynamic. The assumption that the activation barrier for the rate limiting step was the larger of the free energy differences between the various lithiation steps allowed us to develop a kinetic model to calculate the catalytic activity of the various surfaces considered here for the 2-electron process. Following Norskov *et al* [28], we defined maximal surface activity A as:

$$A = k_B T \min_i \left(\ln \left(\frac{k_i}{k_0} \right) \right) \quad (10)$$

The value of k_0 was calculated from the exchange current density reported in Viswanathan *et al.* [8]. The standard formula $i_0 = nFAk_0C$ was used where the concentration was that of oxygen saturation in the electrolyte system used in the experiment reported. The value of k_i was calculated based on an Arrhenius type equation with the frequency factor calculated from collision theory. The value of k_i was calculated from:

$$k_i = A_f e^{-E_a/k_B T} \quad (11)$$

The pre-factor A_f was calculated using a collision theoretic model:

$$A_f = \sigma \left(\frac{8kT}{\pi\mu} \right)^{1/2} N_A \quad (12)$$

The reduced mass (μ) of the various species and the collision cross-section (σ) was calculated as follows:

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \quad (13)$$

$$\sigma = \pi(R_A + R_B)^2 \quad (14)$$

The parameters used in the calculation of reduced mass and the collision cross-section is tabulated in **Table 4**. The collision cross-section was calculated based on the Van der Waal radii (represented by R_A , R_B) of the respective reactants while the reduced mass used the molecular weights of the respective reactants. The calculated pre-factor was used in eqn. (11) to calculate k_i and substituting this value along with the k_0 value in eqn. (10) yielded the activities tabulated in Table 2.

Results and discussion:

The reaction free energy change values presented in **Table 2** were calculated using equation 9 as described in the previous section. The reaction free energy for the first lithiation step was found to be negative and hence the reaction was concluded to be facile. The second lithiation step showed a positive value of reaction free energy for some substrates indicating that it is not the preferred reaction pathway. Since the formation of LiO_2 was predicted to be facile, this along with the poor binding of that intermediate to the surface, as reported in **Table 1**, would serve to explain experimental observations of the subsequent disproportionation reaction to form Li_2O_2 occurring in the electrolyte [21,32,33] or through a hybrid surface-electrolyte mechanism [34]. An electrolyte based disproportionation mechanism could also explain the prior lack of experimental observation of LiO_2 as the final product despite theoretical prediction of that possibility [35]. Previous studies have reported on voltage window controlled closed cells with Li_2O_2 co-doped with Li_2O [36] and, most recently, an open cell configuration with Iridium nanoparticles supported on reduced graphene oxide cathode that produces stable LiO_2 as the end product. Our prior studies have shown that the adsorption of LiO_2 on graphite is strong and also reported the enhancement in bond strength when adsorbed at a defect site [16]. Thus, we speculate that the edge and defect sites on graphene oxide could be one of the reasons for such a stabilizing effect. Further, it is possible that a cathode consisting of a combination of a suitable Pt or Pd alloy supported on graphene oxide could display the same effect.

Figure 3. Volcano plots of 2-electron ORR Catalytic activity calculated from DFT modelled free energy of reaction – (a) Noble metals (Pt, Pd, Au) and carbon basal plane, (b) Skin alloys of Pt, (c) Skin alloys of Pd. The binding energies on the abscissa are calculated w.r.t the binding energy of oxygen on Pt. The error bars represent a 10% error.

The surface catalytic activity results from the electrode kinetic model detailed in the previous section is presented in **Fig. 3**. The activities were calculated from the reaction free energy change values presented in **Table 2**. The activity was plotted as a function of the oxygen binding energy, which was noted to be a key descriptor of the oxygen reduction activity [23, 28]. The trends in **Fig. 3(a)** matched prior experimental observations with porous Au/C, Pt/C and Pd/C electrodes [31] and thus lent confidence to the modelling methodology. The carbon basal plane was used as a comparison and was found to show lower ORR activity as compared to the noble metals. Experimentally, it was expected that carbon would show strong binding with oxygen due to the presence of defect sites as DFT calculations showing stronger binding of Li-O₂ ORR intermediates on defect sites on graphitic carbon has been previously presented by us elsewhere [16]. Prior experimental studies of H⁺ ORR on Pt alloys [29] and Pd Alloys [30] led us to expect higher ORR activity on these alloys as compared to the pure metals themselves. The reason for this was twofold. Firstly, the presence of the dopants on the surface was expected to provide closer or more favorable binding sites. Hence, side-on binding configurations such as Yeager or Griffith type binding could become more favorable, and thus the likelihood of O-O bond breaking as well as subsequent 4-electron transfer was considered to be higher. Even if 4-electron transfer was not achieved, the stronger binding of intermediates led to the expectation that surface electrochemical reactions increase in likelihood and consequently that there was a possibility of 2-electron transfer mechanisms being favored. Secondly, the dopants present in the sub-layers could lead to the so-called “Ligand Effect”. The d-bands of the atoms in the alloy overlap, and the addition of dopants was previously shown to lead to the electron density in those bands changing [43]. This change was hypothesized to result in stronger binding of intermediates and possibly facile electron transfer to the adsorbed species. These arguments were initially

advanced to explain the catalytic activity of these surfaces toward H^+ ORR and were found to be equally applicable to the case of Li^+ ORR [25]. Therefore, the higher activities of the alloys shown in **Fig. 3(b)** and **3(c)** were expected and in accord with extrapolations from experiments in aqueous systems [30]. The relative activities of the various alloys could be a function of the d-electron interactions between the host and dopant atoms. The activities of the Pt alloys shown in **Fig. 3(b)** showed a linear relationship where the atomic radii of the dopant atoms with Pt_3Co showing the highest activity. From **Fig. 3(c)** it was seen that—in the case of the Palladium alloys—the dopant atomic number increase corresponded to a decrease in activity, with the exception of copper. Further work is needed to elucidate the precise mechanism involved.

Figure 4. Comparative screening of high activity substrates for the 1-electron ORR mechanism. Weaker binding (higher binding energy) is preferred. The error bars represent a 10% error.

Figure 5. Comparative screening of high activity substrates for the 2-electron and 4-electron ORR mechanism – (a) Activity vs. Relative Binding Energy of LiO_2 , (b) Activity vs. Relative Binding Energy of Li_2O_2 , (c) Activity vs. Relative Binding Energy of Li_2O . Stronger binding (lower binding energy) is preferred. The error bars represent a 10% error.

The catalytic activity in conjunction with the binding energy of the intermediates could be a valuable guide to the possible ORR mechanisms on a given surface. The comprehensive ORR mechanism detailed above suggested that the LiO_2 binding was the key to the ORR occurring either on the surface or in the electrolyte bulk. The prerequisite for a 1-electron mechanism was found to be the weak binding of LiO_2 . **Fig. 4** compares the activities of the surfaces with the weakest binding of LiO_2 from amongst the noble metals as well as the Pt and Pd alloys. Pt_3Ni showed the highest activity amongst various substrates. Hence, it was reasonable to expect that this substrate will show the least amount of surface electrochemical reactions and accordingly the least amount of deposited Li_2O_2 . This could lead to longer cycle life, since the surface passivation phenomenon has been noted to be a major impediment toward this. The high ORR activity also suggested that conditions such as a high oxygen overpressure could ensure that 2-electron ORR occurs on Pt_3Ni . The requirement for the 2-electron and 4-electron processes was found to be the strong adsorption of LiO_2 to the substrate. Pt, Pt_3Co and Pd_3Fe were found to have the strongest binding with LiO_2 and as a result were evaluated for the occurrence of 2-electron transfers as shown in **Fig. 5**. Pt_3Co showed weaker binding with LiO_2 with a difference of only 0.03 eV compared to Platinum, which had an activity that was 0.64 units higher than Pt. Desorption of the lithium peroxide product, or its nucleation on specific sites rather than uniform surface growth, would be preferable so that more surface area would be available for reaction. Pt_3Co showed weaker binding with Li_2O_2 with a difference of ~ 0.8 eV compared to platinum. While Pt was found to be superior for adsorbing LiO_2 , the small 0.03 eV difference with Pt_3Co suggested that the best candidate for a 2-electron process would be the platinum-cobalt alloy. The same reasoning suggested that 4-electron transfer was unlikely to be observed in the case of the Pt_3Co substrate. The strong binding of Li_2O_2 on Pt and Pd_3Fe raised

the possibility that these surfaces may theoretically exhibit 4-electron transfer. The possible occurrence of surface sites favorable to side-on binding in Pd₃Fe could be an indication that this substrate was the best candidate for a hypothetical 4-electron transfer mechanism. Another mechanism for 4-electron transfer involving initial dissociation of adsorbed oxygen was considered to be unlikely based on prior work showing that dissociation adsorption energy is lowered and dissociation itself is made exothermic in some cases with transition metal doped alloys [43].

The occurrence of surface passivation by deposition of Li₂O₂ is a major problem in Li-O₂ systems. Toroidal nucleates [17] and planar layers [16] are both experimentally observed morphologies for the Li₂O₂ product and it has been previously suggested that modelling the nucleation of the Li₂O₂ would provide valuable insight into the reaction mechanism [8] and could also provide insight into the lack of experimental observation of 4-electron transfer mechanisms. **Fig. 6** shows the variation of Li₂O₂ binding energy with the binding site and the lattice constant on Pt, Au, and Pd. The alloys were not considered because their lattice constants were almost identical within experimental error and thus were unlikely to offer much insight. Following previous work showing the effect of the bonding and coordination number on catalytic activity [44], the two major factors considered were the reaction site and the size of the site in the case of the interstitial sites. **Fig. 6(a)** shows that Li₂O₂ binds relatively strongly to the FCC and HCP interstitial sites as compared to the bridge and top sites. The FCC and HCP sites served as voids, and the interactions with electron clouds of the four immediate neighbor atoms could be the cause of the strong adsorption predicted. The adsorption initiated with the O₂ species and then further reaction occurred to produce Li₂O₂ and so the possible cause of the strong adsorption could be the preference for end-on adsorption for a polar molecule like

oxygen. This would be especially likely if outer sphere electron transfer occurred and the adsorbing species was O_2^- . **Fig. 6(b)** shows that while the binding energy at the interstitial sites appeared to correlate to the lattice constant and hence the size of the site, the lattice constant appeared to have minimal effect on the bridge and top sites. The occurrence of stronger binding on FCC and HCP sites on Pd ($a = 4.01\text{\AA}$) as compared to Pt and Au, which have lower and higher lattice constants respectively, suggested that there was an optimum interstitial site size for the strong adsorption of Li_2O_2 .

Figure 6. $E_{\text{Binding}}(\text{Li}_2\text{O}_2)$ on - (a) Preferential binding sites, (b) correlation between site size and binding energy. Lower binding energy values indicate stronger binding.

Figure 7. Influence of the dopant on $E_{\text{Binding}}(\text{Li}_2\text{O}_2)$. Lower binding energy values indicate stronger adsorption.

Since the adsorption site and the corresponding electron distribution appeared to correlate to the strength of adsorption of the product, the variation of the binding energy of Li_2O_2 with the addition of dopants was considered in **Fig. 7**. A clear correlation between the binding energy and the atomic radii of the dopants was seen in the case of the Pt alloys. This was a clear demonstration of the “Ligand Effect” and further investigation of the structure of the d-band in these alloys [similar to previous work in aqueous systems \[43\]](#) along with models of the

nucleation free energy from the reaction free energy values calculated here could offer insight into the nucleation and growth of Li_2O_2 . The future investigation of the d-bands could also offer insight into the trends seen in case of Pd alloys.

Conclusions

The present study evaluated Pt and Pd skin alloys as possible catalysts for the oxygen reduction reaction on Li- O_2 cell cathodes using *ab initio* DFT modelling and an electrode kinetic model based on collision theory. The issue of surface passivation by the nucleation and growth of peroxide layers was also addressed. The model successfully replicated experimental activity data [31] for noble metals and carbon and also predicted activities for the Pt and Pd alloys that would be expected from our previous work with these alloys in aqueous systems. Pt_3Co and Pd_3Fe are found to show the highest activity and could be possible candidates for use as ORR catalysts. The evaluation of Pt_3Co and Pd_3Fe binding energies, with respect to the proposed requirements for 2-electron transfer, showed that these surfaces may preferentially follow the 2-electron ORR mechanism. Furthermore, the nucleation of Li_2O_2 appears to preferentially occur at interstitial FCC and HCP sites, so decoration of these sites with surface groups may offer an avenue for facile oxygen evolution reactions. The use of Pt and Pd skin alloys appears to be a promising avenue for the realization of high cycle life and high capacity Li- O_2 cells.

Acknowledgements

The authors thank Dr. Mayandi Ramanathan for useful discussions. The use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, and under Contract No. DE-AC02-06CH11357. This work was supported by the Toyota Research Institute of North America (TRINA).

References

1. P.G. Bruce, S.A. Freunberger, L.J. Hardwick, J-M Tarascon, Li-O₂ and Li-S batteries with high energy storage, *Nature Materials* 11 (2011) 19-29.
2. J. Christensen, P. Albertus, R.S. Sanchez-Carrera, T. Lohmann, B. Kozinsky, R. Liedtke J. Ahmed, A. Kojic, A Critical Review of Li/Air Batteries, *J. Electrochem. Soc.* 159(2) (2012) R1-R30.
3. Y-C Lu, H.A. Gasteiger, E. Crumlin, R. McGuire, Jr., Y. Shao-Horn, Electrocatalytic Activity Studies of Select Metal Surfaces and Implications in Li-Air Batteries, *J. Electrochem. Soc.* 157 (9) (2010) A1016-A1025.
4. S.A. Freunberger, Y. Chen, Z. Peng, J.M. Griffin, L.J. Hardwick, F. Barde, P. Novak, P.G. Bruce, Reactions in the Rechargeable Lithium-O₂ Battery with Alkyl Carbonate Electrolytes, *J. Am. Chem. Soc.* 133 (2011) 8040-8047.
5. S.A. Freunberger, Y. Chen, N.E. Drewett, L.J. Hardwick, F. Barde, P.G. Bruce, The Lithium-Oxygen Battery with Ether-Based Electrolytes, *Angew. Chem. Int. Ed.* 50 (2011) 8609-8613.
6. Y. Chen, S.A. Freunberger, Z. Peng, F. Bardé, P.G. Bruce, Li-O₂ Battery with a Dimethylformamide Electrolyte, *J. Am. Chem. Soc.* 134 (2012) 7952-7957.
7. J.S Hummelshøj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K.S. Thygesen, A.C. Luntz, K.W. Jacobsen, J.K Nørskov, Elementary oxygen electrode reactions in the aprotic Li-air battery, *J. Chem. Phys.* 132 (2010) 071101.
8. V. Viswanathan, J.K. Nørskov, A. Speidel, R. Scheffler, S. Gowda, A.C Luntz, Li-O₂ kinetic Overpotentials: Tafel Plots from Experiment and First- Principles Theory, *J. Phys.*

Chem. Lett. 4 (2013) 556-560.

9. J.M. Garcia-Lastra, J.S.G. Myrdal, R. Christensen, K.S. Thygesen, T. Vegge, DFT+U Study of Polaronic Conduction in Li_2O_2 and Li_2CO_3 : Implications for Li-Air Batteries, J. Phys. Chem. C 117 (2013) 5568-5577.
10. F. Mizuno, K. Takechi, S. Higashi, T. Shiga, T. Shiotsuki, N. Takazawa, Y. Sakurabayashi, S. Okazaki, I. Nitta, T. Kodama, H. Nakamoto, H. Nishikoori, S. Nakanishi, Y. Kotani, H. Iba, Cathode reaction mechanism of non-aqueous Li- O_2 batteries with highly oxygen radical stable electrolyte solvent, J. Power Sources 228 (2013) 47-56.
11. S. Higashi, Y. Kato, K. Takechi, H. Nakamoto, F. Mizuno, H. Nishikoori, H. Iba, T. Asaoka, Evaluation and analysis of Li-air battery using ether-functionalized ionic liquid, J. Power Sources 240 (2013) 14-17.
12. A. Debart, J. Bao, G. Armstrong, P.G. Bruce, An O_2 cathode for rechargeable lithium batteries: The effect of a catalyst, J. Power Sources 174 (2007) 1177-1182.
13. H.W. Park, D.U. Lee, L.F. Nazar, Z. Chen, Oxygen Reduction Reaction Using MnO_2 Nanotubes/Nitrogen-Doped Exfoliated Graphene Hybrid Catalyst for Li- O_2 Battery Applications, J. Electrochem. Soc. 160(2) (2013) A344.
14. A. Doble, C. Morein, K.M. Abraham, In 208th ECS Meeting, Los Angeles, CA, USA, 2005, Abstract #823
15. S. Nakanishi, F. Mizuno, T. Abe, H. Iba, Enhancing effect of carbon surface in the non-aqueous Li- O_2 battery, Electrochemistry 80(10) (2012) 783.
16. S. Nakanishi, F. Mizuno, K. Nobuhara, T. Abe, H. Iba, Influence of the carbon surface on cathode deposits in non-aqueous Li- O_2 batteries, Carbon 50 (2012) 4794-4803.

17. R. R. Mitchell, B. M. Gallant, Y. Shao-Horn, C.V. Thompson, Mechanisms of Morphological Evolution of Li_2O_2 Particles during Electrochemical Growth, *J. Phys. Chem. Lett.* 4 (2013) 1060-1064.
18. J. Prakash, D.A. Tryk, E.B. Yeager, Kinetic Investigations of Oxygen Reduction and Evolution Reactions on Lead Ruthenate Catalysts, *J. Electrochem. Soc.* 146 (1999) 4145.
19. W.E. Mustain, K. Kepler, J. Prakash, CoPd_x Oxygen Reduction Electrocatalysts for Polymer Electrolyte Membrane and Direct Methanol Fuel Cells, *Electrochim. Acta* 52 (2006) 2102.
20. W.E. Mustain, J. Prakash, Kinetics and mechanism for the oxygen reduction reaction on polycrystalline cobalt–palladium electrocatalysts in acid media, *J. Power Sources* 170 (2007) 28.
21. C.O. Laoire, S. Mukerjee, K.M. Abraham, E.J. Plichta, M.A. Hendrickson, Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium-Air Battery, *J. Phys. Chem. C* 114 (2010) 9178.
22. W. Torres, N. Mozhzhukhina, A.Y. Tesio, E.J. Calvo, A Rotating Ring Disk Electrode Study of the Oxygen Reduction Reaction in Lithium Containing Dimethyl Sulfoxide Electrolyte: Role of Superoxide, *J. Electrochem. Soc.*, 161 (14) (2014) A2204.
23. J. Greeley, J. K. Nørskov, Combinatorial Density Functional Theory-Based Screening of Surface Alloys for the Oxygen Reduction Reaction, *J. Phys. Chem. C* 113 (2009) 4932.
24. B. Hammer, L.B. Hansen, J.K. Nørskov, Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals, *Phys. Rev. B: Condens. Matter* 59 (1999) 7413.

25. B. Li, J. Greeley, J. Prakash, Understanding the oxygen reduction reaction on Pd-based alloys (Pd-M, M=Ni, Co) surfaces using density functional theory calculations, *ECS Trans.* 19 (2009) 109.
26. E.J. Lamas, P.B. Balbuena, Oxygen Reduction on Pd_{0.75}Co_{0.25}(111) and Pt_{0.75}Co_{0.25}(111) Surfaces: an Ab Initio Comparative Study, *J. Chem. Theory Comput.* 2 (2006) 1388.
27. R. Padbury, X. Zhang, Lithium-oxygen batteries-limiting factors that affect performance, *J. Power Soc.* 196 (2011) 4436.
28. J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jonsson, Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode, *J. Phys. Chem. B* 108 (2004) 17886.
29. S. Mukerjee, S. Srinivasan, Enhanced electrocatalysis of oxygen reduction on platinum alloys in proton exchange membrane fuel cells, *J. Electroanal. Chem.*, 357 (1993) 201-224.
30. M. Ramanathan, V. Ramani, J. Prakash, Kinetics of the oxygen reduction reaction on Pd₃M (M= Cu, Ni, Fe) electrocatalysts synthesized at elevated annealing temperatures, *Electrochim. Acta*, 75 (2012) 254.
31. Y-C Lu, H.A. Gasteiger, Y. Shao-Horn, Catalytic Activity Trends of Oxygen Reduction Reaction for Nonaqueous Li-Air Batteries, *J. Am. Chem. Soc.* 133 (2011) 19048.
32. C.J. Allen, J. Hwang, R. Kautz, S. Mukerjee, E.J. Plichta, M.A. Hendrickson, K.M. Abraham, Oxygen Reduction Reactions in Ionic Liquids and the Formulation of a General ORR Mechanism for Li-Air Batteries, *J. Phys. Chem. C* 116 (2012) 20755.
33. M.J. Trahan, S. Mukerjee, E.J. Plichta, M.A. Hendrickson, K.M. Abraham, Studies of Li-Air Cells Utilizing Dimethyl Sulfoxide-Based Electrolyte, *J. Electrochem. Soc.* 160(2)

(2013) A259.

34. L. Johnson, C. Li, Z. Liu, Y. Chen, S.A. Freunberger, P.C. Ashok, B.B. Praveen, K. Dholakia, J-M Tarascon, P.G. Bruce, The Role of LiO_2 Solubility in O_2 Reduction in Aprotic Solvents and its Consequences for LiO_2 batteries, *Nature Chemistry* 6 (2014) 1091.
35. U. Das, K.C. Lau, P.C. Redfern, L.A. Curtiss, Structure and Stability of Lithium Superoxide Clusters and Relevance to Li-O_2 Batteries, *J. Phys. Chem. Lett.* 5 (2014) 813.
36. S. Okuoka, Y. Ogasawara, Y. Suga, M. Hibino, T. Kudo, H. Ono, K. Yonehara, Y. Sumida, Y. Yamada, A. Yamada, M. Oshima, E. Tochigi, N. Shibata, Y. Ikuhara, N. Mizuno, A New Sealed Lithium-Peroxide Battery with a Co-Doped Li_2O Cathode in a Superconcentrated Lithium Bis(fluorosulfonyl)amide Electrolyte, *Sci. Rep.* 4 (2014) 5684, DOI:10.1038/srep05684.
37. J. Lu, Y.J. Lee, X. Luo, K.C. Lau, M. Asadi, H-H Wang, S. Brombosz, J. Wen, D. Zhai, Z. Chen, D.J. Miller, Y.S. Jeong, J-B Park, Z.Z. Fang, B. Kumar, A. Salehi-Khojin, Y-K Sun, L.A. Curtiss, K. Amine, A lithium–oxygen battery based on lithium superoxide, *Nature* 529 (2016) 377.
38. N.W. Ashcroft, N.D. Mermin, *Solid State Physics* (1976), Saunders College, Orlando, FL.
39. R. Black, J.H. Lee, B. Adams, C.A. Mims, L.F. Nazar, The Role of Catalysts and Peroxide Oxidation in Lithium–Oxygen Batteries, *Angew. Chem., Int. Ed.* 52 (2013) 392.
40. R.W. Murray, J.B. Goodenough, W.J. Albery, Modified Electrodes: Chemically Modified Electrodes for Electrocatalysis, *Phil. Trans. R. Soc. Lond. A* 302 (1981) 253.
41. R.G. Egdell, J.B. Goodenough, A. Hamnett, C.C. Naish, *Electrochemistry of*

- ruthenates. Part 1. —Oxygen reduction on pyrochlore ruthenates, J. Chem. Soc., Faraday Trans. 1, 79 (1983) 893.
42. D.T. Sawyer, J.S. Valentine, How Super Is Superoxide?, Acc. Chem. Res. 14 (1981) 393.
- 43.** J.R. Kitchin, J.K. Nørskov, M.A. Barteau, J.C. Chen, Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3d transition metals, J. Chem. Phys. 120(21) (2004) 10240.
44. L. M. Falicov, A. Somorjai, Correlation between catalytic activity and bonding and coordination number of atoms and molecules on transition metal surfaces: Theory and experimental evidence Proc. Natl. Acad. Sci. USA 82 (1985) 2207.

Figure captions:

Fig. 1. (a) The postulated mechanism of Li-O₂ ORR, including the effect of surface binding energies on reaction routes. The dashed line represents the 1-electron mechanism, the solid line represents the 2-electron mechanism and the dashed-dot line represents the 4-electron mechanism; (b) schematic of the possible adsorption orientations considered – (i) Pauling (end-on), (ii) Yeager (bridge), (iii) Griffith (side-on). The adsorbed intermediates are shown on surface sites denoted by “S”.

Figure 2. (a) Molecular structures used in the calculations (i) O₂, (ii) LiO₂, (iii) Li₂O₂, (iv) Li₂O, (v) LiO ; (b) Structure of various surfaces used for calculation - (i) Pt slab (top view), (ii) Pt slab (side view), (iii) Typical FCC(111) unit cell for noble metals and alloys, (iv) Various adsorption sites and adsorbed species orientation (EO:=End-on, SO:=Side-on).

Fig. 3. Volcano plots of 2-electron ORR Catalytic activity calculated from DFT modelled free energy of reaction – (a) Noble metals (Pt, Pd, Au) and carbon basal plane, (b) Skin alloys of Pt, (c) Skin alloys of Pd. The binding energies on the abscissa are calculated w.r.t the binding energy of oxygen on Pt. The error bars represent a 10% error.

Fig. 4. Comparative screening of high activity substrates for the 1-electron ORR mechanism. Weaker binding (higher binding energy) is preferred. The error bars represent a 10% error.

Fig. 5. Comparative screening of high activity substrates for the 2-electron and 4-electron ORR mechanism – (a) Activity vs. Relative Binding Energy of LiO₂, (b) Activity vs. Relative Binding Energy of Li₂O₂, (c) Activity vs. Relative Binding Energy of Li₂O. Stronger binding (lower binding energy) is preferred. The error bars represent a 10% error.

Fig. 6. E_{Binding} (Li₂O₂) on - (a) Preferential binding sites, (b) correlation between site size and binding energy. Lower binding energy values indicate stronger binding.

Fig. 7. Influence of the dopant on E_{Binding} (Li₂O₂). Lower binding energy values indicate stronger adsorption.

Table captions:

Table 1. Optimized lattice constants of the various surfaces and reaction intermediate binding energies. The binding energies tabulated are for the strongest binding site and orientation. The lower the value of the binding energy, the stronger is its adsorption.

Table 2. Reaction free energies for the first and second lithiation steps used to calculate the surface activity. The larger of the two reaction free energies is taken to be the activation energy on that substrate and used to calculate activity.

Table 3. Parameters used in the calculation of the pre-factor (A_f).

Table 1. Optimized lattice constants of the various surfaces and reaction intermediate binding energies. The binding energies tabulated are for the strongest binding site and orientation. The lower the value of the binding energy, the stronger is its adsorption.

	Optimized Lattice Constant (Å)	Binding energy (E_{Binding}) (eV)					
		O ₂ *	LiO ₂ *	Li ₂ O ₂ *	O*	LiO*	Li ₂ O*
Au	4.15	0.23	0.77	-3.17	-1.96	-1.8	-2.36
Pt	3.95	-0.09	0.17	-3.61	-3.25	-2.38	-2.49
Pt ₃ Fe	3.91	0.32	0.86	-2.55	2.49	-2.35	-2.74
Pt ₃ Co	3.89	0.27	0.20	-2.83	-2.68	-1.85	-2.83
Pt ₃ Cu	3.90	0.17	0.30	-3.06	-2.73	-2.03	-2.85
Pt ₃ Ni	3.87	0.26	0.86	-2.79	-2.73	-1.93	-2.79
Pd	4.01	-0.61	0.18	-3.96	-3.49	-3.13	-0.77
Pd ₃ Fe	3.96	0.41	0.27	-3.29	-3.09	-2.92	-2.65
Pd ₃ Co	3.93	-0.01	0.40	-0.91	-3.12	-2.54	-2.83
Pd ₃ Cu	3.95	-0.82	0.49	-3.61	-3.12	-2.54	-2.85
Pd ₃ Ni	3.93	-0.03	0.61	-3.11	-2.95	-2.6	-2.88

Table 2. Reaction free energies for the first and second lithiation steps used to calculate the surface activity. The larger of the two reaction free energies is taken to be the activation energy on that substrate and used to calculate activity.

	ΔG_1 (eV)	ΔG_2 (eV)	Activity (eV)
Pt	-0.75	-0.15	0.253
Au	-0.47	-0.32	-0.027
Pd	-0.04	-0.69	0.203
Pt ₃ Fe	-0.88	0.04	1.077
Pt ₃ Co	-1.49	0.42	0.894
Pt ₃ Cu	-1.29	0.08	1.232
Pt ₃ Ni	-0.82	-0.20	0.324
Pd ₃ Fe	-1.89	-0.43	1.397
Pd ₃ Co	-1.43	-0.47	-0.018
Pd ₃ Cu	-0.28	-0.81	0.327
Pd ₃ Ni	-2.27	0.44	-0.499

Table 3. Parameters used in the calculation of the pre-factor (A_f).

	$O_2^* + Li^+ + e^- \rightarrow LiO_2^*$	$LiO_2^* + Li^+ + e^- \rightarrow Li_2O_2^*$
Reduced mass μ	5.70	5.89
Collision cross-section σ (m ²)	4.75×10^{-20}	7.16×10^{-20}
Arrhenius type pre-factor A_f (s ⁻¹)	1.23×10^{-06}	1.83×10^{-06}

Graphical abstract: