# **PCCP**



## COMMUNICATION

View Article Online
View Journal | View Issue



# Multi-spin-state at a Li<sub>3</sub>PO<sub>4</sub>/LiCoO<sub>2</sub> (104) interface†

Masato Sumita\*a and Takahisa Ohno\*abc

Cite this: Phys. Chem. Chem. Phys., 2016, **18**, 4316

Received 15th December 2015, Accepted 19th January 2016

DOI: 10.1039/c5cp07735d

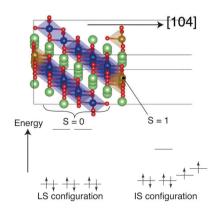
www.rsc.org/pccp

We have found the disproportion between the intermediate spin (IS) and low spin (LS) configurations of Co atoms at a Li<sub>3</sub>PO<sub>4</sub>/LiCoO<sub>2</sub> (104) interface through density functional molecular dynamics (DF-MD). The manifold of the spin state at the interface, however, does not affect the band alignment between the Li<sub>3</sub>PO<sub>4</sub> and LiCoO<sub>2</sub> regions.

All-solid state Li ion secondary batteries (ALBs) are regarded as next-generation rechargeable electronic cells.<sup>1</sup> Although various materials have already been synthesized for electrolytes and electrodes, solid Li ion secondary batteries fabricated from these materials do not always show the expected performance because there are some problems caused by the interfaces between the electrolyte and electrode materials. Experimental results imply that the problems are attributed to harmful products at the atomistic level<sup>2</sup> or to a space charge layer at electrode/electrolyte interfaces,<sup>3</sup> which result in interfacial resistance. Investigation and the control of the interfaces at the atomistic level, therefore, are indispensable in ALB development.

In this communication, we report a theoretical study on the interface between amorphous Li<sub>3</sub>PO<sub>4</sub> and LiCoO<sub>2</sub>, which is a typical electrode/electrolyte interface in ALBs, to give some insight into the interfacial properties. LiCoO<sub>2</sub> is widely used as a 4 V-class electrode and Li<sub>3</sub>PO<sub>4</sub> is also a fundamental electrolyte material. A battery that uses a Li/LiPON/LiCoO<sub>2</sub> structure, where LiPON is nitrogen-doped Li<sub>3</sub>PO<sub>4</sub>,<sup>4</sup> exhibits a high cyclic performance,<sup>5</sup> indicating the existence of a stable electrolyte/electrode interface. Furthermore, Haruta *et al.*<sup>6</sup>

Here, we consider the LiCoO<sub>2</sub> (104) surface, which is a stable active surface for Li<sup>+</sup> intercalation/deintercalation. On the surface of nanosize stoichiometric LiCoO<sub>2</sub>, Co atoms have various spin configurations depending on the facets. The (104) surface has five-coordinated Co atoms (Co<sub>5C</sub>) whose spin configuration is reported to be the intermediate-spin (IS) state (S=1, Fig. 1). The present calculations also indicate that the Co<sub>5C</sub> on the surface prefers the IS state to the low-spin (LS) configuration *in vacuo* (see the ESI†). However, the fate of radical electrons on the Co<sub>5C</sub> after forming the interface with the electrolyte remains unknown. We have investigated the spin configuration of Co<sub>5C</sub> on the (104) surface at the interface with the amorphous Li<sub>3</sub>PO<sub>4</sub> phase using density functional molecular dynamics (DF-MD; molecular dynamics



**Fig. 1** Low-spin (LS) configuration (S=0) in the d orbitals of Co in bulk LiCoO $_2$  (left) and intermediate-spin (IS) configuration (S=1) of five-coordinated Co (Co $_5$ C) on the (104) surface (right). Orange balls indicate IS Co (Co $_5$ C) atoms and blue balls indicate LS Co atoms.

have recently succeeded in lowering the resistance at the LiPON/LiCoO<sub>2</sub> interface *via* all-in-vacuum fabrication than that in a liquid electrolyte-based battery. In addition to the use as an electrolyte, Li<sub>3</sub>PO<sub>4</sub> plays an important role as a coating material for enhancing the performance of LiCoO<sub>2</sub>.<sup>7</sup> Li<sub>3</sub>PO<sub>4</sub>-coated LiCoO<sub>2</sub> shows higher voltage than a pure LiCoO<sub>2</sub> cathode with a polymer electrolyte.<sup>8</sup>

<sup>&</sup>lt;sup>a</sup> National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. E-mail: SUMITA.Masato@nims.go.jp

<sup>&</sup>lt;sup>b</sup> Global Research Center for Environment and Energy based on Nanomaterials Science (GREEN), NIMS, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>&</sup>lt;sup>c</sup> Institute of Industrial Science, University of Tokyo, Meguro, Tokyo 153-8505, Japan. E-mail: OHNO.Takahisa@nims.go.jp

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Computational details, cell parameters of the LiCoO2 (104) slab with thickness. See DOI: 10.1039/ c5cp07735d

**PCCP** Communication

calculation with density functional theory) with an NPT ensemble. See the ESI† about the setup of an initial interface structure and the recipes for making a model structure for amorphous Li<sub>3</sub>PO<sub>4</sub>.

We have performed three types of DF-MD calculation. One is the system where all Co<sub>5C</sub> atoms at the interface are set to the IS configuration. Hereafter, we refer to this system as I. Another is the system where all Co<sub>5C</sub> atoms at the interface are set to the LS state, which we refer to as II. After running a 100 ps DF-MD calculation, we have obtained the energetic equilibrium conditions during 40.0 ps for sampling. In I and II, some PO<sub>4</sub> anions adsorbed onto the LiCoO2 (104) surface via two Co-O bonds (coverage;  $\Theta = 0.75$ , including both sides of the LiCoO<sub>2</sub> slab, see also Fig. 3), but one monolayer coverage (all Co<sub>5C</sub> atoms are covered by PO<sub>4</sub> anions) is not reached during this DF-MD calculation. To explore the possibility of the monolayercoverage situation (III), we have performed another DF-MD calculation whose initial structure has one monolayer, i.e., all Co<sub>5C</sub> atoms at the interface are covered by PO<sub>4</sub> anions. For this one monolayer system, we have calculated only the LS state because PO<sub>4</sub> adsorbed Co atoms prefer the LS configuration, as will be explained later.

The average total energies  $(E_A)$ , their standard deviations (SD), and average enthalpies  $[H_A = E_A + PV_A; P (= 1.01325 \text{ bar})]$ and  $V_A$  are pressure and average volume] of all states are tabulated in Table 1 with the average cell parameters in the direction of the c-axis. Because the differences between the average cell parameters of the respective systems are within 3%, the comparison between the statistical energies of the systems is allowed. Indeed, there is no large discrepancy between  $E_A$  and  $H_A$  (including volume fluctuation). As shown in Table 1, the LS state (II) is more stable than the IS state (I) by 101.23 kJ mol<sup>-1</sup>. From this result, PO<sub>4</sub> adsorbed Co atoms at the interface prefer the LS configuration. The PO<sub>4</sub> adsorption is therefore expected to induce intersystem crossing from the IS state to the LS state. Although the one monolayer situation is maintained during the 40.0 ps DF-MD calculation, the one monolayer system III has no energetic advantage over the unsaturated LS state II because the one monolayer system III also shows a comparable energetic level with the system II. This indicates the possible existence of uncovered Co<sub>5C</sub> even at the interface with the amorphous Li<sub>3</sub>PO<sub>4</sub> phase.

As shown in Fig. 2, each distribution of energies of I-III (histograms) overlaps with each other. The IS and LS states have the possibility of taking an energetically and structurally common area by thermal fluctuation. This suggests that the

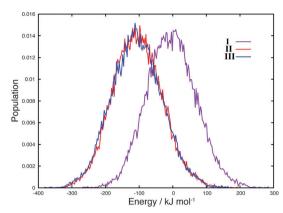


Fig. 2 Normalized histograms of total energies (in kJ mol<sup>-1</sup> relative to the average energy of I) of system I (IS system), II (LS system), and III (monolayer LS system) during 40.0 ps DF-MD.

Co5C atoms at the interface could thermally undergo a spin crossover between the LS and IS configurations similar to perovskite LaCoO3. 10 Consequently, disproportionation involving LS and IS might appear at the interface.

Three-dimensional and schematic structures of PO<sub>4</sub> adsorbed on the LiCoO<sub>2</sub> (104) surface are shown in Fig. 3. The average Co-O (PO<sub>4</sub>) bond lengths, which are relevant to PO<sub>4</sub> adsorption to the LiCoO<sub>2</sub> (104) surface, are tabulated in Table 2 with the Co-O bond lengths in the bulk region of the LiCoO<sub>2</sub> (104) slab.

The average Co-O (PO<sub>4</sub>) lengths in all the systems are estimated to be above 2.0 Å, which is larger than the average bond lengths of the bulk region of the LiCoO2 (104) slab [Co-O (LCO)]. The large bond length Co-O (PO<sub>4</sub>) is probably attributed to the Li ion neighbouring the oxygen of PO<sub>4</sub>. With the adsorption of the PO4 anion, one/two Li ions released from one PO<sub>4</sub> anion exist because three Li ions electrostatically coordinate to four oxygen atoms of one PO4 anion, and two oxygen atoms of PO<sub>4</sub> are used for the adsorption on the surface. Some Li ions can be located in a position that can be shared by two oxygen atoms: one is an oxygen atom of the adsorbed PO4 [broken lines in Fig. 3(b)] and the other is an oxygen atom on the LiCoO<sub>2</sub> (104) surface [hashed lines in Fig. 3(b)].

The average Co-O (PO<sub>4</sub>) bond lengths of the LS systems II and III are estimated to be 2.07 and 2.16 Å, respectively. On the other hand, the average Co-O (PO<sub>4</sub>) bond length of the IS system I is estimated to be 2.37 Å, which is larger than that of the LS systems II and III. This indicates that the IS Co atom certainly prefers the PO<sub>4</sub> desorption. Although PO<sub>4</sub> adsorption

**Table 1** Average total energies  $(E_A)$ , standard deviations (SDs), and average enthalpies  $(H_A)$  in kJ mol<sup>-1</sup> [values in parentheses are in  $E_h$  (Hartree)] of the systems I (all Co<sub>5C</sub> are IS), II (all Co<sub>5C</sub> are LS), III [one monolayer situation (all Co<sub>5C</sub> are LS)] during the 40.0 ps DF-MD calculation. Average cell parameters in the direction of the c-axis are also tabulated

	I (IS)	II (LS)	III (monolayer)
$E_{\rm A}$ kJ mol <sup>-1</sup> $(E_{\rm h})$ SD/kJ mol <sup>-1</sup>	0.0 (-7330.67908)	-101.24 (-7330.71764)	-103.02 (-7330.71832)
SD/kJ mol <sup>-1</sup>	72.97	73.23	74.64
c-axis/Å	47.26	46.17	46.90
$H_{\rm A}/{\rm kJ~mol}^{-1}$ $(E_{\rm h})$	$0.0\ (-7330.67901)$	$-101.24 \left(-7330.71757\right)$	-103.02 (-7330.71825)

PCCP Communication

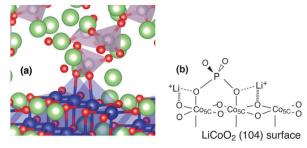


Fig. 3 (a) Structure of  $PO_4$  anion adsorbed on the  $LiCoO_2$  (104) surface. (b) Schematic structure of  $PO_4$  adsorbed with two free Li ions shared by oxygen atoms of  $PO_4$  and  $LiCoO_2$ .

Table 2 Average bond lengths of Co–O (PO<sub>4</sub>), which are relevant to PO<sub>4</sub> adsorption, and Co–O (LCO) bond length in bulk LiCoO<sub>2</sub>, in the systems I (all Co<sub>5C</sub> atoms are IS), II (all Co<sub>5C</sub> atoms are LS), III [one monolayer situation (all Co<sub>5C</sub> atoms are LS)] during 40.0 ps DF-MD calculation

	I (IS)	II (LS)	III (monolayer)
Co-O (PO <sub>4</sub> )/Å	2.371	2.068	2.162
Co-O (LCO)/Å	1.941	1.940	1.933

on the (104) surface contributes to the destabilization of IS Co atoms on the surface, it stabilizes LS Co atoms. Consequently, the LS interface systems II and III lie at an energetically lower level than the IS interface system I.

The  $PO_4$  adsorption decreases the positive charge of Co atoms at the interface. As tabulated in Table 3, the average Mulliken charges of the interfacial Co atoms in the LS systems II and III decrease to the same extent as bulk Co (about 0.5), in contrast to the interfacial Co in the IS system I (0.65). Therefore, the  $PO_4$  adsorption induces the electron transfer from an oxygen atom of the  $PO_4$  anion to a Co atom.

Fig. 4 shows the contour maps of LDOS of alpha spin electrons along the *c*-axis at the average structures of all systems during the 40.0 ps DF-MD calculation. The IS system I has an interfacial level attributed to an unoccupied d orbital of IS Co at the interface, as shown in Fig. 4. On the other hand, the LS system II has an interfacial level due to the uncapped LS Co atoms at the interface (one side) that disappears in the one monolayer system III. For all these systems, band gaps in the bulk regions [LDOS in Fig. 4] of LiCoO<sub>2</sub> (104) slabs and in the Li<sub>3</sub>PO<sub>4</sub> phases are estimated to be approximately 2.3 eV [comparable to the experimental result (2.7 eV)<sup>11</sup>] and 5.0 eV, respectively. The band offset of the valence band maximum (VBM) between the bulk LiCoO<sub>2</sub> and Li<sub>3</sub>PO<sub>4</sub> phases is estimated to be 0.7 eV.

**Table 3** Average Mulliken charges of Co atoms (bulk Co and interface Co) at average structures in the systems **I** (all  $Co_{5C}$  atoms are IS), **II** (all  $Co_{5C}$  atoms are LS), **III** [one monolayer situation (all  $Co_{5C}$  atoms are LS)] during 40.0 ps DF-MD calculation

	I (IS)	II (LS)	III (monolayer)
Interface Co (Co <sub>5C</sub> )	0.65	0.54	0.55
Bulk Co	0.51	0.50	0.49

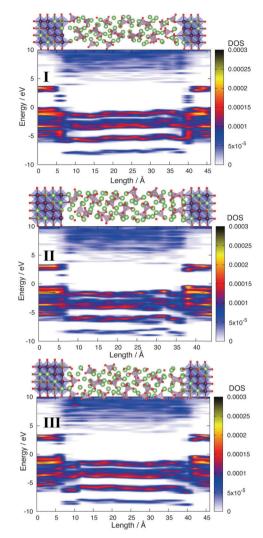


Fig. 4 Contour maps of alpha spin LDOS of the systems **I–III** along the c-axis for the average structure obtained from all the structures during the 40.0 ps DF-MD calculation. Fermi levels are set to zero. Irrespective of the system, the gaps between the valence band maximum (BVM) and the conduction band minimum (CBM) of the LiCoO<sub>2</sub> and  $\rm Li_3PO_4$  phases are estimated to be 2.3 and 5.0 eV respectively.

Irrespective of the spin state, no reaction products grow during the 40.0 ps DF-MD calculations. Moreover, the IS Co atoms in the IS system I remain at the interface during the DF-MD calculation as shown in Fig. 4, that is, the radical electrons at the interface do not become one of the factors for producing some harmful products in this system at the current computational level. We speculate that a similar interface is obtained by fabrication under all-vacuum conditions<sup>6</sup>, which exclude impurities from the interface as much as possible.

#### Conclusions

Our simulation indicates that  $PO_4$  anions adsorb on the  $LiCoO_2$  (104) surface via two Co–O bonds without the growth of an impurity phase. With the  $PO_4$  adsorption, the IS Co atoms on the surface are destabilized, whereas the LS Co atoms on the

Communication

surface are stabilized. Consequently, the LS system of the LiCoO<sub>2</sub> (104)/Li<sub>3</sub>PO<sub>4</sub> amorphous interface lies at an energetically lower level than the IS system; however, the one monolayer situation has no advantage in terms of energy against the unsaturated LS system. On the other hand, the difference in energy between the LS and IS interface systems is not large. Therefore, the multi-spin-state where the IS and LS state Co atoms coexist at the LiCoO<sub>2</sub> (104)/Li<sub>3</sub>PO<sub>4</sub> interface emerges similar to those in perovskite LaCoO3 that shows a thermally induced spin-crossover. 10 The manifold of the spin state at the interface, however, does not significantly affect the band alignment between the Li<sub>3</sub>PO<sub>4</sub> and LiCoO<sub>2</sub> regions and the Li<sub>3</sub>PO<sub>4</sub> electrolyte is found to have a wide electrochemical window against the LiCoO<sub>2</sub> electrode. The manifold in the spin states of interfacial Co atoms does not affect this system significantly. We will investigate the effect on charging process and of sulfide electrolytes.

### Acknowledgements

We thank Dr. T. Suzuki for his advice on this communication. This work was supported by the JST ALCA project. The computations in this work were carried out on the supercomputer centers of NIMS.

#### Notes and references

- 1 K. Takada, Acta Mater., 2013, 61, 759.
- 2 A. Sakuda, A. Hayashi and M. Tatsumisago, Chem. Mater., 2010, 22, 949.
- 3 K. Takada, N. Ohta, L. Zhang, K. Fukuda, I. Sakaguchi, R. Ma, M. Osada and T. Sasaki, Solid State Ionics, 2008, 179, 1333.
- 4 X. Yu, J. B. Bates, G. E. Jellison and F. X. Hart, J. Electrochem. Soc., 1997, 144, 524.
- 5 B. Wang, J. B. Bates, F. X. Hart, B. C. Sales, R. Z. Zuhr and J. D. Robertson, J. Electrochem. Soc., 1996, 143, 3203.
- 6 M. Haruta, S. Shiraki, T. Suzuki, A. Kumatani, T. Ohsawa, Y. Takagi, R. Shimizu and T. Hitosugi, Nano Lett., 2015, 15, 1498.
- 7 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, Solid State Ionics, 1981, 3/4, 171.
- 8 S. Seki, Y. Kobayashi, H. Miyashiro, Y. Mita and T. Iwahori, Chem. Mater., 2005, 17, 2041.
- 9 D. Qian, Y. Hinuma, H. Chen, L.-S. Du, K. J. Carroll, G. Ceder, C. P. Grey and Y. S. Meng, J. Am. Chem. Soc., 2012, 134, 6096.
- 10 A. Doi, T. Fukuda, S. Tsutsui, D. Okuyama, Y. Taguchi, T. Arima, Q. R. Baron and Y. Tokura, Phys. Rev. B: Condens. Matter Mater. Phys., 2014, 90, 081109.
- 11 J. V. Elp, J. L. Wieland, H. Eskes, P. Kuiper, G. A. Sawatzky, F. M. F. D. Groot and T. S. Turner, Phys. Rev. B: Condens. Matter Mater. Phys., 1991, 44, 6090.