Supplementary Information

# First Principle Calculations Study of α-$MnO_2$ as a Potential Cathode for Al-Ion Battery Application

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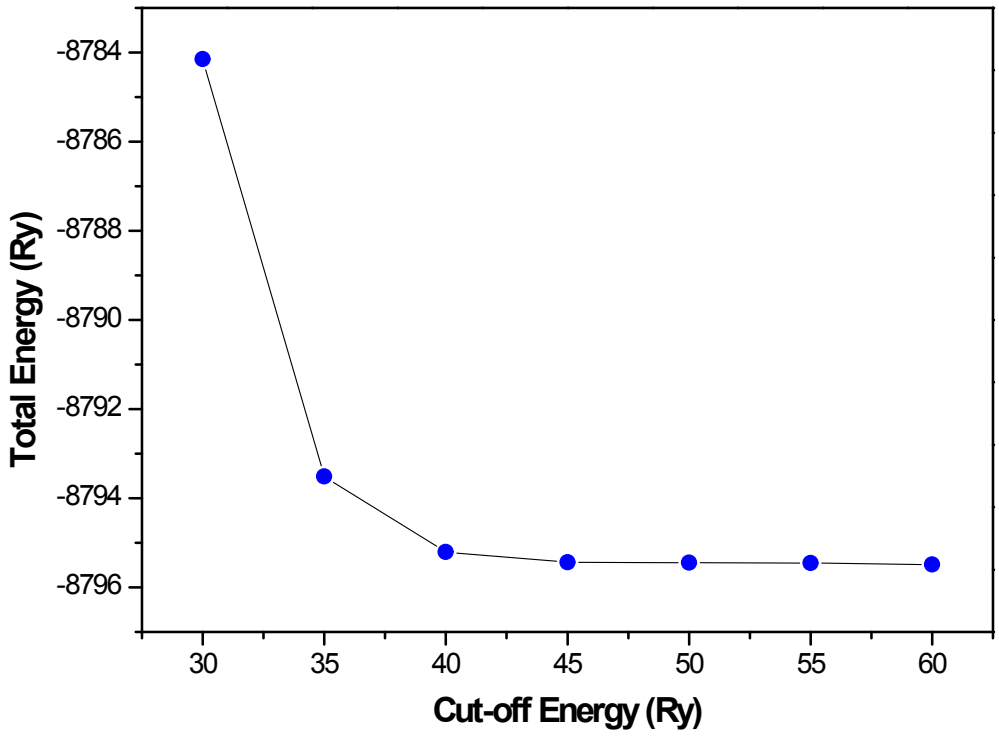


**Fig. S1** Convergence test results for determination of the cut-off energy.[S1-S3]

**Table S1** Lattice parameters of α-$MnO_2$ calculated with and without *U* values and from JCPDS.

| ***U*** | ***a* (Å)** | ***c* (Å)** |
|---|---|---|
| Without *U* | 9.729144 | 2.843746 |
| 1 | 9.737103 | 2.854406 |
| 1.6 | 9.744911 | 2.861916 |
| 3 | 9.769505 | 2.881524 |
| 3.3 | 9.776334 | 2.886177 |
| 3.6 | 9.784281 | 2.891126 |
| 3.9 | 9.79276 | 2.896217 |
| 4 | 9.795763 | 2.897954 |
| 5 | 9.833247 | 2.916991 |
| JCPDS No. 44-0141 | 9.7847 | 2.863 |

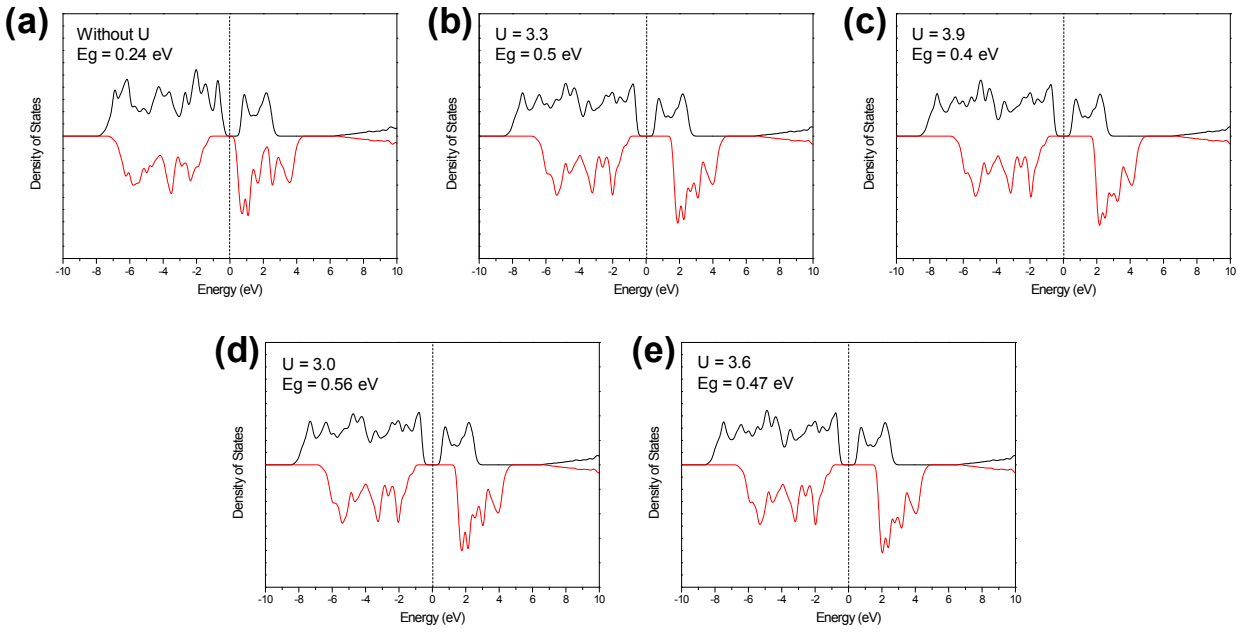


**Fig. S2** Total density of state α-$MnO_2$ obtained using with and without *U* values.

**Table S2** Al insertion energies in the dilute concentration limit of α-$Al_{0.04}MnO_2$

| Site | E (eV) |
|---|---|
| 2*a* | -2.03 |
| 2*b* | -0.66 |
| 4*c* | -4.03 |
| 8*h* | -5.43 |

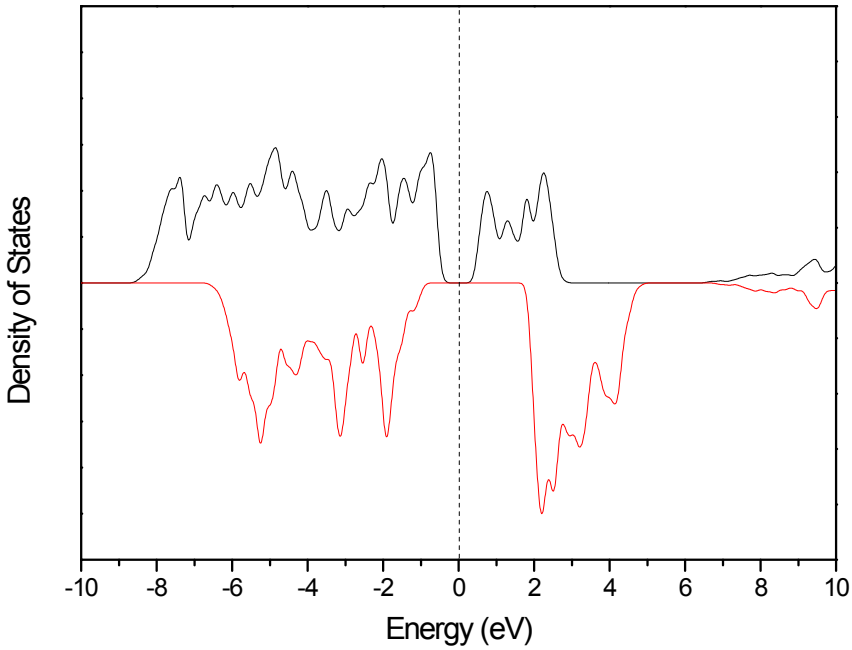


**Fig. S3** Density of states plot of α-$MnO_2$ phase using PBEsol functional with k-points of 6 × 6 × 6.

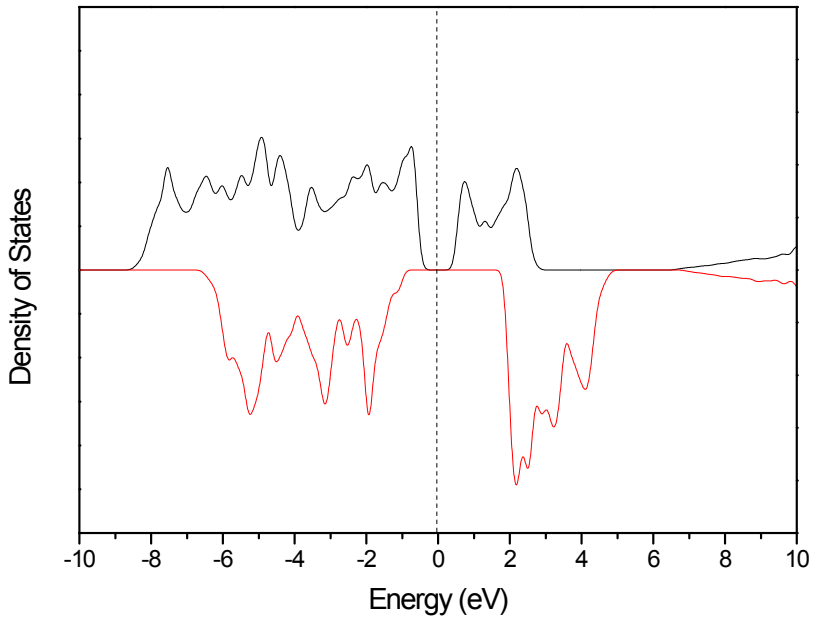


**Fig. S4** Density of states plot of α-$MnO_2$ phase using PBEsol functional with k-points of 20 × 20 × 20.

**Table S3** Bader charge analysis results.

| Atom | Δ Charge | Atom | Δ Charge | Atom | Δ Charge |
|---|---|---|---|---|---|
| Mn1 | 0.002441 | O1 | 0.004545 | O25 | 0.005473 |
| Mn2 | 0.005624 | O2 | 0.006329 | O26 | 0.003704 |
| Mn3 | 0.005739 | O3 | 0.02135 | O27 | 0.003278 |
| Mn4 | 0.001708 | O4 | 0.00336 | O28 | 0.001801 |
| Mn5 | 0.009707 | O5 | 0.023711 | O29 | -0.00089 |
| Mn6 | 0.006249 | O6 | 0.019432 | O30 | 0.001023 |
| Mn7 | 0.001889 | O7 | 0.009143 | O31 | 0.001609 |
| Mn8 | 0.051787 | O8 | 0.056623 | O32 | -0.01583 |
| Mn9 | 0.002556 | O9 | 0.035879 | O33 | 0.004583 |
| Mn10 | 0.005714 | O10 | 0.007104 | O34 | 0.006402 |
| Mn11 | 0.005827 | O11 | 0.056004 | O35 | 0.021388 |
| Mn12 | 0.001844 | O12 | 0.006272 | O36 | 0.003415 |
| Mn13 | 0.000692 | O13 | -0.00074 | O37 | 0.10782 |
| Mn14 | -0.00083 | O14 | 0.001179 | O38 | 0.078464 |
| Mn15 | 4.9E-05 | O15 | 0.001707 | O39 | 0.026509 |
| Mn16 | 0.006452 | O16 | -0.01593 | O40 | 1.023389 |
| Mn17 | 0.0193 | O17 | 0.000891 | O41 | 0.035935 |
| Mn18 | 0.005329 | O18 | 0.006259 | O42 | 0.007073 |
| Mn19 | 0.083862 | O19 | -0.0004 | O43 | 0.056061 |
| Mn20 | 0.003217 | O20 | 0.001863 | O44 | 0.006257 |
| Mn21 | 0.009836 | O21 | 0.023716 | O45 | 0.002687 |
| Mn22 | 0.006327 | O22 | 0.019353 | O46 | -0.00172 |
| Mn23 | 0.002055 | O23 | 0.009233 | O47 | 0.002102 |
| Mn24 | 0.052191 | O24 | 0.056766 | O48 | 0.00743 |

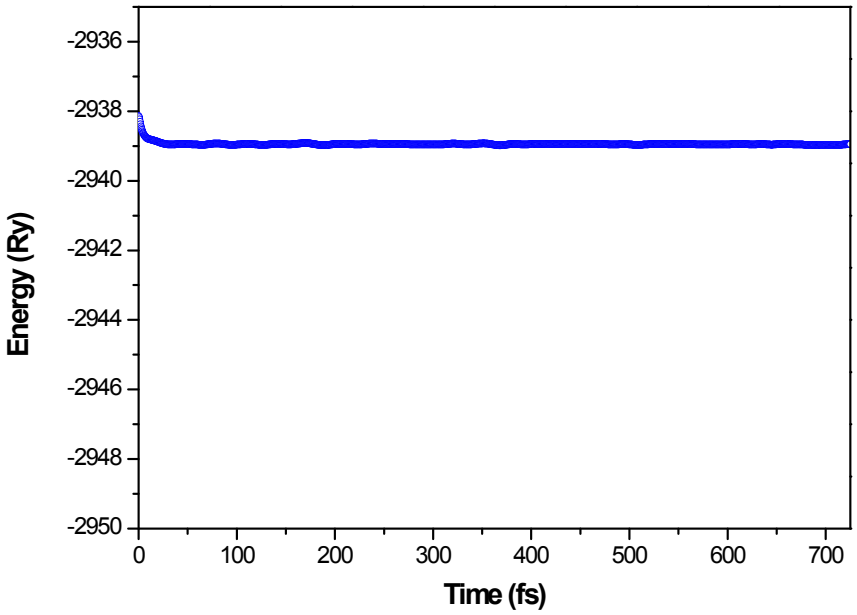


**Fig. S5** Total energy variation as a function of time in the AIMD simulation at 300 K.

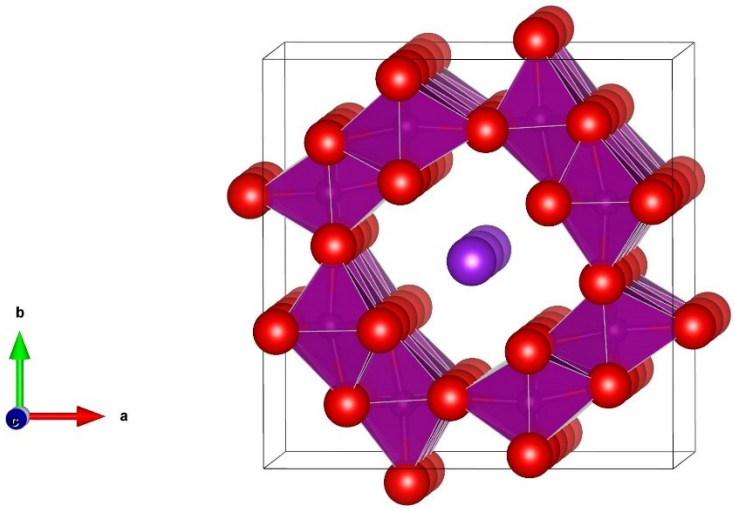


**Fig. S6** Relaxed structure of K-doped α-$MnO_2$ phase.

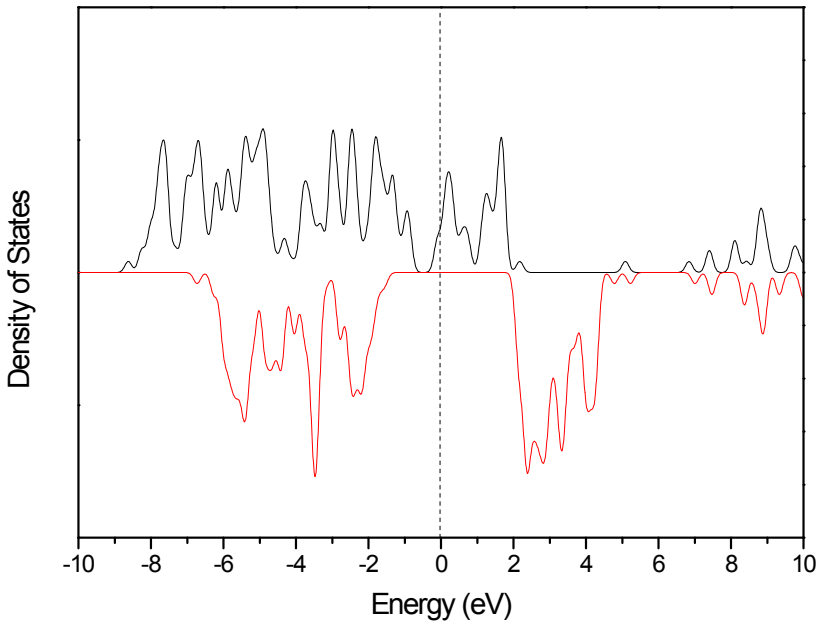


**Fig. S7** Total density of states of K-doped α-$MnO_2$ phase.

**ESI Note I**

We have performed test calculations for the Hubbard (*U*) parameter for Mn. Initially, we performed structural relaxation for α-$MnO_2$ using *U* = 1, 1.6, 3, 3.3, 3.6, 3.9, 4, 5 eV and without applying *U*. Some of the U values were selected based on previous reports.[S4-S7] The obtained lattice parameters for *U* = 3.9 eV, which was used in the our calculation and is commonly used for the DFT studies of electrode materials, are reasonable and close to the standard JCPDS No. 44-0141. Furthermore, we also performed density of states (DoS) calculation for *U* = 3, 3.3, 3.6, 3.9 eV and without *U*. It can be seen that DoS results without applying *U*, the spin-down in the conduction band is located near the Fermi level, while after applying *U*, the spin-down in the conduction band moves further away from the Fermi level. We can observe also as the *U* values increase, the band gaps decrease.

**References**


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