Supporting Information for

Jahn-Teller type small polaron assisted Na diffusion in $NaMnO_2$ as a cathode material for Na-ion batteries

Lumin Zheng[1], Zhiqiang Wang*[2, 3], Musheng Wu[1], Bo Xu[1], Chuying Ouyang*[1]

[1]Department of Physics, Laboratory of Computational Materials Physics, Jiangxi Normal University, Nanchang, 330022, China

[2] Department of Physics, Xiamen University, Xiamen, 361005, China

[3] Department of Physics, National University of Singapore, Singapore 117542, Singapore.

*Wang ZQ E-mail: wangzq3614@stu.xmu.edu.cn

*Ouyang CY E-mail: cyouyang@jxnu.edu.cn

SI-1. The lattice parameters of the $NaMnO_2$.

Table S1. The calculated lattice parameters and ground state energy per formula unit of E-$NaMnO_2$, C-$NaMnO_2$, and Na_0MnO_2 under the PW91, PBE and LDA level. Exp-$NaMnO_2$ is the experimental lattice parameters of $NaMnO_2$.

	a (Å)	*c* (Å)	Energy (eV)
exp-$NaMnO_2$	5.950	8.671	—
E-$NaMnO_2$	6.069 (PW91)	9.609	-24.781
	6.045 (PBE)	9.638	-24.863
	6.045 (LDA)	9.637	-24.810
C-$NaMnO_2$	6.418 (PW91)	8.516	-24.691
	6.394 (PBE)	8.487	-24.763
	6.397 (LDA)	8.483	-24.709
Na_0MnO_2	5.853 (PW91)	8.265	-20.471
	5.851 (PBE)	8.291	-20.465
	5.845 (LDA)	8.275	-20.428

As shown in Table S1, the lattice constant *c* of the E-$NaMnO_2$ model (9.609 Å) is substantially larger than the experimentally observed value (8.671 Å), while the lattice constant *a* of the C-$NaMnO_2$ (6.418 Å) is also substantially larger than the experimental value (5.950 Å). Taken into account the DFT overestimated lattice constant, we can still judge that the E-$NaMnO_2$ model overestimates the *c* substantially while C-$NaMnO_2$ overestimates *a*. Although the above lattice parameters are obtained from PW91 functional, lattice parameters obtained from PBE and LDA functionals demonstrate that the above conclusion is independent of the functional. Meanwhile, both models do not reproduce the experiment lattice constant, and therefore a mixture of both distortion modes is possibly occurred to the $NaMnO_2$ at room temperatures.

SI-2. Evaluation of the configurational entropy contribution to the free energy of the $NaMnO_2$.

All the Mn atoms are in the oxidation state of Mn^{3+} in the $NaMnO_2$. For each Mn^{3+} ion, there are two types of Jahn-Teller distortion: elongated distortion or compressive distortion. On other hand, the orientation of the distortion should also be considered, namely the elongation (compression) of the Mn-O bonds along x, y, or z directions. Therefore, the total configurations for each Mn atom are 6. Then the configurational entropy for each Mn atom is:

$$S_{\text{conf}} = k_B \ln \Omega = k_B \ln(3 \times 2) \approx 1.792 k_B$$

Therefore, the configurational entropy contribution to the free energy of the unitcell is evaluated to be -46.59 meV per formula unit at room temperature (300 K).

Assuming that the two types of distortion occur with the same probability, the ground state energy of the system takes the average of the ground state energies from E-$NaMnO_2$ (-24.781 eV per formula unit) and C-$NaMnO_2$ (-24.691 eV per formula unit), which is calculated to be -24.736 eV per formula unit. Then, the free energy of the $NaMnO_2$ with

mixed distortions of the MnO_6 octahedron is obtained to be -24.783 eV, which is lower than both of the ground state energies of E-$NaMnO_2$ (-24.781 eV) and C-$NaMnO_2$ (-24.691 eV).

SI-3. Technical points on how to localize an electron to a specific Mn site.

In this study, localization of electrons to a chosen Mn atom is technically difficult. Here we show how these calculations have been done.

Firstly, we must confirm that the electron localized state (or Jahn-Teller distorted structure) is thermodynamically favorable. Namely, the electron is preferred to be localized at the Mn-3d orbital and the ground state energy of the localized structure is lower than the delocalized state. Then, in order to describe the localized electron and the Jahn-Teller distortion, DFT+U (or hybrid functional method) should be applied in our study. In this study, we used GGA+U in order to save the computational expense.

From physics point of view, the electron localization is strongly associated with the distorted local structure of the MnO_6 octahedron. Technically, we cannot "force" the electron to localize at certain Mn atom, but we can adjust the Mn-O bond lengths to a properly distorted local structure, which "attracts" the electron to localize there, because the electron localized at the distorted MnO_6 octahedron is energetically favorable. Therefore, in order to localize an electron to a chosen Mn atom, we manually adjust the Mn-O bond lengths of the objective MnO_6 octahedron according to the theory of Jahn-Teller theory. For example, if we want to localize one electron to the Mn-3dz^2 orbital, we need to elongate two Mn-O bond lengths along the z-axis direction. On the other hand, if we want to localize one electron to the Mn-3d(x^2-y^2) orbital, we need to elongate four Mn-O bond lengths in the x-y plane. Then, we need to check if the distorted structure will be retained during the structural relaxation. If the initial Mn-O bond lengths are set properly, the distorted structure will be retained and the electron will automatically be localized to the specific Mn atom. As a result, the band gap will be opened and the electronic structure is insulating. On the other hand, if the electron is

delocalized, the charge distributes to all Mn atoms almost equally. In this case, we obtained a metallic electronic structure. Of course, the ground state energy of the metallic system is higher comparing with the insulating system with electrons localized at Mn-3*d* states (Jahn-Teller distorted structure).

Taking as examples, we present the optimized atomic position files (CONTCAR file) with the electron localized at Mn1-Mn3 (shown in Fig. 3) in the fully de-intercalated structure.

The optimized atomic positions for the polaron located at Mn-1

```
====================================
Na1-Mn16O32
      1.00000000000000
     11.7093000412000006     0.0000000000000000     0.0000000000000000
     -0.0000405399000000     5.8548002241999999     0.0000000000000000
      0.0000000000000000     0.0004045523000000     8.2783002754999995
   Na      Mn      O
    1      16      32
Direct
  0.2500141520888020     0.2591315868664445     0.6215885397885065
  0.2500137818629680     0.0012831281527284     0.0121324712534219
  0.9907093173618875    -0.0030636207271078     0.5049256464535452
  0.1237241379024015     0.2439711834005906     0.2589429281879467
  0.3772471630617538     0.7571605997386256     0.7576226341334652
  0.1227806390534788     0.7571603661158770     0.7576225750287667
  0.3763037956427386     0.2439707097795330     0.2589429382405980
  0.9936494992547887     0.5012827464018066     0.5054545307643931
  0.2500139709609208     0.5071719541576906     0.0166126839237741
  0.7500136338287707     0.0002178015752874     0.0062011672600586
  0.5093187226817538    -0.0030633480529580     0.5049259467251397
  0.6261453733205694     0.2505255656950908     0.2540345080683014
  0.8737139658010877     0.7488585852357054     0.7584492227949913
  0.6263136617771007     0.7488585859259840     0.7584493123728508
  0.8738825334911037     0.2505256840178437     0.2540341890978315
  0.5063783520925342     0.5012828885908119     0.5054545123972161
  0.7500136302495668     0.4997353051687359     0.0064314204627390
  0.9953797277722118     0.9721974954963090     0.7407699124074962
  0.9944966023540600     0.0266382478129085     0.2706912990982857
  0.2500132328161299     0.0228645421502933     0.2459870891828777
  0.2500144711806355     0.9750617525177436     0.7778114020361638
  0.1381484115400974     0.7579355539173098     0.9911179883375179
  0.3601354481051866     0.2496079733831215     0.0299051372921258
  0.0980255431832573     0.2444167843326812     0.4919385093354241
  0.3964135642144010     0.7533557825139799     0.5204710723932978
  0.1036142944034702     0.7533576506689691     0.5204708401128371
  0.4020025414629887     0.2444145194411971     0.4919385956385485
  0.1398926671917574     0.2496070827056316     0.0299048197183379
  0.3618788394846939     0.7579369327892171     0.9911184792311758
  0.2500146681890440     0.4490201086410259     0.2745424628169081
  0.2500132603670514     0.5554014942085778     0.7589390979386068
 -0.0002390788179918     0.5324385150576781     0.7412584407883623
 -0.0015103408567346     0.4682711901821979     0.2713760502708831
  0.5046492327933718     0.9721976178988669     0.7407702457080391
  0.5055303101973755     0.0266377490492794     0.2706917396300033
  0.7500133515901070     0.0305268341044639     0.2393582817017391
  0.7500143550913320     0.9683007288896077     0.7718978073727494
  0.6403235727204121     0.7498345743710503     0.9917360209605092
  0.8595549912621738     0.2501484473575679     0.0198326807816662
  0.6167126793207163     0.2518603837416132     0.4886360036395220
  0.8839768142182092     0.7463660624364807     0.5227617878122063
  0.6160509926882383     0.7463683791139740     0.5227619578982624
  0.8833153249217984     0.2518577559011095     0.4886357001750967
  0.6404721965058088     0.2501461220030116     0.0198331012581328
```

0.8597036357192883	0.7498368672292516	0.9917359716467126
0.7500145015469040	0.4715976804331216	0.2391290437825508
0.7500131854649490	0.5285611084113008	0.7725972779731179
0.5002654517928520	0.5324385468816363	0.7412585003552448
0.5015394021439229	0.4682709959781974	0.2713761293876631

The optimized atomic positions for the polaron located at Mn-2

```
====================================
Na1-Mn16O32
      1.00000000000000
     11.7093000412000006     0.0000000000000000     0.0000000000000000
     -0.0000405399000000     5.8548002241999999     0.0000000000000000
      0.0000000000000000     0.0004045523000000     8.2783002754999995
   Na   Mn   O
   1    16   32
Direct
```

0.2533823693150118	0.7480886107418084	0.3789476693998672
0.2457309320925362	0.0027671149056530	-0.0063195567515387
0.9949840935672521	0.0018840608095590	0.5021374587136065
0.1211709954444998	0.2506584974787139	0.2461413564824335
0.3791012973564368	0.7558438935461800	0.7573857807729369
0.1225450472176634	0.7494665146259304	0.7519829292653172
0.3797117560633914	0.2443849728966777	0.2421463156540042
0.9950970800977025	0.4982279066940410	0.5021607848249754
0.2487049378162141	0.4976726113090784	-0.0061322594185384
0.7538206479004713	0.0001124675410204	0.0013159697921453
0.5057845088946675	0.0006458538805413	0.5019996626942927
0.6248100682438065	0.2447547788132989	0.2451583974123261
0.8733168485911196	0.7492509919650912	0.7525518838133261
0.6248329304129591	0.7558369760125691	0.7578561738365284
0.8729083015187883	0.2510623598365815	0.2501614929364355
0.5066991402768877	0.4958784079272893	0.5042727059902671
0.7507507477705280	0.5005759878009740	0.0014002399584516
-0.0022367757050585	0.9698197500903971	0.7363409963387382
-0.0015741102300807	0.0308728563866742	0.2662729569603247
0.2460638096331099	0.0346725935168520	0.2263203995656899
0.2464399512262869	0.9701463093371637	0.7621249692428622
0.1374419453355068	0.7476008868846067	0.9831101666488361
0.3568528398539721	0.2462315651382697	0.0049578247193971
0.1071352642317623	0.2501263821579903	0.4829375228620892
0.3979247237616506	0.7511907946148192	0.5266653793999910
0.1028908324696538	0.7500267746499434	0.5184620793620210
0.3926606768553255	0.2453831299475359	0.4758221167228096
0.1359623180968638	0.2529226229440134	0.0102178471127568
0.3555042826619876	0.7544598006020723	0.9890450984243603
0.2499819296454901	0.4608121878269748	0.2263126537522132
0.2504832350264409	0.5349197151438017	0.7624721087480111
-0.0021633647221866	0.5277947020162134	0.7358541513107867
-0.0013300198644050	0.4718390795577861	0.2667622596145717
0.5022673354193075	0.9798514037134167	0.7388413567726362
0.5010869866684055	0.0207789453450130	0.2637644053055542
0.7528620933606767	0.0286260074080317	0.2354053263986616
0.7530923855458189	0.9724515288132838	0.7682501081885041
0.6437875677431079	0.7545273030151621	0.9920166072175409
0.8624488778052417	0.2530709378902031	0.0178063869280987
0.6147801317643079	0.2442097721444479	0.4786520203112755
0.8866666859576490	0.7498142862825194	0.5167738788473946
0.6152206067306599	0.7532816020980443	0.5253794421345789
0.8871557111197713	0.2502830045429837	0.4868470592530046
0.6435345997007167	0.2462348795991393	0.0117829288477097
0.8623527960560197	0.7475637824864745	0.9858469268543795
0.7488975467705514	0.4674939275189480	0.2354774505480065
0.7490457407723567	0.5322585443952286	0.7684645602077924
0.5015054075116353	0.5465423438299941	0.7641402334759796
0.5006903242348412	0.4542976364042089	0.2405970539109452

The optimized atomic positions for the polaron located at Mn-3

```
====================================
Na1-Mn16O32
      1.00000000000000
     11.7093000412000006     0.0000000000000000     0.0000000000000000
```

-0.0000405399000000 5.8548002241999999 0.0000000000000000
0.0000000000000000 0.0004045523000000 8.2783002754999995
Na Mn O
1 16 32
Direct
0.2535927900905456 0.7498525216968108 0.3742784649180599
0.2464843964516987 0.0048042526785098 -0.0122938951453972
0.9949802183463303 0.0015361102118349 0.4998732923963620
0.1212593700106628 0.2498958422180823 0.2417671625587626
0.3772363986033970 0.7499272251761203 0.7528478748533227
0.1220344713177566 0.7499105968232563 0.7489370955618894
0.3795884824744277 0.2499184427633733 0.2438321466419185
0.9949818732686020 0.4983452897747439 0.4998701939756864
0.2464917838097056 0.4949421915328496 -0.0123290970011073
0.7503430859269802 -0.0005277979219833 0.0037333794096652
0.5071626670989361 0.0049089229073920 0.5087835401397598
0.6275499028512940 0.2499779966553456 0.2555373836193572
0.8734312603815700 0.7499592369249820 0.7527332074027354
0.6260596549497938 0.7499691044368146 0.7566914453856771
0.8739036151673588 0.2499524405270254 0.2494690625221795
0.5071679019369727 0.4950399591016958 0.5087702326497574
0.7503444157800521 0.5004815370610014 0.0037450632640700
0.9970112334457886 0.9713731767963991 0.7338413522517520
-0.0018867072180308 0.0291976047551953 0.2641227918190561
0.2473993026089672 0.0361085001163495 0.2198455288159973
0.2479012374278413 0.9657230934240125 0.7555433194565949
0.1365914516339979 0.7498611424931427 0.9784626643124740
0.3519096243060978 0.2498616882173082 0.9841817056848197
0.1072318405748068 0.2499344397913871 0.4796583356555290
0.3996398115686979 0.7499724749431447 0.5221066777443301
0.1023132061080974 0.7499421569927558 0.5142125317815516
0.4001887340600102 0.2499815173025068 0.5079586929120341
0.1342476843304431 0.2498744483604867 0.0054963016267149
0.3555506729361223 0.7498749060486303 0.9825563093293550
0.2474238509439340 0.4636372683814485 0.2198152252830350
0.2479064200311384 0.5341004910949403 0.7555171990217493
-0.0030033721669492 0.5284946772911474 0.7338412637989354
-0.0018660584192973 0.4706671157768036 0.2641149310590146
0.5030122373292863 0.9685286269833541 0.7441597855704699
0.5047673525502431 0.0289614050990822 0.2743921293286443
0.7518154934963116 0.0296720385917522 0.2381772371164079
0.7505203807438303 0.9708757157453756 0.7704267641181569
0.6415736472853754 0.7499753626089601 0.9921913993947262
0.8600577361608068 0.2499773351755432 0.0171981783468983
0.6171272497514309 0.2499699277255311 0.4913499392144074
0.8860176565154519 0.7499452975452550 0.5165661130803288
0.6162207715819067 0.7499842491945384 0.5245293211569652
0.8872122066299956 0.2499409497558156 0.4851698353372764
0.6406027459672041 0.2499811154795007 0.0207229298732356
0.8604545132752206 0.7499767587343198 0.9873117184267255
0.7518238697729186 0.4702573071301798 0.2381823638683691
0.7505148967100019 0.5290678148468984 0.7704380046921107
0.5030246213448824 0.5313802603480423 0.7441541799671326
0.5047774342647053 0.4709943387695538 0.2743899481668521

SI-4. AIMD simulation to show the bulk structure of the E-$NaMnO_2$ is stable under high temperatures.

In order to evaluate the stability of E-$NaMnO_2$, *ab initio* molecular dynamic simulation is performed at a temperature of 500 K. as shown in Figure S1, the free energy of E-$NaMnO_2$ converged to a stable value. Furthermore, the atomic structure of E-$NaMnO_2$ during the *ab initio* molecular dynamic simulation at t=5, 6, 7 and 8 ps are shown in Figure S2. Except for some small distortions, the overall structure of E-$NaMnO_2$ maintains well

under 500 K, showing the good thermal stability of E-$NaMnO_2$ under high temperature. Upon structural relaxation, the atomic structures selected randomly from any step of the AIMD simulation can easily go backs to the ground state structure.

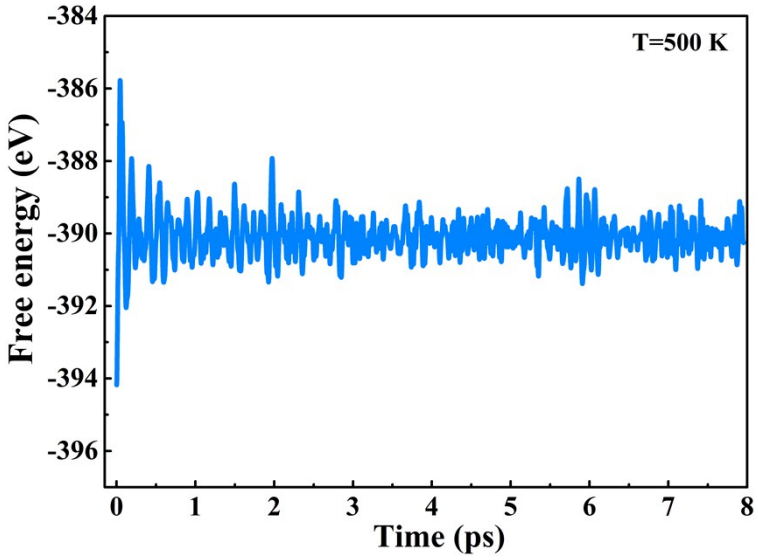

Fig. S1. Variation of free energy of E-$NaMnO_2$ during *ab initio* molecular dynamic simulation at a temperature of 500 K.

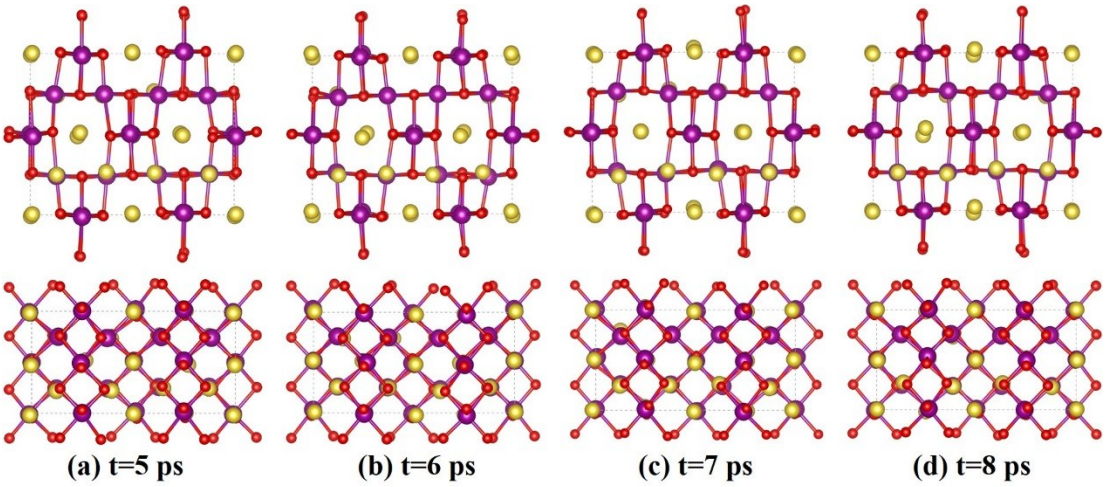

Fig. S2. Atomic structures of E-$NaMnO_2$ during *ab initio* molecular dynamic simulation at t=5 (a), 6 (b), 7 (c) and 8 (d) ps.