Electronic Supplementary Information

Composite $A_2M_6O_{13}$ Anodes (A = Li, Na; M = Ti, Zr) for Li-Na Dual Cation Batteries: A Theoretical Investigation

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Table S1: Number of ionic species in each sample, including cations, vacancies, and defect concentrations.

Sample	N_{Na}^+	N_{Li}^+	N_{Ti}^{4+}	N_{Zr}^{4+}	N_O^{2-}	Vac-O^{2-}	Vac-A^+	A^+ defect concentration
NTO	1400		4320		9340	40	20	0.0927
NZO	1400			4320	9340	40	20	0.0927
bi-NTO	1546		4762		10297		34	0.0931
bi-NZO	1546			4762	10297		34	0.0931
NTZO	1546		2386	2376	10297		34	0.0931
NZTO	1546		2376	2386	10297		34	0.0931
LTNZO	774	772	2376	2386	10297		34	0.0931
LZNTO	774	772	2386	2376	10297		34	0.0931

Examples of LAMMPS input files (at 900K) of NTO, bi-NTO samples, and LTNZO composite are included for reproducibility providing further simulation details for the readers. A zip file is included with the simulation boxes.

1. Input file of NTO

```
##########################################################
##
#------------Variables and cell-------------------------#
##########################################################
##

clear
```

```
units         metal       #eV,atomic charge,angstroms,ps,kelvin,bars,g/mol
dimension 3
boundary p p p
atom_style charge
#processors * * * grid numa
read_data 4x15x6NeutralNTO.lmp

group          Na type 1
group          Ti type 2
group          O  type 3
#group                Zr type 4


mass 1   23                #Na
mass 2   47.867          # Ti
mass 3   15.99900000          # O

variable T1 equal 900
variable Timer equal step*dt
log ${T1}.lammps

#########################################################
#
#---------- Pair styles and electrostatics--------------#
#########################################################
#

pair_style buck/coul/long 10
pair_coeff * *  0.0 1.0 0.0
pair_coeff 1 1  0.0 1.0 0.0
pair_coeff 1 2  0.0 1.0 0.0
pair_coeff 1 3  1271.504 0.3 0.0 #Na-O
pair_coeff 2 2  0.0 1.0 0.0
pair_coeff 2 3 5111.7  0.2625   0.0 #Ti-O
pair_coeff 3 3  22764.3 0.149 27.627 #O-O



kspace_style pppm 1e-05

#########################################################
# -------------- Run Minimization ---------------------#
#########################################################

reset_timestep 0
```

```
timestep 0.5
thermo 10
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000


#########################################################
# ---------- Relax Cell -------------------------#
#########################################################

reset_timestep 0
timestep 0.5
fix 1 all box/relax aniso 1.0 vmax 0.003
thermo 1
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000
unfix 1

#########################################################
# ------------ Run NPT T1----------------------------#
#########################################################

reset_timestep 0
timestep 0.002
velocity all create ${T1} 49284 rot yes dist gaussian
fix     2 all npt temp ${T1} ${T1} 0.01 aniso 1.0 1.0 0.1
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
thermo 1000
run 5000
unfix 2

reset_timestep 0
timestep 0.002

compute       mymsdNa Na msd com yes
compute       mymsdO O msd com yes
variable      msdxNa equal "c_mymsdNa[1]"
variable      msdyNa equal "c_mymsdNa[2]"
variable      msdzNa equal "c_mymsdNa[3]"
variable      msdtotNa equal "c_mymsdNa[4]"
variable      msdoxO equal "c_mymsdO[1]"
variable      msdoyO equal "c_mymsdO[2]"
variable      msdozO equal "c_mymsdO[3]"
```

```
variable       msdototO equal "c_mymsdO[4]"

fix          msdT2 O ave/time 1 1 2500 v_msdoxO v_msdoyO v_msdozO v_msdototO
file msdOxygen${T1}
fix          msdT1 Na ave/time 1 1 2500 v_msdxNa v_msdyNa v_msdzNa v_msdtotNa
file msdSodium${T1}
fix          3 all nvt temp ${T1} ${T1} 0.01
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
v_msdtotNa v_msdototO
thermo 5000
dump dynamics all xyz 5000 monoNTO_${T1}.xyz
dump_modify dynamics every 5000 element Na Ti  O  first yes
run          1000000
unfix 3
unfix msdT1
unfix msdT2
```

2. Input file of bi-crystalline bi-NTO

```
#########################################################
##
#------------Variables and cell-------------------------#
#########################################################
##

clear
units          metal       #eV,atomic charge,angstroms,ps,kelvin,bars,g/mol
dimension 3
boundary p p p
atom_style charge
#processors * * * grid numa
read_data NeutralNTO-1.lmp

group          Na type 1
group          Ti type 2
group          O  type 3
#group                 Zr type 4


mass 1   23                #Na
mass 2   47.867          # Ti
mass 3   15.999          # O

variable T1 equal 900
variable Timer equal step*dt
```

```
log ${T1}.lammps

#############################################################
#
#---------- Pair styles and electrostatics-------------#
#############################################################
#

pair_style buck/coul/long 10
pair_coeff * *  0.0 1.0 0.0
pair_coeff 1 1  0.0 1.0 0.0
pair_coeff 1 2  0.0 1.0 0.0
pair_coeff 1 3  1271.504 0.3 0.0 #Na-O
pair_coeff 2 2  0.0 1.0 0.0
pair_coeff 2 3 5111.7  0.2625   0.0 #Ti-O
pair_coeff 3 3  22764.3 0.149 27.627 #O-O
kspace_style pppm 1e-05

#############################################################
# -------------- Run Minimization ---------------------#
#############################################################

reset_timestep 0
timestep 0.5
thermo 10
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000


#############################################################
# -------------- Relax Cell --------------------------#
#############################################################

reset_timestep 0
timestep 0.5
fix 1 all box/relax aniso 1.0 vmax 0.003
thermo 1
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000
unfix 1

#############################################################
# ------------- Run NPT T1----------------------------#
```

```
#########################################################

reset_timestep 0
timestep 0.002
velocity all create ${T1} 49284 rot yes dist gaussian
fix     2 all npt temp ${T1} ${T1} 0.01 aniso 1.0 1.0 0.1
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
thermo 1000
run 5000
unfix 2

reset_timestep 0
timestep 0.002

compute       mymsdNa Na msd com yes
compute       mymsdO O msd com yes
variable      msdxNa equal "c_mymsdNa[1]"
variable      msdyNa equal "c_mymsdNa[2]"
variable      msdzNa equal "c_mymsdNa[3]"
variable      msdtotNa equal "c_mymsdNa[4]"
variable      msdoxO equal "c_mymsdO[1]"
variable      msdoyO equal "c_mymsdO[2]"
variable      msdozO equal "c_mymsdO[3]"
variable      msdototO equal "c_mymsdO[4]"

fix          msdT2 O ave/time 1 1 2500 v_msdoxO v_msdoyO v_msdozO v_msdototO
file msdOxygen${T1}
fix          msdT1 Na ave/time 1 1 2500 v_msdxNa v_msdyNa v_msdzNa v_msdtotNa
file msdSodium${T1}
fix          3 all nvt temp ${T1} ${T1} 0.01
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
v_msdtotNa v_msdototO
thermo 5000
dump dynamics all xyz 5000 2grainsNTO_${T1}.xyz
dump_modify dynamics every 5000 element Na Ti  O  first yes
run          1000000
unfix 3
unfix msdT1
unfix msdT2
```

3. Input file of LTNZO composite

```
#########################################################
##
#------------Variables and cell-------------------------#
```

```
#########################################################
##

clear
units         metal       #eV,atomic charge,angstroms,ps,kelvin,bars,g/mol
dimension 3
boundary p p p
atom_style charge
#processors * * * grid numa
read_data LZNTO-1.lmp

group          Na type 1
group         Li type 2
group          Ti type 3
group          O  type 4
group          Zr type 5


mass 1   23          # Na
mass 2   6.94         # Li
mass 3   47.867       # Ti
mass 4   15.999       # O
mass 5   91.224       # Zr



set              group O charge -2.0
set              group Li charge 1.0
set              group Ti charge 4.0
set              group Zr charge 4.0
set              group Na charge 1.0

variable T1 equal 1000
variable Timer equal step*dt
log ${T1}.lammps

#########################################################
#
#---------- Pair styles and electrostatics--------------#
#########################################################
#

pair_style buck/coul/long 10
pair_coeff * *  0.0 1.0 0.0
pair_coeff 1 4  1271.504 0.3 0.0 #Na-O
```

```
pair_coeff 2 4  632.1018 0.2906  0.0 #Li-O
pair_coeff 3 4 5111.7  0.2625   0.0 #Ti-O
pair_coeff 4 5 985.87 0.3760  0.0 #Zr-O
pair_coeff 4 4  22764.3 0.149 27.627 #O-O



kspace_style pppm 1e-05

#########################################################
# -------------- Run Minimization --------------------#
#########################################################

reset_timestep 0
timestep 0.5
thermo 10
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000


#########################################################
# -------------- Relax Cell --------------------------#
#########################################################

reset_timestep 0
timestep 0.5
fix 1 all box/relax aniso 1.0 vmax 0.003
thermo 1
thermo_style custom step enthalpy fmax lx ly lz vol press
min_style cg
minimize 1e-25 1e-25 5000 10000
unfix 1

#########################################################
# ------------- Run NPT T1----------------------------#
#########################################################

reset_timestep 0
timestep 0.002
velocity all create ${T1} 4928 rot yes dist gaussian
fix     2 all npt temp ${T1} ${T1} 0.01 aniso 1.0 1.0 0.1
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
thermo 1000
```

```
run 5000
unfix 2

reset_timestep 0
timestep 0.002
compute       mymsdNa Na msd com yes
variable      msdx equal "c_mymsdNa[1]"
variable      msdy equal "c_mymsdNa[2]"
variable      msdz equal "c_mymsdNa[3]"
variable      msdtotNa equal "c_mymsdNa[4]"

compute       mymsdLi Li msd com yes
variable      msdx equal "c_mymsdLi[1]"
variable      msdy equal "c_mymsdLi[2]"
variable      msdz equal "c_mymsdLi[3]"
variable      msdtotLi equal "c_mymsdLi[4]"

fix           msdT1 Li ave/time 1 1 5000 v_msdx v_msdy v_msdz v_msdtotLi file
MSDLi${T1}
fix           msdT2 Na ave/time 1 1 5000 v_msdx v_msdy v_msdz v_msdtotNa file
MSDNa${T1}
fix           3 all nvt temp ${T1} ${T1} 0.01
thermo_style custom step v_Timer cpu temp etotal fmax lx ly lz vol press
v_msdtotLi v_msdtotNa
thermo 5000
dump dynamics all xyz 5000 2grainsLZNTO_${T1}.xyz
dump_modify dynamics every 5000 element Li Na Ti O Zr  first yes
run           1000000
unfix 3
unfix msdT1
unfix msdT2
```

Trajectory density maps

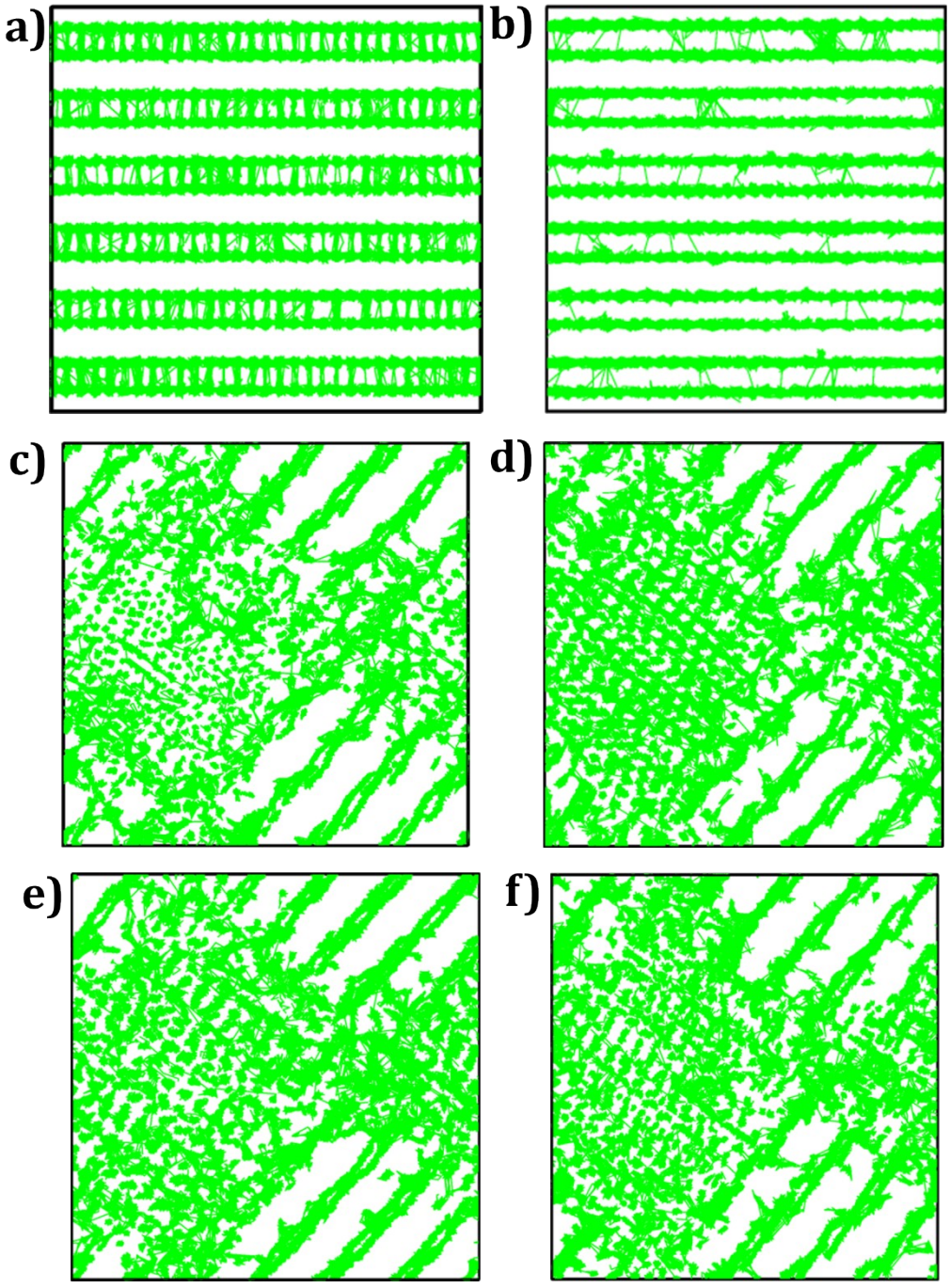

Figure S1: Na^+ trajectory density maps (green lines) of: a) NTO and b) NZO, c) bi-NTO, d) bi-NZO, e) NTZO and f) NZTO samples.