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Atomistic level aqueous dissolution dynamics of NASICON-Type $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP)

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ABSTRACT: Advancing the atomistic level understanding of aqueous dissolution of multicomponent materials is essential. We combined ReaxFF and experiments to investigate the dissolution at the Li1+xAlxTi2-x(PO4)3-water interface. We demonstrate that surface dissolution is a sequentially dynamic process. The phosphate dissolution destabilizes the NASICON structure, which triggers a titanium-rich secondary phase formation.

Table of Contents

1. Supplementary Figures
2. Supplementary Tables
3. Supplementary Movie
4. References

1. Supplementary Figures

Radial distribution functions:

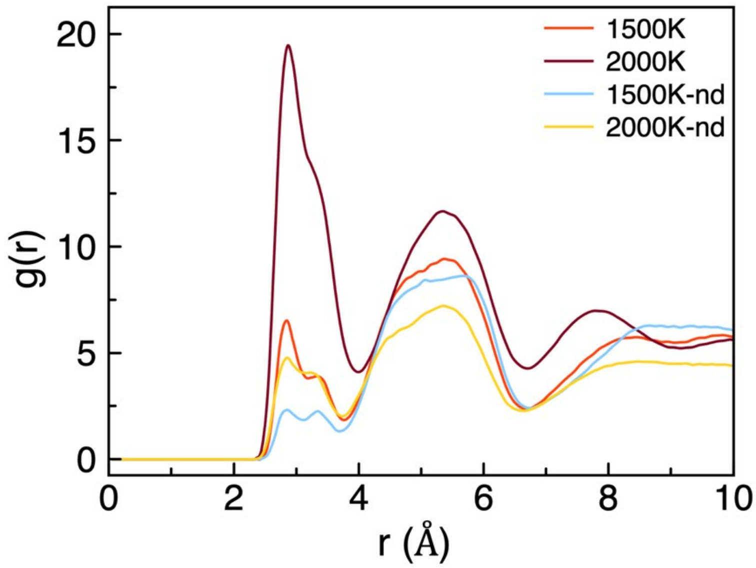

Figure S1. The titanium-titanium RDFs of LATP crystal inside water (red and claret red) and in vacuum (blue and yellow) at two different temperatures. Dissolution of phosphates were prevented in vacuum which results in a preservation of crystallinity in the crystal.

As discussed in the main text, there is a switch to a more stable phase inside crystal between TiO_6 groups due to the dissolution of PO_3 groups. In order to avoid artificial effects on dissolution coming from the thermal fluctuations caused by the elevated simulation temperatures, we conducted separate simulations using same LATP structures for temperatures larger than 1500K. We removed the water from the system and reduced the vacuum region to prevent the dissolution of LATP. As can be seen in the radial distribution function in Figure S1, Ti-Ti distance dramatically decreases during the transition from 1500K (red line) to 2000K (claret red line) because PO_3 groups are dissolved during this transition. However, when the dissolution of PO_3 groups is suppressed by removing the liquid phase, the transition (blue line to yellow line) does not affect the Ti-Ti distance, thus does not affect the stability of the structure.

TEM images after incongruent dissolution:

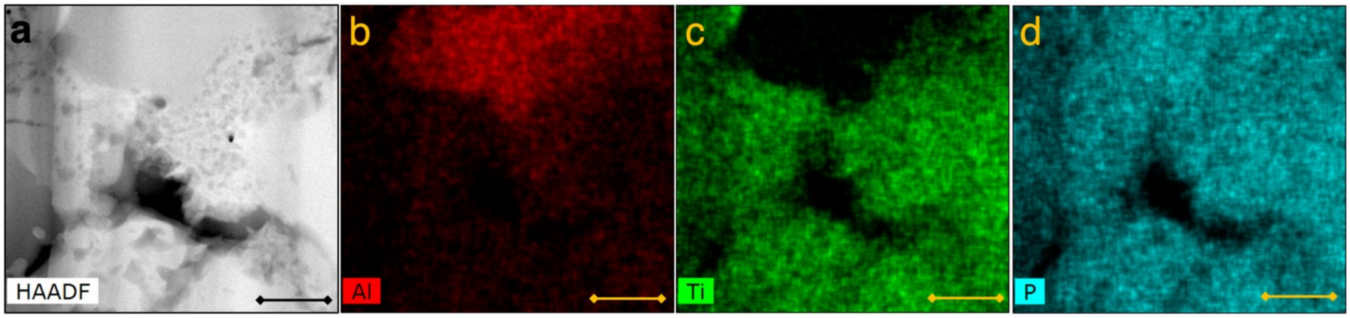

Figure S2. The HAADF-TEM and EDS elemental mapping images obtained from the cold sintered sample. The images indicate the segregation of Ti and Al whereas P is homogenously distributed through most of the sample. All the scale bars are 90nm.

The SEM images of initial powder:

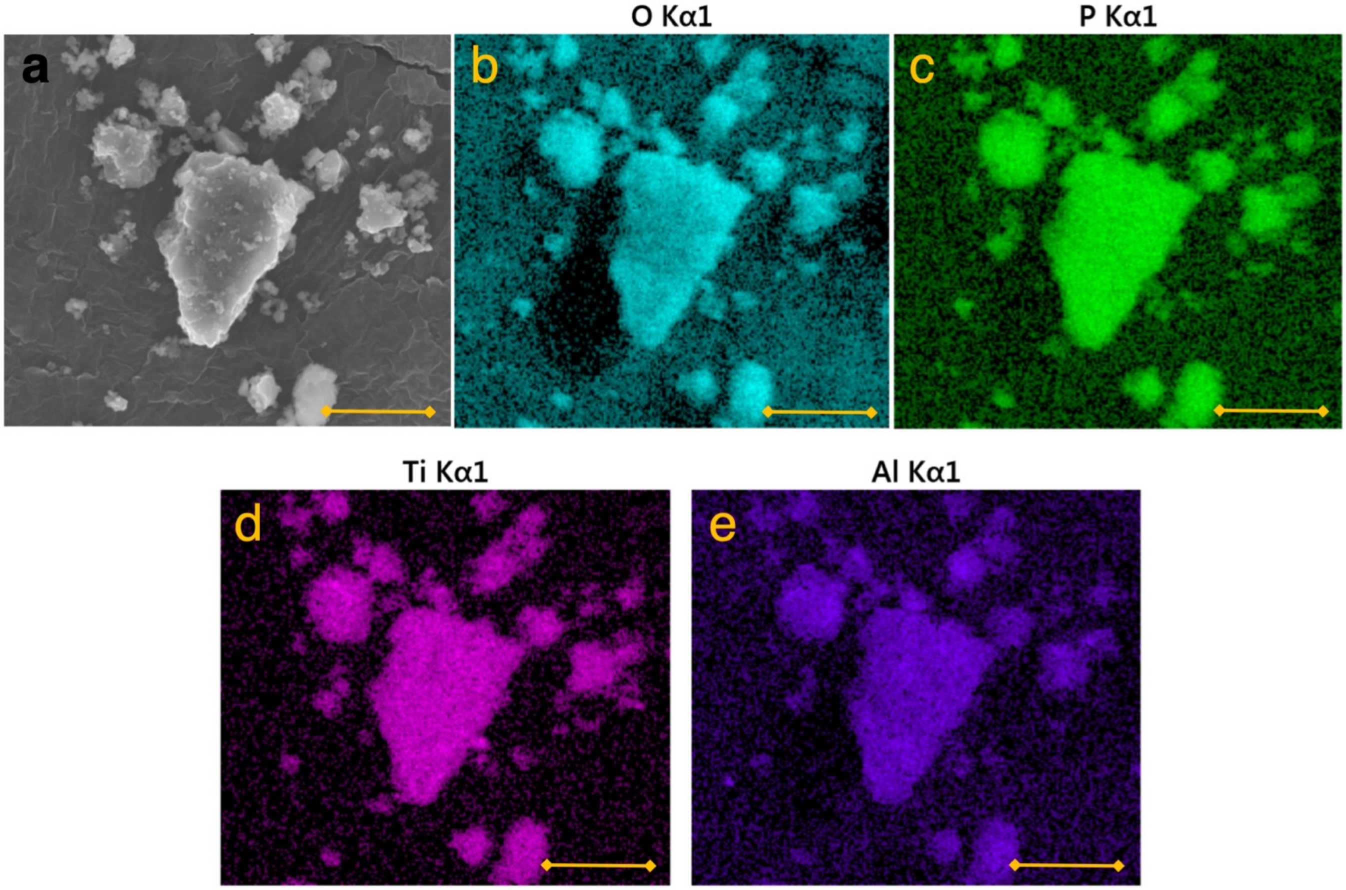

Figure S3. The SEM and EDS elemental mapping images obtained from initial powder. The details about the powder can be seen in experimental methods sections. As can be seen, there are no segregation of Al and Ti species in initial powder. All the scale bars are 5μm.

2. Supplementary Tables

Table S1. The dissolution ratio obtained from experiments and model. In order to calculate the dissolution ratio, the ratio of the dissolved species to dissolved lithium is divided by the congruent dissolution ratios. The lithium ratios are normalized based on the dissolved lithium amount for each case. Results are calculated by averaging over 1ns long simulation. The simulated surface is 15.3 nm^2 and system is composed of 19072 atoms. For details, please see computational methods sections.

Element	**Li**	**Al**	**Ti**	**P**
Dissolution Ratio (experimental)	100%	15%	7%	41%
Dissolution Ratio (ReaxFF)	100%	5.3%	1.1%	43.6%

Table S2. The dissolution concentrations of each specie obtained from experiments at room temperature.

Element	**Li**	**Al**	**Ti**	**P**
Concentration (μmol/mL)	5.06	0.24	0.33	4.07

3. Supplementary Movie

Movie S1. The video shows the dissolution of $AlPO_6$-PO_4 chain from the crystal phase to aqueous phase. As can be seen, the chain is very stable and stays as a chain after dissolved into aqueous phase, which is one of the reasons of incongruent dissolution. The video was recorded from 0.6 ns long ReaxFF simulations. To increase visibility, the background liquid phase is represented using blurred colors. Key: Ti (green); P (cyan); Al (red); Li (purple); O (orange). The atoms in chain structure are represented as bigger spheres than others to increase visibility.

4. References

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