



Cite this: *J. Mater. Chem. A*, 2016, 4, 6998

Feeling the strain: enhancing ionic transport in olivine phosphate cathodes for Li- and Na-ion batteries through strain effects†

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Olivine-type phosphates LiFePO_4 and NaFePO_4 are among the most widely studied cathode materials for rechargeable batteries. To improve their rate behaviour for future electronic and vehicle applications, it is vital that the Li^+ and Na^+ conductivities be enhanced. In this study, atomistic simulation methods (including molecular dynamics) are used to investigate the effect of lattice strain on ion transport and defect formation in olivine-type LiFePO_4 and NaFePO_4 , as these properties are directly related to their intercalation behaviour. The results suggest that lattice strain can have a remarkable effect on the rate performance of cathode materials, with a major increase in the ionic conductivity and decrease in blocking defects at room temperature. Such understanding is important for the future optimization of high-rate cathodes for rechargeable batteries, and is relevant to the growing interest in developing thin film solid-state batteries.

Received 20th November 2015

Accepted 21st February 2016

DOI: 10.1039/c5ta09418f

www.rsc.org/MaterialsA

1. Introduction

The successful development of next-generation lithium- and sodium-ion batteries depends to a large degree on the ability to fabricate cathode materials with superior electrochemical and mechanical properties.^{1–3} Cathodes based on olivine LiFePO_4 have been widely studied for this purpose and continue to be important.^{4–6} One advantage of such polyoxyanion-type materials compared with the conventional layered transition metal oxides is that the binding of oxygen in the polyoxyanions enhances the material's stability and thus safety.^{6,7} Sodium-ion battery materials such as NaFePO_4 have attracted increasing attention recently, largely because the high natural abundance of sodium should make them less expensive.^{8,9} The development of cheap and safe cathode materials is a particularly important goal in the case of large-scale batteries. However, the improvement of the rate performance of both LiFePO_4 and NaFePO_4 for portable electronic or electric vehicle applications will require significantly improved ionic conductivities.

Previous strategies to optimize intercalation properties have mainly involved chemical doping and morphology modulation, with nanosizing and carbon coating so far proving to be the

most successful approaches.^{10,11} The charge/discharge rate performance of olivine-type LiFePO_4 has been improved by shortening the diffusion distances by preparing nanosized particles, but higher rates are required for specific applications such as electric vehicles.⁴ Higher energy storage capability will also require materials with faster ionic transport so that thicker electrodes can be used.⁵

In the case of intercalation compounds, charge/discharge rates are related to lithium and sodium diffusion kinetics which, in turn, are highly dependent upon structural and defect properties. Manipulation of lattice strain is increasingly being considered as a possible design strategy to improve the functional properties of various materials, such as superconductivity,^{12,13} ionic conductivity,¹⁴ ferroelectricity¹⁵ and colossal magnetoresistance.¹⁶ In particular, there has been considerable interest in the application of lattice strain in the modulation of ionic conductivity in oxide materials for solid oxide fuel cells (SOFCs).^{17,18} Several studies have highlighted the positive effect of tensile lattice strain on migration barriers and ion diffusion coefficients in SOFC electrolytes. Following the report of colossal ionic conductivity in epitaxial heterostructures formed by thin layers of Y/ZrO_2 and SrTiO_3 ,¹⁹ lattice strain effects on fluorite- and perovskite-type materials have been systematically studied using computational techniques.^{20–25} It should be noted that there is still much debate as to the nature of the charge-carriers with evidence pointing towards electronic conduction in SrTiO_3 .²⁶ In contrast, the effects of mechanical strain on battery cathode materials have not been extensively considered, with only a limited number of studies to date.^{27–34} Shahid *et al.*³⁰ report that at the nanoscale level for LiFePO_4 there is an order of magnitude enhancement in the electronic (polaron)

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† Electronic supplementary information (ESI) available: List of potential parameters; comparison between calculated and experimental structures; alkali-ion migration barrier for along path A and C; formation energy for pair clusters in the case of *ab* and *bc* biaxial applied strain. See DOI: 10.1039/c5ta09418f

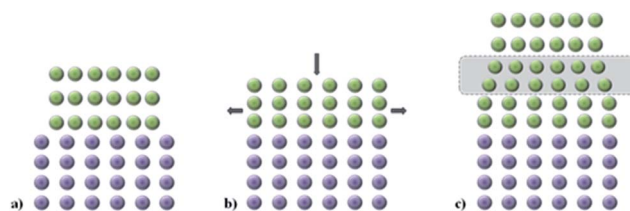


It is apparent that there are limited fundamental studies in this area comparing Li- and Na-ion systems. Here we investigate the effect of lattice strain on the ion conduction and defect properties of both LiFePO_4 and NaFePO_4 olivine-type cathode materials using atomistic simulation techniques. In general, the results highlight the importance of lattice strain effects as an alternative strategy to optimize the electrochemical properties of Li- and Na-ion intercalation compounds.

Olivine-type LiFePO_4 and NaFePO_4 unit cells (*Pnma* space group) were allowed to relax at constant pressure with zero applied strain. Subsequently, the energy minimized cells were subjected to biaxial compressive ($<0\%$) and tensile ($>0\%$) strains between -3% and $+3\%$ in the *ab*, *ac* and *bc* planes. Besides representing a physically accessible range of values, this strain range was chosen in order to avoid instabilities due to structure failure. Energy minimization of the structures with respect to the third cell parameter and all the atomic coordinates was then carried out. The strained energy-minimized structures were used as the starting configurations for ion migration and defect calculations. Similar methodology has been applied successfully to the study of SOFC oxide-ion conductors.^{23,25}

MD simulations were performed, using the DL_Poly code,⁴⁹ at 500 K. Such an elevated temperature was chosen to allow both efficient thermalization of the defective solid and sufficient ionic diffusion during the simulation time span, thereby improving the statistics of the calculations. The unstrained system was first equilibrated at the desired temperature for 100 ps with a time step of 0.5 fs. The main simulation run of 750 ps was then performed in the NVT ensemble (Nose–Hoover thermostat). For the strained systems, the energy-minimized cell parameters were expanded according to the thermal expansion coefficient derived for the same composition in the absence of applied strain. Simulations in the NVT ensemble were then carried out as described above. Data analysis was performed using the Visual Molecular Dynamics package (VMD).⁵⁰

For experimental work, lattice strain in thin film samples is generated by substrate/film mismatch (*i.e.* differences in d spacing), as schematically shown in Fig. 1a. In the case of similar or related lattice symmetries and small mismatch values, a coherent interface is often formed. The lattice mismatch leads to in-plane tensile or compressive strain in the deposited layer. In the case of thin films deposited onto



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a crystalline substrate, this will be a biaxial strain. For perfectly elastic systems, the unit cell volume remains unchanged and the out-of-plane cell parameters increase or decrease as appropriate (Fig. 1b). In practice, most oxide materials have a Poisson coefficient, ν , in the range $0 < \nu < 0.5$,⁵⁴ which means that in the case of in-plane tensile strain, the out-of-plane parameter decreases in a way such that film undergoes a net positive volume change. The effect of lattice strain due to film/substrate mismatch is restricted to thin films on the nanometre scale; in thick film samples, the strain is released as the greater distance from the film/substrate interface into the bulk of the film (Fig. 1c).

Since many electrical properties are strongly influenced by the type and number of defects and ion diffusion barriers in a crystalline material, strained systems may exhibit behaviour different from the corresponding bulk material. The application of biaxial strain on the olivine system, regardless of the plane considered, has the effect of producing a net change in unit cell volume (Fig. 2), indicative of non-ideal Poisson behaviour commonly exhibited by oxide materials.⁵⁴

Li^+ migration pathways in LiFePO_4 , as initially predicted from theoretical calculations⁴⁵ and subsequently confirmed by neutron diffraction maximum entropy methods,⁵⁵ zigzag along the $[010]$ direction (path B of Fig. 3). Na^+ migration in olivine-type NaFePO_4 was subsequently shown to follow the same zigzag path, characterized by a lower migration barrier compared to the Li analogue (0.31 vs. 0.55 eV).⁴⁶

Fig. 4 shows the calculated migration barrier along the $[010]$ direction as a function of applied strain for LiFePO_4 and NaFePO_4 . For both systems, the energy barrier increases slightly along with the applied strain for the ab and bc cases. Interestingly, the migration energy decreases along with strain for the ac case, reaching a value that is approximately half the value for the unstrained system, corresponding to 3% tensile strain. The calculated migration barrier for Li^+ decreases from 0.55 eV to

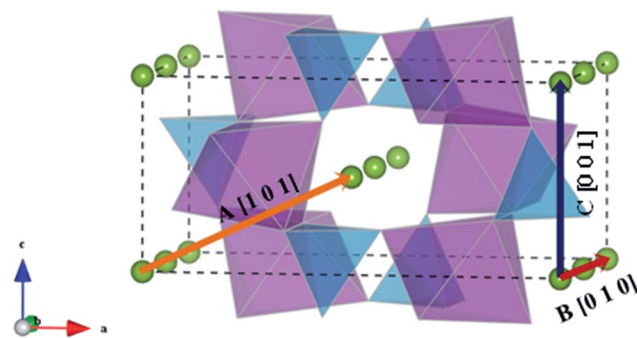


Fig. 3 Schematic representation of the possible migration paths in olivine-type AFePO_4 ($\text{A} = \text{Li}^+$ or Na^+). Blue: PO_4 tetrahedra; purple: FeO_6 octahedra; green: Li/Na .

0.28 eV while the migration barrier for Na^+ decreases from 0.37 eV to 0.16 eV. This significant reduction in migration energy with tensile strain is consistent with a previous DFT study of Lee *et al.*²⁹ on olivine LiFePO_4 .

Changes in migration barrier for ion diffusion can be interpreted in terms of structural modifications. In particular, our results show a relation between the variation in migration barrier and the ion-ion hopping distance along with the applied strain. For example, in the case of LiFePO_4 , the Li-Li hopping distance for migration along the $[010]$ direction decreases for the ac strained case, while it increases for the other two cases (Fig. S2a†). A decrease in ion hopping distance is expected to favour alkali-ion diffusion in the structure. Other structural parameters such as the available free volume at the saddle point position may also influence the migration barrier. Hence, the overall variation of the migration barrier along with strain is the

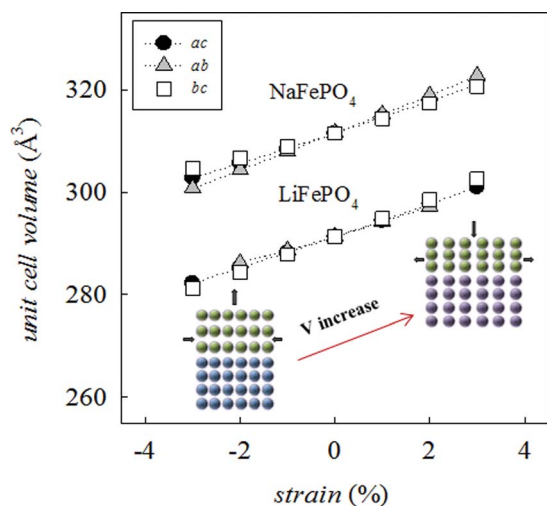


Fig. 2 Change in the calculated unit cell volume as a function of strain for LiFePO_4 and NaFePO_4 together with a schematic representation of the effect of compressive ($<0\%$) or tensile ($>0\%$) lattice strain on the thin film system.

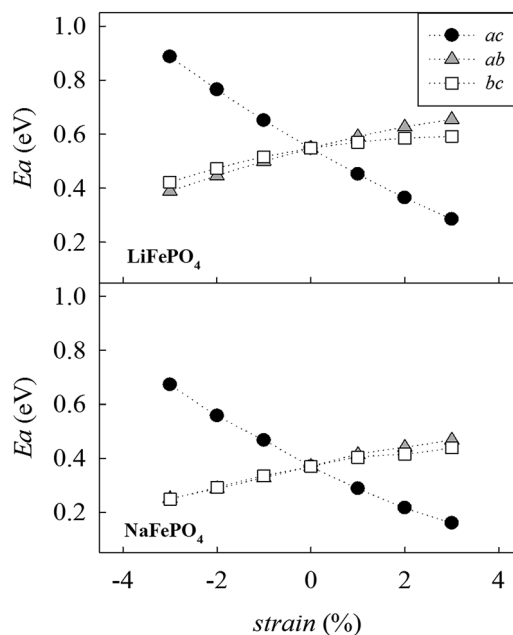


Fig. 4 Change in the alkali-ion migration barrier along the $[010]$ direction as a function of strain for LiFePO_4 (upper panel) and NaFePO_4 (lower panel).

result of a fine interplay between different structural parameters whose nature depends on the particular structure and the migration path considered (Fig. S2-ESI†).

In the olivine system, two other migration paths are potentially accessible, labelled in Fig. 3 as paths A (along the [101] direction) and C (along the [001] direction). Both paths are characterized by energy barriers >2.5 eV for the unstrained system and, as a consequence, alkali-ion transport in olivine-type materials is considered a one dimensional process. In order to determine if the dimensionality of Li^+ and Na^+ ion transport is affected by applied strain, the activation energies for paths A and C were calculated as a function of the applied strain. Calculated activation energies for migration along the [001] and [101] directions still remain above 2 eV for the 3% tensile strained systems (Fig. S1-ESI†) and therefore they are not comparable to the most favourable migration path running parallel to the b axis (Fig. 4). This result suggests that, even for the strained systems, Li^+ and Na^+ ion transport will remain a 1D diffusion process, as is found for unstrained LiFePO_4 and NaFePO_4 .^{45,46}

MD simulations performed on both the unstrained and the ac -plane strained systems confirmed that Li and Na ion

diffusion proceeds through a zig-zag path parallel to the b -axis. The 1D and curved nature of such paths are not altered by the application of tensile strain, as shown in Fig. 5 for the Na-based system, selected as an example.

Visual analysis of Fig. 5 already indicates that the application of tensile strain has a positive effect on the alkali-ion mobility within the system showing greater Na-ion density in the trajectory plot. To better quantify such effects, Li and Na ion diffusion coefficients were derived from the slope of the mean square displacement (MSD) parameters *vs.* simulation time plots (Fig. 6) through the use of the following standard relation:

$$\langle |r_i(t) - r_i(0)|^2 \rangle = 6D + B \quad (1)$$

where on the left side the quadratic displacement of the Li/Na atom from its initial position is represented, D is the diffusion coefficient and B is the atomic displacement parameter attributed to thermal vibration. The diffusion coefficients (D) derived for the systems under investigation are reported in Table 1. Direct comparison with experiment is not straightforward due to significant scatter in measured values of diffusion coefficients. Nevertheless, our calculated D_{Li} and D_{Na} are consistent with available observed values for LiFePO_4 and related Na-ion cathode materials.^{56–58}

Analysis of the MD results indicate two main points: first, Na-ion diffusion coefficients are predicted to be higher than Li-ion diffusion coefficients in the olivine system, in line with the calculated difference in the absolute values between Na-ion and Li-ion migration barriers (Fig. 4); second, the application of tensile strain increases the alkali-ion diffusion. The predicted effect is comparable for Li and Na-based systems and, at the simulation temperature used in this study (500 K), is roughly one order of magnitude.

The overall results derived from MD simulations are in good agreement with the trend observed from static lattice simulations, *i.e.* tensile strain applied perpendicularly to the main diffusion direction is enhancing ion transport in the system.

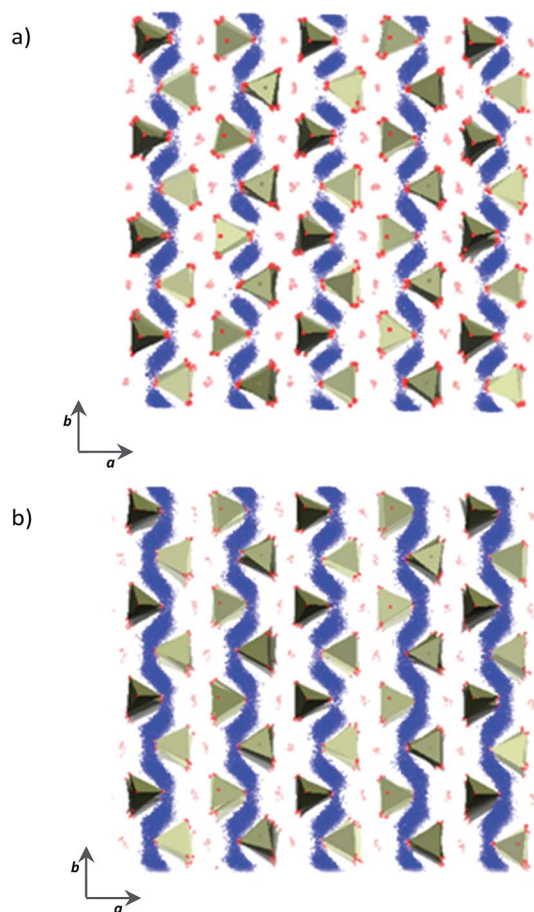


Fig. 5 Na-ion trajectory plot for (a) unstrained $\text{Na}_{0.9}\text{FePO}_4$ and (b) 3% ac -strained $\text{Na}_{0.9}\text{FePO}_4$ showing the Na-ion zig-zag path. Projection along the c axis. Blue spheres represent the positions occupied by Na ions over the simulation time; pink spheres represent the Fe ions in their final configuration while the tetrahedra represent the PO_4 units.

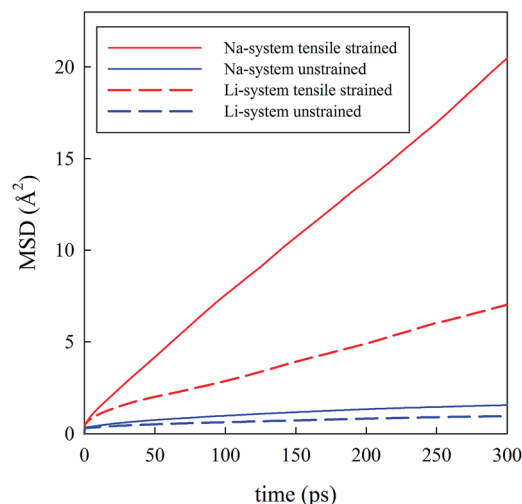


Fig. 6 Mean square displacement (MSD) *vs.* time for $\text{Li}_{0.9}\text{FePO}_4$ (dashed lines) and $\text{Na}_{0.9}\text{FePO}_4$ (solid lines).



Table 1 Comparison between the Li and Na ion calculated diffusion coefficients at 500 K for the unstrained and the 3% tensile strained systems

Strain (%)	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	D_{Na} ($\text{cm}^2 \text{s}^{-1}$)
0.0	3.36×10^{-8}	6.69×10^{-8}
3.0	3.42×10^{-7}	1.08×10^{-6}

Based on the calculated changes in activation energy along with strain (Fig. 4), we can estimate the change in ionic conductivity due to the application of 3% biaxial strain in the *ac* plane based on standard Arrhenius equations. Previous work of De Souza²³ shows that with regard to oxygen diffusion in fluorite-type CeO_2 , ΔH^{mig} can be conveniently approximated by the calculated activation barrier, E_{mig} , within a certain range of applied strain. Using the values shown in Fig. 4, and approximating ΔH^{mig} by the calculated activation barrier, E_{mig} , we can predict an enhancement in Li^+ and Na^+ conductivity of approximately three orders of magnitude at room temperature. We recognize that the calculated enhancement based on MD results is significantly lower. However, a number of factors should be taken into consideration. First, MD simulations were conducted at 500 K while the estimation of conductivity increase based on the static lattice simulations result was performed at 300 K. The predicted change in activation energy along with strain (Fig. 4) suggests that differences in conductivity will be more pronounced as the temperature is reduced; for example, this has been computationally predicted²⁰ and experimentally observed⁵⁹ for oxygen diffusion in strained fluorite structures and perovskite-type materials.⁶⁰ This is also in line with the predicted large effect of temperature in the exponential factor of the Arrhenius equation.

Therefore, the key conclusion of this study is that tensile biaxial strain applied in the plane perpendicular to the main diffusion path will promote alkali-ion diffusion. Even within the limits of our estimate, this is a major enhancement in ionic conductivity which should greatly improve the rate behaviour of olivine-type cathode materials. Even taking into account possible effects of interfaces (*e.g.* dislocations, grain boundaries and space charge regions), the ionic conductivity should undergo a significant enhancement. There are of course experimental technical challenges associated with the fabrication of epitaxial thin-films (using, for example, pulsed laser deposition) and their electrical characterisation. In particular, the evolution of dislocation defects may introduce a lower degree of strain compared to that expected on the basis of substrate/lattice mismatch. Nevertheless, our clear predictions warrant further investigation.

3.2 Strain effects on defect formation

Due to the 1D nature of alkali-ion transport in olivine-type materials, the presence of intrinsic anti-site defects (eqn (2) and (3), and Fig. 7), which involve the exchange of an Li/Na ion for a neighbouring Fe atom, can be detrimental to ion intercalation properties:

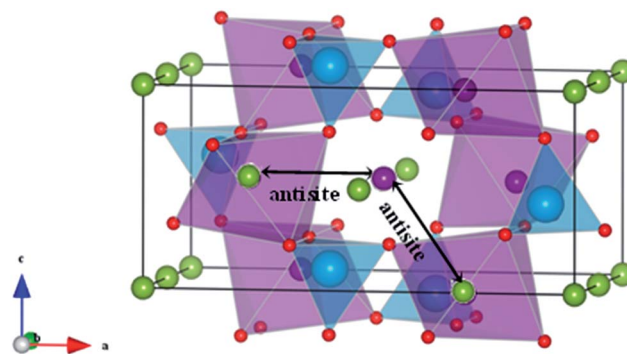
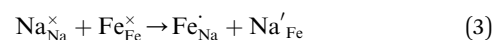
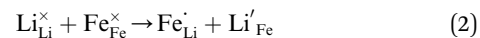


Fig. 7 Schematic representation of two configurations of Li/Fe or Na/Fe anti-site defects in olivine-type AFePO_4 ($\text{A} = \text{Li}^+$ or Na^+).



Such intersite cation exchanges represent the most energetically favourable intrinsic defect in olivine-type materials.⁴⁵ Their formation has been frequently observed experimentally, for example, by refinement of site occupancies in diffraction experiments⁶¹ or by direct visualization using electron microscopy methods.⁶² Since alkali-ion transport in olivine-type materials occurs one-dimensionally along [010], these types of defect negatively affect the intercalation properties by blocking the ion transport pathways.

In order to determine if the application of biaxial strain affects the formation energy of such defects, we calculated the energies of anti-site pair cluster formation and the binding energies for such defects as a function of strain. Fig. 8 shows the

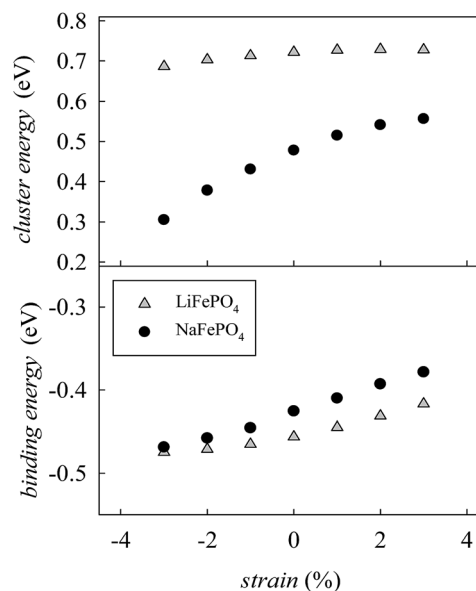


Fig. 8 Anti-site defect energies for olivine-type AFePO_4 ($\text{A} = \text{Li}^+$ or Na^+) as a function of the applied biaxial tensile/compressive strain in the *ac* plane; (upper) cluster formation energy (based on eqn (1) and (2)); (lower) binding energy.



Finally, the effect of strain on the anti-site cluster formation energy is negligible (LiFePO_4) or positive (NaFePO_4) when tensile strain is applied in the ac plane. The application of biaxial strain in directions different from the ac plane is predicted to be unfavourable for the intercalation properties of olivine-type materials since it is expected to increase the amount of anti-site defects in the system (Fig. S3-ESI†).

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