Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

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

Table S1. Buckingham pair potential and shell model parameters for $LiFePO_4$ and $NaFePO_4$.

Buckingham	**A (eV)**	**ρ (Å)**	**C (eV·Å^6)**	**Y (e)**	**K (eV·Å^{-2})**
Li^+ --O^{2-}	632.1018	0.2906	0.00	1.000	99999
Na^+--O^{2-}	560.0	0.3200	0.00	1.000	99999
Fe^{2+} --O^{2-}	1105.2409	0.3106	0.00	2.997	19.26
P^{5+} --O^{2-}	897.2648	0.3577	0.00	5.000	99999
O^{2-} -- O^{2-}	22764.30	0.1490	27.89	-2.860	65.0

Three-body	**K (eV · rad^{-2})**
O -- P -- O	1.322626

Table S2. Calculated lattice parameters for olivine $LiFePO_4$ and NaFePO4 with comparison to experimental values.

	$LiFePO_4$		**$NaFePO_4$**	
Parameter	**Expt.**	**Calc.**	**Expt.**	**Calc.**
a / Å	10.3380	10.3701	10.4109	10.3402
b / Å	6.0110	6.0136	6.2283	6.1647
c / Å	4.6950	4.6722	4.9521	4.8872

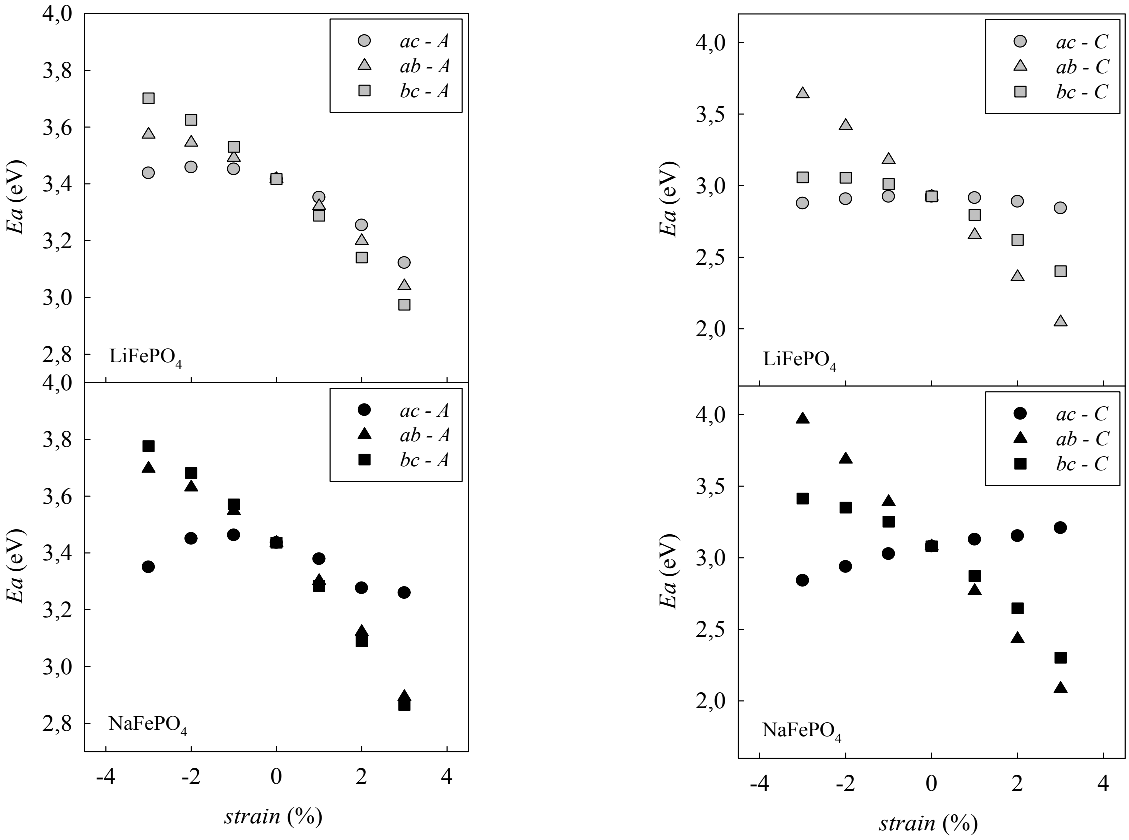

Figure S1. Change in the alkali-ion migration barrier along the [101] direction (left) and the [001] direction as a function of strain for $LiFePO_4$ (upper panel) and $NaFePO_4$ (lower panel).

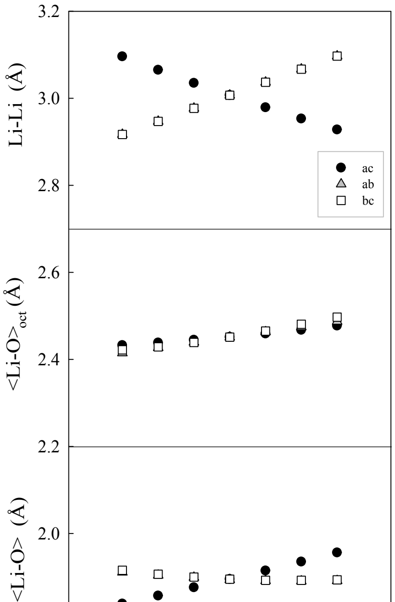

Figure S2. Structural variation as a function of the applied strain in olivine-type $LiFePO_4$ related to the migration path along the [0 1 0] direction. a) Li-Li hopping distance; b) average Li-O distance for the octahedral environment at the saddle point configuration; c) average Li-O shortest distances at the saddle point configuration.

Our results indicate that diffusion of Li^+ and Na^+ ions in the olivine system is highly favoured by the application of tensile strain in the *ac* plane. The reasons behind such changes may be correlated to structural modifications such as the ion hopping distance and the available migration space at the saddle point configuration. As shown in Figure S2a for $LiFePO_4$, 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. A decrease in ion hopping distance is expected to result in a decrease in the migration barrier. The migration barrier is usually the result of a fine interplay between the strength of the bond to be broken during the hopping of the ion, and the available migration space at the saddle point configuration. For both aspects, if the bond lengths around the migrating ion become longer, the migration barrier will be lower. Figure S2b shows that the average bond length of the LiO_6 environment increases with strain for all the three cases, which means that such parameter tends to lower the migrating barrier along with strain. In Figure S2c the trend along with strain of the two shorter Li-O distances at the saddle point configuration is shown (calculated using the relaxed positions around the migrating ion). Such distances represent the effective bottleneck for the migrating ion at the saddle point configuration.

The balance between the three parameters presented in Figure S2 results in a considerable lowering of the activation energy for Li ion migration in the case of *ac* strain, as all the three parameters have the effect to lower the migrating barrier along with strain. For the other two cases (*ab* and *bc*), the activation barrier increases, however this is to less of an extent than expected from the *ac* case, the increase in Li-Li hopping distance with strain is tempered by the other two parameters, reflecting an increase in the available space.

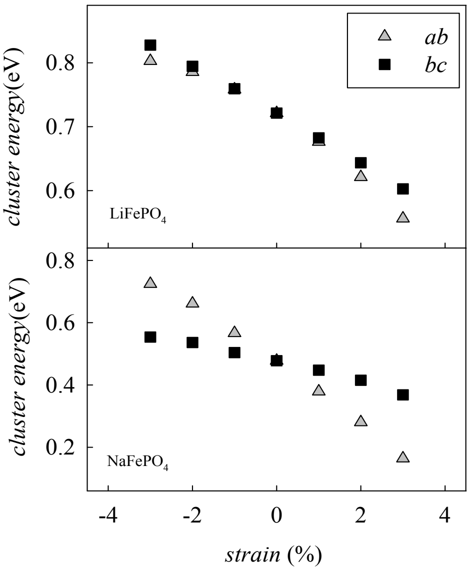

Figure S3. Formation energy for Li/Na-Fe pair clusters as a function of the applied strain in the *ab* and *bc* planes for $LiFePO_4$ (upper panel) and $NaFePO_4$ (lower panel).