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


*Supporting Information*

# $MgFeSiO_4$ as a potential cathode material for Mg-ion Batteries: defects, ion diffusion and voltage trends

Jennifer Heath, Hungru Chen and M. Saiful Islam

**Table S1. Interatomic potential parameters for $MgFeSiO_4$ a) Formal charge model (static lattice defect calculations) b) Pedone partial charge model (MD calculations)**

a) **Formal Charge** $\Phi_{ij}(r_{ij}) = A_{ij}\exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6$

| Bond type | A (eV) | ρ (Å) | C (eV Å$^6$) |
|---|---|---|---|
| Mg-O | 946.627 | 0.31813 | 0.0 |
| Fe-O | 1105.2409 | 0.3106 | 0.0 |
| Si-O | 1283.91 | 0.32052 | 10.66 |
| O-O | 22764.3 | 0.149 | 44.53 |

**Three-body:** $\Phi_{ijk} = \frac{1}{2}K_{ijk}(\theta - \theta_0)^2$

| Bond type | K (eV rad$^{-2}$) | $\Theta_0$ (deg) |
|---|---|---|
| O-Si-O | 2.09724 | 109.47 |

b) **Partial Charge**

| Bond type | $D_{ij}$ (eV) | α (Å$^{-2}$) | $r_0$ (Å) |
|---|---|---|---|
| $Mg^{1.2}$-$O^{-1.2}$ | 0.001114 | 3.429506 | 2.681360 |
| $Fe^{1.2}$-$O^{-1.2}$ | 0.078171 | 1.822638 | 2.658163 |
| $Fe^{1.8}$-$O^{-1.2}$ | 0.418981 | 1.620376 | 2.382183 |
| $Si^{2.4}$-$O^{-1.2}$ | 0.340554 | 2.006700 | 2.100000 |
| $O^{-1.2}$-$O^{-1.2}$ | 0.042395 | 1.379316 | 3.618701 |

**Table S2. Calculated and experimental lattice parameters and bond lengths for $MgFeSiO_4$.**

| Parameter | Experimental (Å)[1] | Calculated (rigid ion) (Å)[(a)] | Δ (Å) | Calculated (Pedone model) (Å)[(b)] | Δ (Å) |
|---|---|---|---|---|---|
| *a* | 4.807 | 4.854 | 0.047 | 4.863 | -0.056 |
| *b* | 10.376 | 10.336 | -0.040 | 10.125 | -0.251 |
| *c* | 6.061 | 6.026 | -0.035 | 6.005 | -0.056 |
| Mg-O | 2.168 | 2.131 | -0.037 | 2.132 | -0.036 |
| Fe-O | 2.125 | 2.140 | 0.015 | 2.148 | 0.023 |
| Si-O | 1.624 | 1.639 | 0.015 | 1.600 | -0.024 |

(a) Formal charge model best used to calculate energies of ionic defects and charge-compensation for dopant ions

(b) Pedone model is also able to reproduce the structure well (within 2.5%) and has shown previously to work particularly well for MD simulations of polyanion materials where the focus is on Li, Na or Mg transport.[2]

**Table S3. Interatomic potential parameters for trivalent dopant cations**

| Bond type | A (eV) | ρ (Å) | C (eV Å$^6$) |
|---|---|---|---|
| Al-O | 1114.9 | 0.3118 | 0.0 |
| Ga-O | 2901.12 | 0.2742 | 0.0 |
| V-O | 1790.2 | 0.3061 | 0.0 |

**Table S4. Experimental and calculated (DFT) structural parameters for $MgFeSiO_4$**

| | ***a*(Å)** | ***b*(Å)** | ***c*(Å)** |
|---|---|---|---|
| Experimental[24] | 4.8065 | 10.3759 | 6.0609 |
| Calculated | 4.7552 | 10.2621 | 6.0473 |
| Δ | -0.0513 | -0.1138 | -0.0136 |

**References:**


1. Redfern, S. A. T.; Artioli, G.; Rinaldi, R.; Henderson, C. M. B.; Knight, K. S.; Wood, B. J., Phys. Chem. Miner. 2000, 27, 630-637.
2. Deng Y, Eames C, Chotard J-N, Lalere F, Seznec V, Emge S, Pecher O, Grey C P, Masquelier C and Islam M S, J. Am. Chem. Soc., 2015, 137, 9136-9145.