

# Defect Chemistry of LiFePO<sub>4</sub> Based on Single Crystal Experiments

Ruhul Amin, Katja Weichert and Joachim Maier

Max Planck Institute for Solid State Research, Heisenbergstraße 1, D-70569 Germany

## Introduction

The clarification of defect chemistry is the prerequisite for understanding the concentrations of ionic and electronic charge carriers as well as their dependencies on control parameters such as temperature, component activities and doping concentration. While atomistic modelling on various types of point defects and point defect activation has been performed, a defect model in the sense of a thermodynamic treatment (Kröger-Vink diagrams etc.) has not yet been given. Based on accurate single crystal data obtained by extensive electrochemical analysis such a defect model is presented below (see also Ref. [1]). Migration enthalpies for ionic and electronic charge carriers as well as defect reaction energies can be extracted.

## Experimental Data

Using single crystals of LiFePO<sub>4</sub> [2], ionic and electronic conductivities were separated and measured as a function of temperature for the nominally pure material as well as for various dopants [3]. In addition the chemical diffusion coefficient was determined. The properties were measured along the different crystallographic directions. The values for b- and c-direction were similar while the transport along a-axis was significantly less. For simplicity we concentrated on data along b, c-direction.

Activation energies of electronic and ionic conductivity and lithium diffusivity for LiFePO<sub>4</sub> (Table I), LiFe<sub>0.99</sub>Si<sub>0.01</sub>PO<sub>4</sub> (Table II) and LiFe<sub>0.99</sub>Al<sub>0.01</sub>PO<sub>4</sub> (Table III) at 300 K [1]

Properties	a-axis	b-axis	c-axis
E <sub>con</sub>	0.59 eV	0.59 eV	0.55 eV
E <sub>ion</sub>	0.74 eV	0.62 eV	0.62 eV
E <sub>D</sub>	0.95 eV	0.70 eV	0.75 eV

Properties	a-axis	b-axis	c-axis
E <sub>con</sub>	0.65 eV	0.66 eV	0.66 eV
E <sub>ion</sub>		0.70 eV	0.71 eV
E <sub>D</sub>		1.01 eV	0.98 eV

Properties	a-axis	b-axis	c-axis
E <sub>con</sub>	0.43 eV	0.15 eV (assoc. reg.) 0.69* eV (non-assoc. reg.)	0.16 eV (assoc. reg.) 0.65* eV (non-assoc. reg.)
E <sub>ion</sub>		1.04 eV (assoc. reg.) 0.46 eV (non-assoc. reg.)	0.90 (assoc. reg.) 0.44 eV (non-assoc. reg.)
E <sub>D</sub>		0.47 eV (average) > 0.7 eV (assoc. reg.) < 0.3 eV (non-assoc. reg.)	0.49 eV (average) > 0.7 eV (assoc. reg.) < 0.3 eV (non-assoc. reg.)

\* asymptotical value

## Ingredients of the Defect Model

- 1) Major mobile defects (see Ref. [4]): lithium vacancies V<sub>Li</sub><sup>'</sup> and holes h<sup>\*</sup> (Fe<sub>Fe</sub><sup>3+</sup>)
- 2) Frozen-in defects: anti-site defects (Fe<sub>Li</sub><sup>•</sup>) dopants (e.g. Al<sub>Fe</sub><sup>•</sup>)
- 3) Electroneutrality equation and mass balance

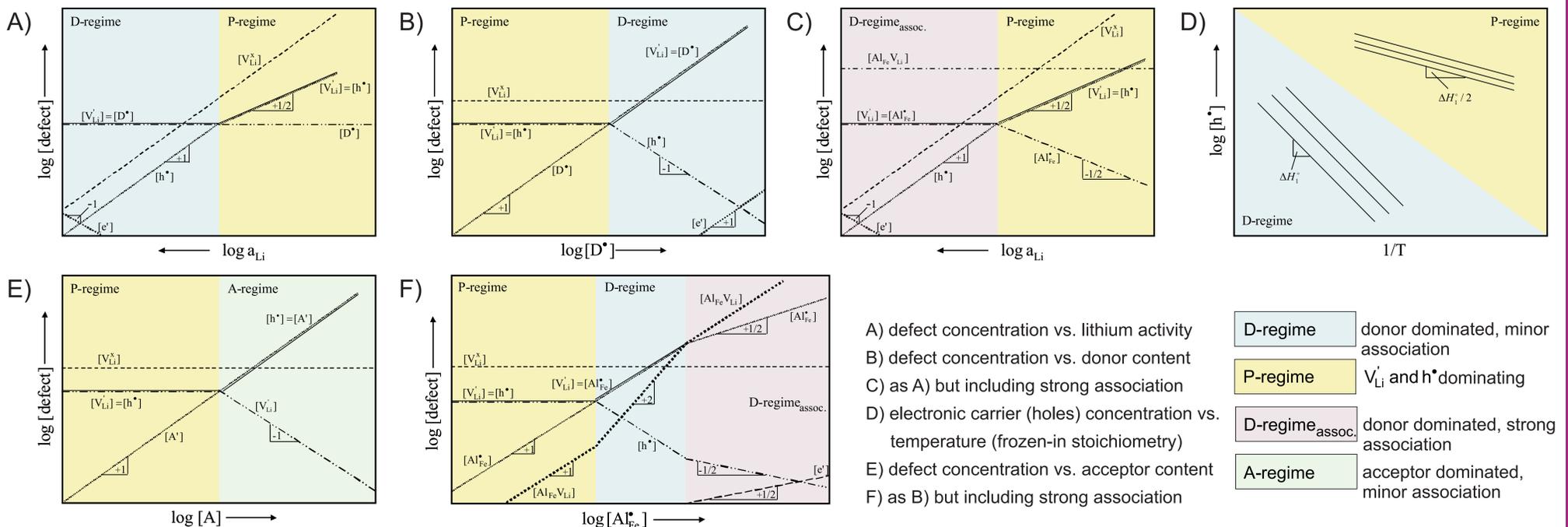
- 4) Defect interactions and equilibria: lithium in-/excorporation (reversible at high T and/or very long waiting times)  
 $V_{Li}^{\prime} + h^{\bullet} + Li_{(g)} \rightleftharpoons Li_{Li}$   
 association between V<sub>Li</sub><sup>'</sup> and h<sup>\*</sup>  
 $V_{Li}^{\prime} + h^{\bullet} \rightleftharpoons V_{Li}^{\times}$   
 association between donor defects D<sup>\*</sup> and V<sub>Li</sub><sup>'</sup>  
 $V_{Li}^{\prime} + D^{\bullet} \rightleftharpoons V_{Li}D$

$$5) \sigma_{\text{eon}} = F [h^{\bullet}] u_h, \quad \sigma_{\text{ion}} = F [V_{Li}^{\prime}] u_v$$

$$6) D = \frac{RT}{F^2} \frac{\sigma_v \sigma_h}{\sigma} \left( \frac{\chi_v}{[V_{Li}^{\prime}]} + \frac{\chi_h}{[h^{\bullet}]} \right)$$

χ<sup>-1</sup>: differential degree of trapping [5]  
 u: mobility  
 D: diffusion coefficient  
 σ: conductivity

## Brouwer- and Arrhenius-Diagrams



## Extracted Data

Table IV. Activation energies in the defect model

Properties	P-regime	D-regime
E <sub>h</sub> (T > T <sub>A</sub> )	-ΔH <sub>Li</sub> <sup>o</sup> /2 + h <sub>h</sub>	-ΔH <sub>Li</sub> + h <sub>h</sub>
E <sub>v</sub> (T > T <sub>A</sub> )	-ΔH <sub>Li</sub> <sup>o</sup> /2 + h <sub>v</sub>	h <sub>v</sub>
E <sub>h</sub> (T < T <sub>A</sub> )	-ΔH <sub>Li</sub> <sup>o</sup> /2 + h <sub>h</sub>	-ΔH <sub>Li</sub> <sup>o</sup> + h <sub>h</sub>
E <sub>v</sub> (T < T <sub>A</sub> )	-ΔH <sub>Li</sub> <sup>o</sup> /2 + h <sub>v</sub>	h <sub>v</sub>

Table V. Activation energies for Li-diffusion coefficient

Properties	D-regime <sub>non-assoc.</sub>	D-regime <sub>assoc.</sub>
E <sub>D</sub> (small δ)	ΔH <sub>Li</sub> + h <sub>v</sub>	ΔH <sub>Li</sub> - ΔH <sub>2</sub> <sup>o</sup> + h <sub>v</sub>
E <sub>D</sub> (large δ)	ΔH <sub>Li</sub> - ΔH <sub>1</sub> <sup>o</sup> + h <sub>v</sub>	ΔH <sub>Li</sub> - ΔH <sub>1</sub> <sup>o</sup> - ΔH <sub>2</sub> <sup>o</sup> /2 + h <sub>v</sub>

h<sub>h</sub>: migration energy for holes  
 h<sub>v</sub>: migration energy for Li vacancies  
 ΔH<sub>1</sub><sup>o</sup>: enthalpy of V<sub>Li</sub><sup>'</sup> and h<sup>\*</sup> association  
 ΔH<sub>2</sub><sup>o</sup>: enthalpy of V<sub>Li</sub><sup>'</sup> and D<sup>\*</sup> association  
 ΔH<sub>Li</sub>: enthalpy of Li incorporation

Table VI. Extracted values for migration and reaction energies

Properties	Values
h <sub>h</sub>	0.05 eV
h <sub>v</sub>	0.55 eV
ΔH <sub>1</sub> <sup>o</sup>	-0.60 eV
ΔH <sub>2</sub> <sup>o</sup> (Al-doped 1%)	-0.9 eV ± 0.3 eV
(ΔH <sub>Li</sub> )	(-0.5 eV ... -1 eV)

## Conclusions

- Based on extensive electrochemical investigations [3] and also taking into account atomistic defect modelling [6-8] a defect model is given that explains all our observed dependencies of ionic and electronic conductivities on temperature, doping content and Li-stoichiometry
- Migration and reaction enthalpies can be extracted (Table VI)
- While reaction enthalpies are isotropic the migration energies depend on orientations (similar in b- and c-direction, very different in a-direction)
- The defect model allows predictive material research through doping or stoichiometry control in particular in view of optimizing D<sub>Li</sub>

## References

- [1] J. Maier, R. Amin, *J. Electrochem. Soc.*, 155 (2008) A339-A344  
 [2] D. P. Chen, A. Maljuk, C. T. Lin, *J. Cryst. Growth*, 284 (2005) 86-90  
 [3] a) R. Amin, P. Balaya, J. Maier, *Electrochem. Solid-State Lett.*, 10 (2007) A13-A16; b) R. Amin, J. Maier, P. Balaya, D. P. Chen, C. T. Lin, *Solid State Ionics*, in press; c) R. Amin, C. T. Lin, J. Maier, submitted; d) R. Amin, K. Weichert, C. T. Lin, J. Maier, submitted  
 [4] R. Amin, J. Maier, *Solid State Ionics*, 178 (2008) 1831-1836  
 [5] J. Maier, *J. Am. Ceram. Soc.*, 76 (1993) 1212-1217  
 [6] D. Morgan, A. Van der Ven, G. Ceder, *Electrochem. Solid-State Lett.*, 7 (2004) A30-A32  
 [7] C. Ouyang, S. Shi, Z. Wang, X. Huang, L. Chen, *Phys. Rev. B*, 69 (2004) 104303  
 [8] M. S. Islam, D. J. Driscoll, C. A. J. Fisher, P. R. Slater, *Chem. Mater.* 17 (2005) 5085-5092