



# Heterosite $\text{FePO}_4$ : Defect Chemistry and Transport Properties

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## Introduction

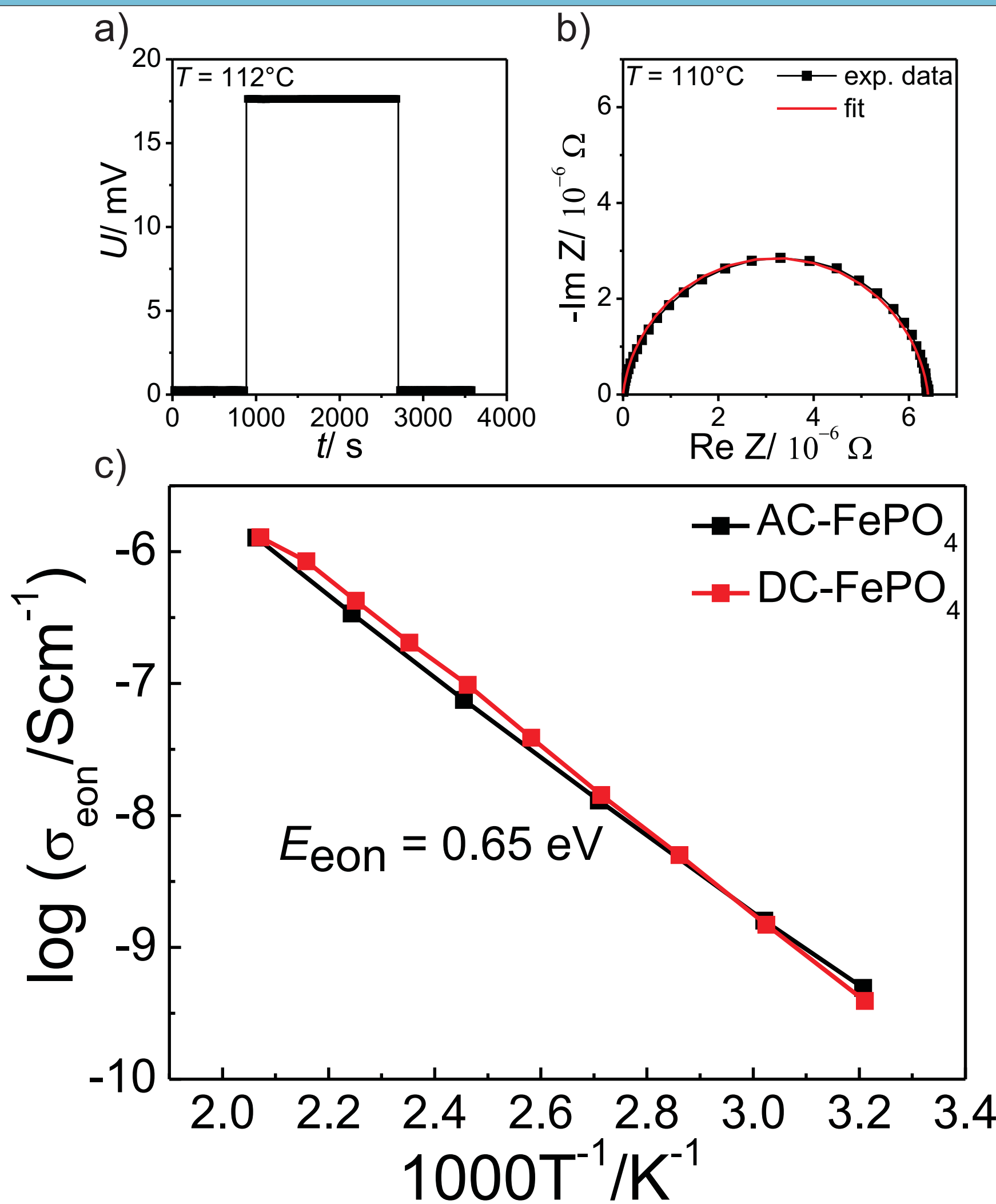
Owing to excellent performance combined with low cost, safety, non-toxicity, and environmental benignity  $\text{LiFePO}_4$  [1] has become a promising cathode material for secondary Li-ion batteries. A lot of research regarding doping, coating with conductive media, and particle size minimization has been done on this material to overcome its sluggish transport properties and improve the battery performance. That also includes a detailed study of the point defect chemistry of  $\text{LiFePO}_4$ , which led to a complex defect model that was established only recently [2]. In contrast, only little information of heterosite  $\text{FePO}_4$ , which features the same space group as  $\text{LiFePO}_4$  ( $Pnma$ ), is available.

Here we report on our investigations concerning the electronic conductivity of  $\text{FePO}_4$  from which we extract a tentative defect chemistry model for this material.

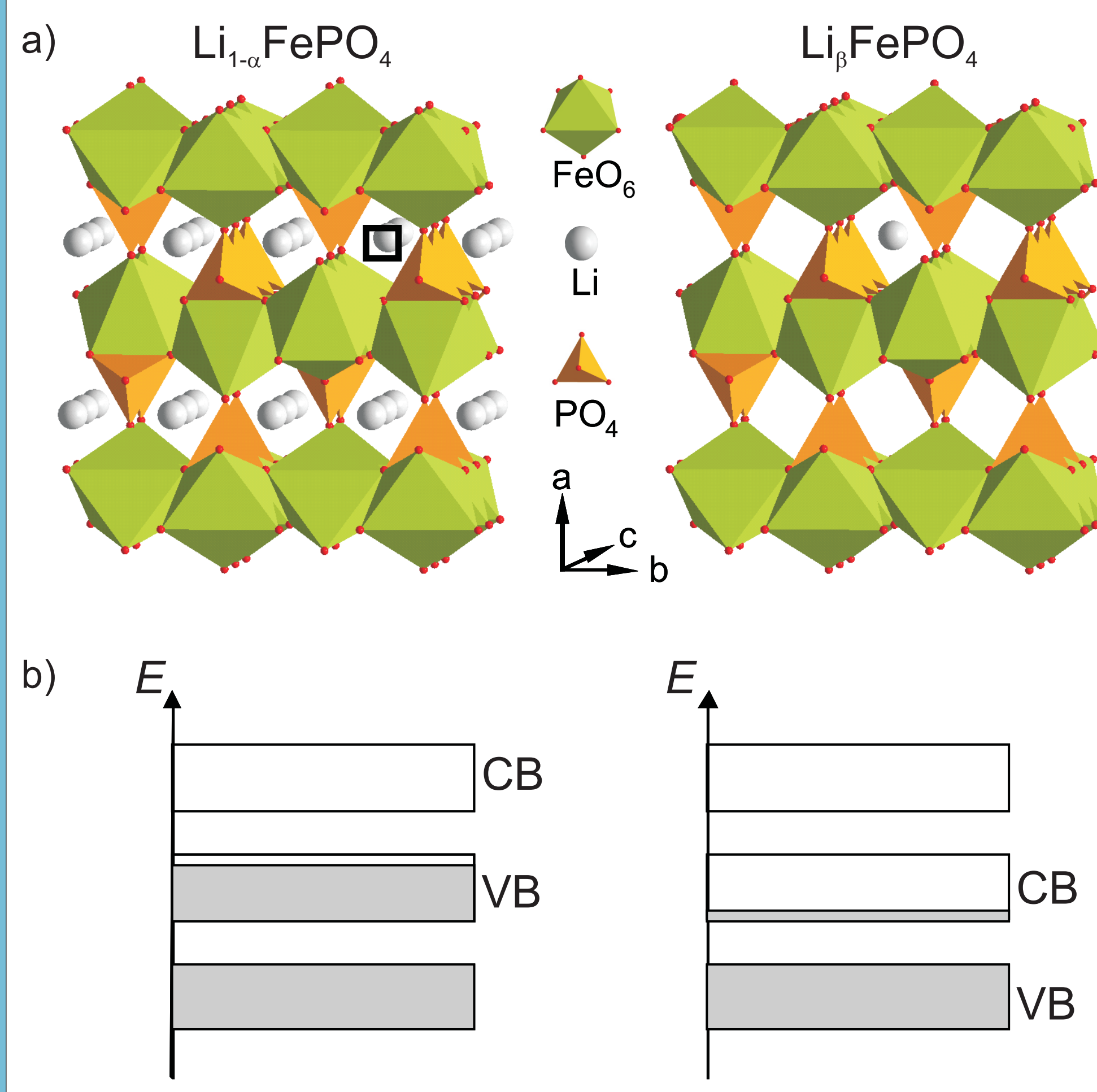
## Electronic Conductivity

The step-like voltage increase after applying a constant DC current (Fig. 1a) as well as no Warburg response in the low frequency regime of the impedance spectra (Fig. 1b) indicate a predominant electronic conductivity. Indeed, the electronic conductivity measured by polarization experiments using the ion blocking cell  $\text{Ti}/\text{FePO}_4/\text{Ti}$  is the same as the total conductivity derived from impedance measurements as shown in Fig. 1c.

Fig. 1: Representative data plots measured by a) galvanostatic DC polarization, and b) AC impedance spectroscopy (frequency range 1 MHz–0.01 Hz). c) Conductivity data derived from both techniques.



## Major defects in the $\text{LiFePO}_4/\text{FePO}_4$ System



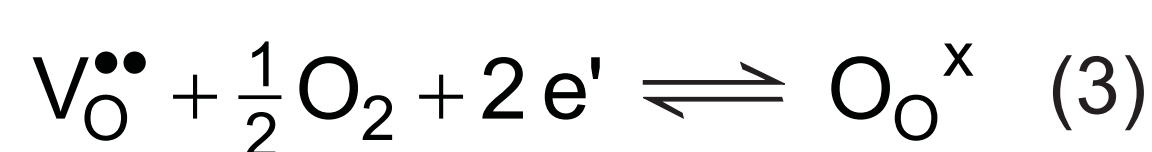
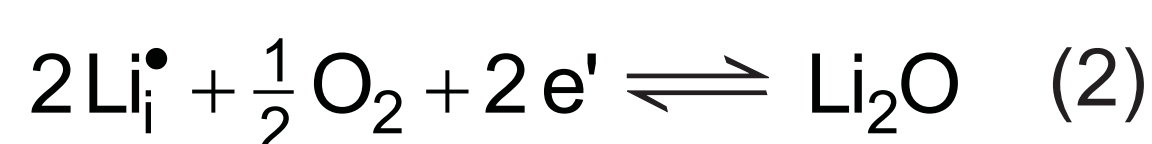
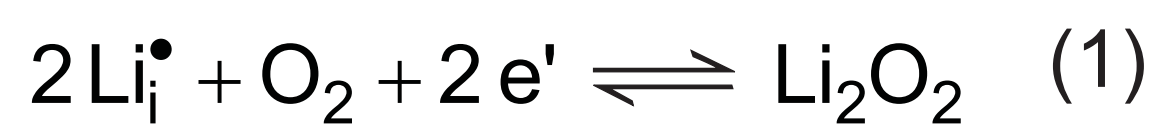
The defect chemistry of  $\text{LiFePO}_4$  is dominated by lithium vacancies and holes. [2,3] Delithiation leads to a phase transformation at which lithium saturated  $\text{FePO}_4$  is formed. Due to the altered ionic (Fig. 2a) and electronic ground states (Fig. 2b), the lithium ions in  $\text{FePO}_4$  have to be treated as interstitial defects which are compensated by excess electrons.

Fig. 2: a) Sketch of the crystal structure of Li deficient  $\text{LiFePO}_4$  and Li saturated  $\text{FePO}_4$ . b) Band structure showing the presence of holes in the valence band (VB) of  $\text{LiFePO}_4$  and of electrons in the conduction band (CB) of  $\text{FePO}_4$ , respectively.

## $\text{O}_2$ Partial Pressure Dependence

Electronic conductivity is decreased with increasing oxygen partial pressure. Since the reaction with oxygen (independent of the exact mechanism) consumes electrons, it can be concluded that the conductivity of  $\text{FePO}_4$  is  $n$ -type.

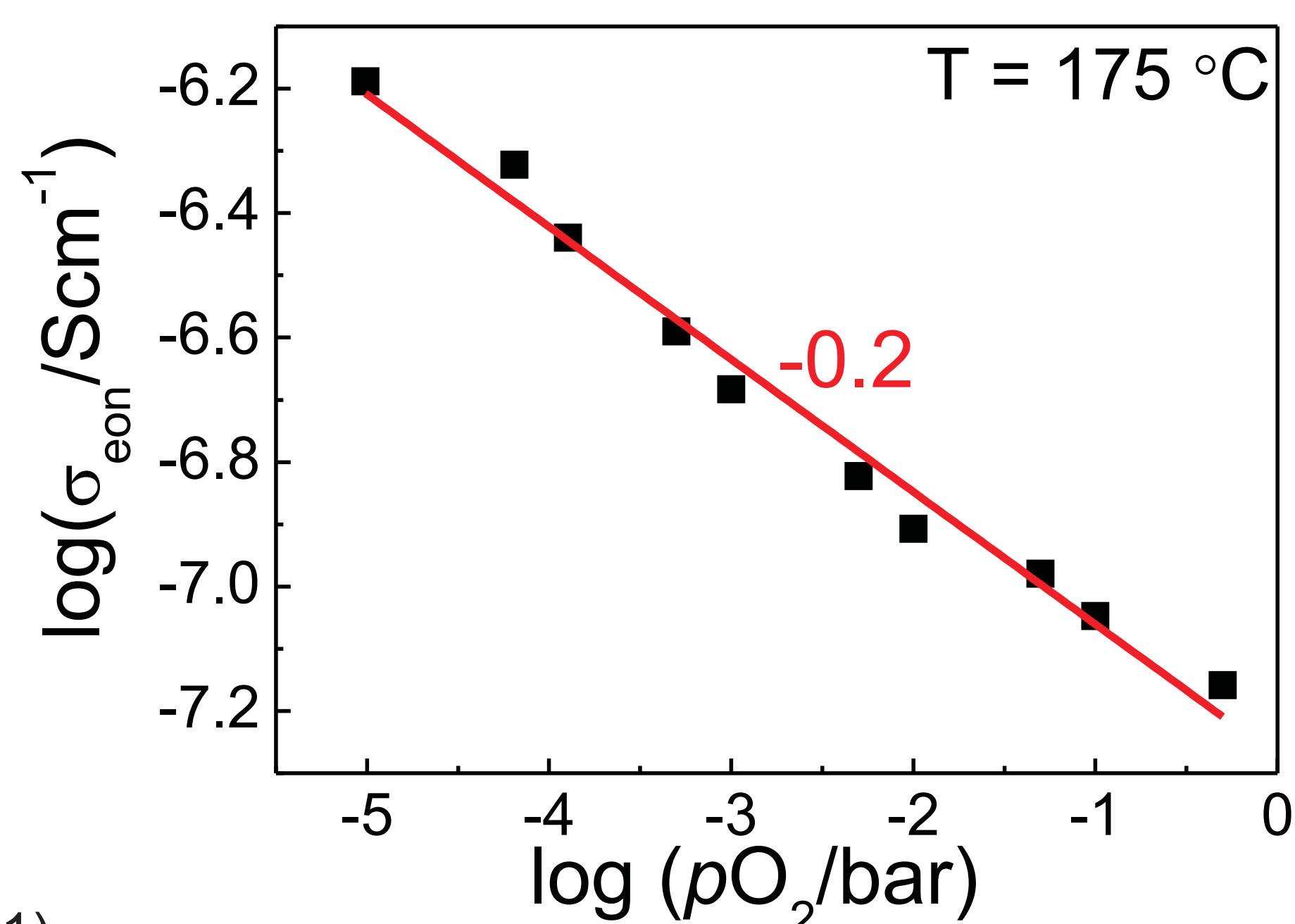
For the reaction with oxygen lithium interstitials ( $\text{Li}_i^\bullet$ ) (Eq. 1,2) or oxygen vacancies ( $\text{V}_\text{O}^\bullet$ ) (Eq. 2) can be considered, e.g.:



$$K_1 = \frac{[\text{Li}_2\text{O}_2]}{[\text{Li}_i^\bullet]^2 [\text{pO}_2] [e^-]^2}$$

$$[\text{Li}_i^\bullet] = [e^-]$$

$$\frac{d \ln [e^-]}{d \ln [\text{pO}_2]} \propto -\frac{1}{4}$$



Although the existence of oxygen vacancies at least as minor defects cannot be ruled out, the almost identical activation energies of nominally pure  $\text{FePO}_4$  and its solid solutions (see on the right-hand side of the poster) suggest that lithium interstitials and electrons are the main defects.

The theoretical slope amounts to -1/4 and -1/8 considering the formation of  $\text{Li}_2\text{O}_2$  and  $\text{Li}_2\text{O}$  respectively. The experimental slope of 0.2 is in good agreement with the value of -1/4.

## Experimental Data

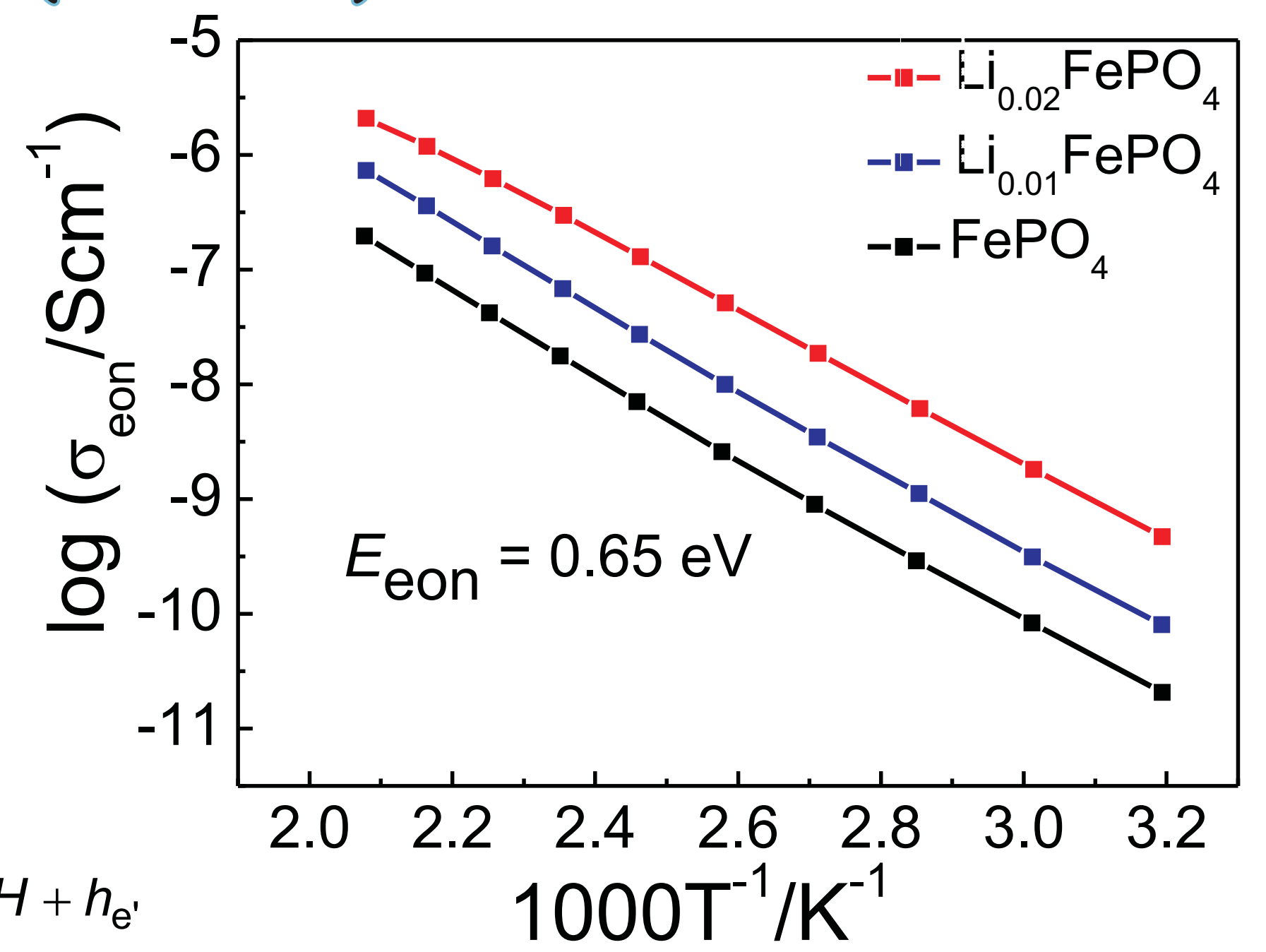
Polycrystalline  $\text{LiFePO}_4$  was chemically delithiated with  $\text{NO}_2\text{BF}_4$  in acetonitrile solution according to the reaction:  $\text{LiFePO}_4 + \text{NO}_2\text{BF}_4 \rightleftharpoons \text{FePO}_4 + \text{NO}_2 + \text{LiBF}_4$ . The resulting heterosite  $\text{FePO}_4$  contains a residual Li content of ca. 0.03 wt% corresponding to the formula  $\text{Li}_{0.007}\text{FePO}_4$ . Solid solutions  $\text{Li}_x\text{FePO}_4$  with  $x \leq 0.02$  were prepared by partial reduction using stoichiometric amounts of  $\text{LiI}$  in acetonitrile solution. The electronic conductivity was determined using a symmetric ion blocking cell with titanium or platinum electrodes (e.g.,  $\text{Ti}/\text{FePO}_4/\text{Ti}$ ). Impedance as well as DC polarization measurements have been performed.

## Solid Solutions $\text{Li}_x\text{FePO}_4$ ( $x \leq 0.02$ )

In the solid solutions  $\text{Li}_x\text{FePO}_4$  ( $x \leq 0.02$ ) the electronic conductivity increases with increasing Li content due to the formation of lithium interstitials ( $\text{Li}_i^\bullet$ ) and electrons ( $e^-$ ) corresponds to  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . Association (trapping) of these defects is assumed to be responsible for the  $T$  dependence of the electronic conductivity.



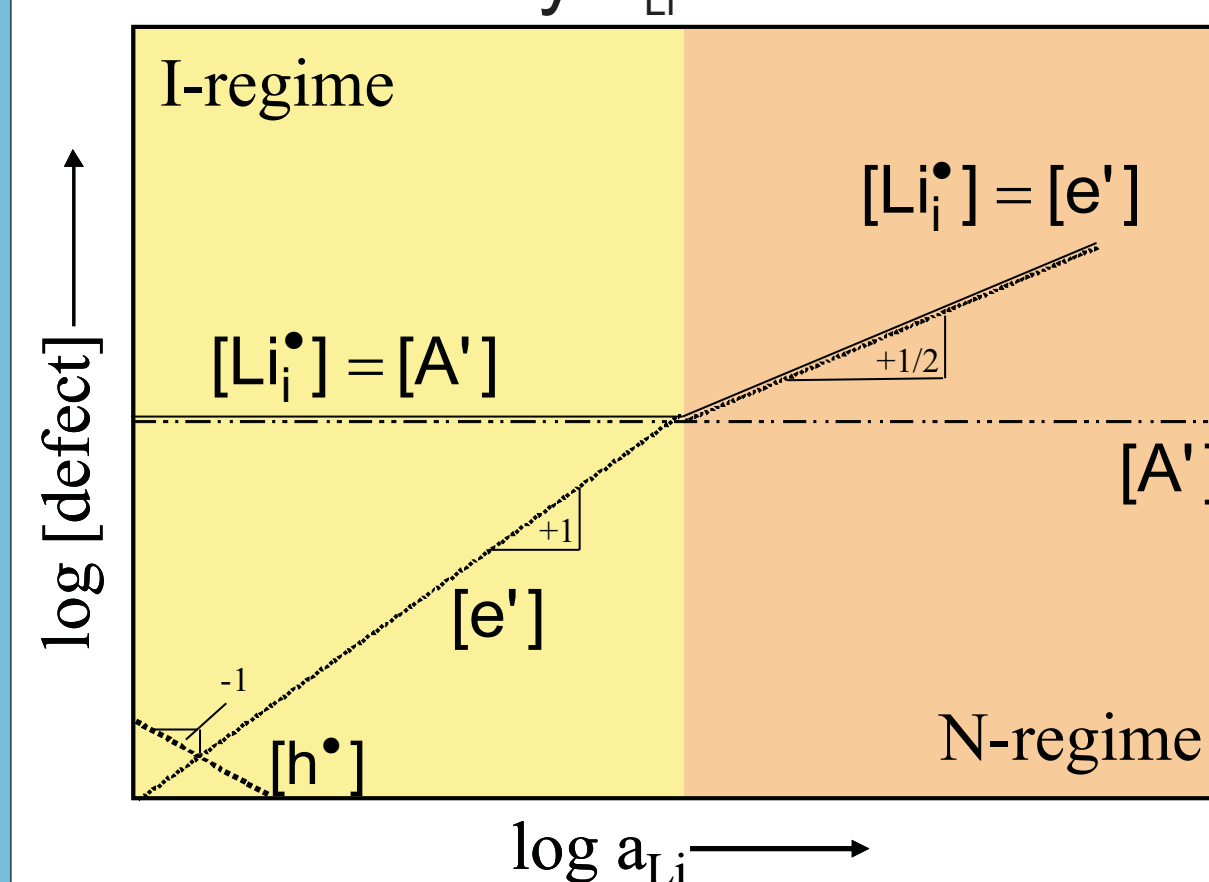
$$K = \frac{[\text{Li}_i^x]}{[\text{Li}_i^\bullet] [e^-]} \quad h_{e^-} \approx 0.2 \text{ eV} [4]$$



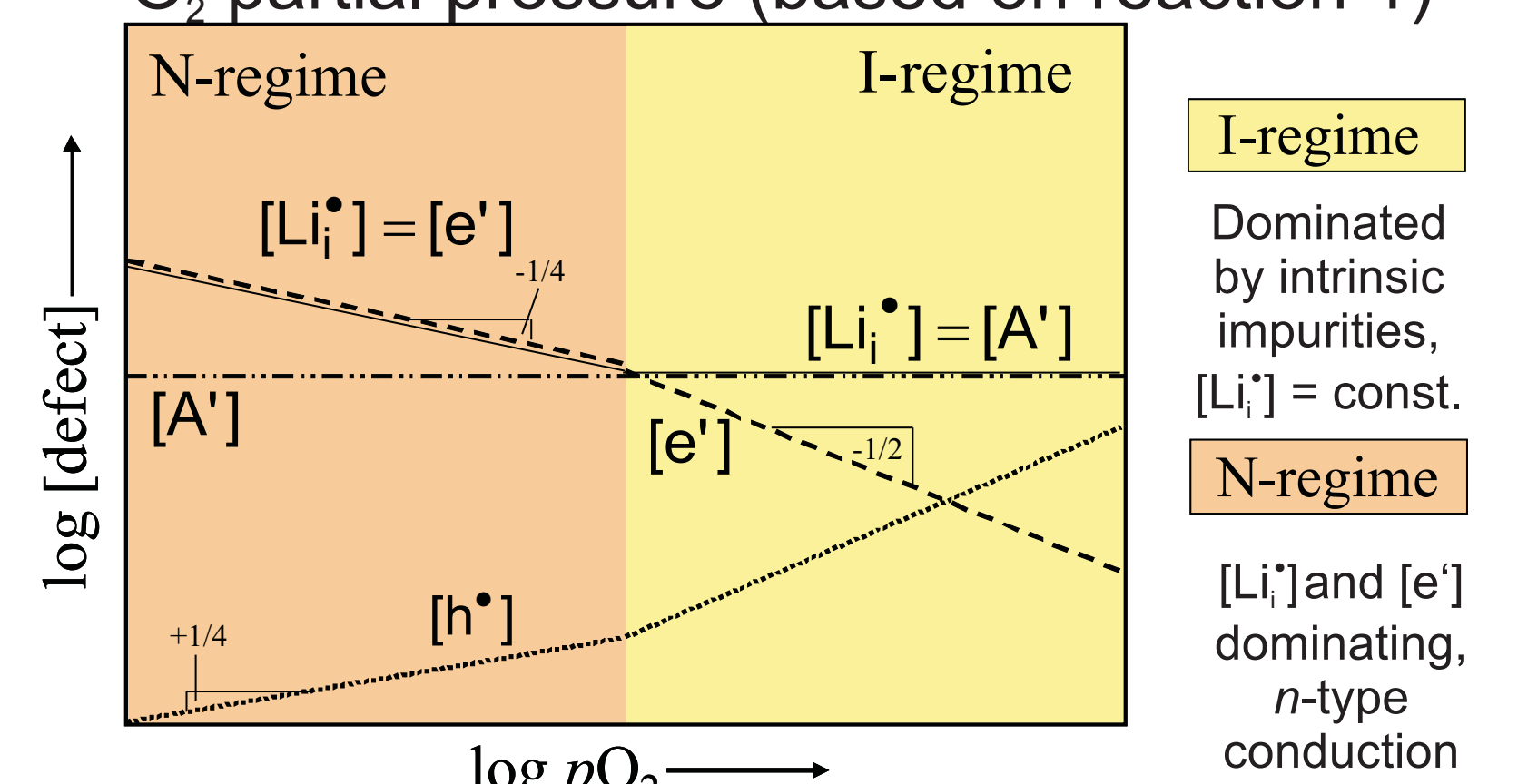
$$\Delta H \approx -1 \text{ eV}$$

## Kröger-Vink Diagrams

Dependence of defect concentration on Li activity  $a_{\text{Li}}$



Dependence of defect concentration on  $\text{O}_2$  partial pressure (based on reaction 1)



## Conclusions

- ✦  $\text{FePO}_4$  exhibits a predominant electronic conductivity which is  $n$ -type.
- ✦ The major defects in chemically delithiated  $\text{FePO}_4$  are lithium interstitials and electrons.
- ✦ An association enthalpy of -1 eV could be extracted (assuming a migration energy of electrons of 0.2 eV [4]).

## References

- [1] A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* **144** (1997) A1188  
[2] J. Maier, R. Amin, *J. Electrochem. Soc.* **155** (2008) A339

- [3] R. Amin, J. Maier, *Solid State Ionics* **178** (2008), 1831  
[4] T. Maxisch, F. Zhou and G. Ceder, *Phys. Rev. B*, **73** (2006) 104301