

Surface adsorption and disordering in LiFePO₄ based battery cathodes

Archana Kayyar,¹ Haijun Qian,² and Jian Luo^{1,3,a)}

¹School of Materials Science and Engineering, Clemson University, Clemson, South Carolina 29634, USA

²Electron Microscope Facility, Clemson University, Anderson, South Carolina 29625, USA

³Center for Optical Materials Science and Engineering Technology, Clemson University, Anderson, South Carolina 29625, USA

(Received 20 September 2009; accepted 10 November 2009; published online 3 December 2009)

A recent study [Kang and Ceder, *Nature (London)* **458**, 190 (2009)] suggested that a Li₄P₂O₇-like “fast ion-conducting surface phase” could form on the surfaces of LiFePO₄ particles, enabling ultrafast discharging of Li-ion batteries. We demonstrate that these nanoscale surface films exhibit a self-selecting or “equilibrium” thickness, akin to those observed in simpler binary oxides [Luo and Chiang, *Annu. Rev. Mater. Res.* **38**, 227 (2008)]. These observations can be interpreted as a case of coupled prewetting and premelting. Similar nanoscale intergranular films are also observed. These nanoscale interfacial phenomena can be utilized to tailor nanoparticles for battery and many other applications. © 2009 American Institute of Physics. [doi:10.1063/1.3270106]

Olivine LiFePO₄ is a promising cathode material to enable the commercial applications of Li-ion batteries in electric or hybrid vehicles, because it is cheap and safe. However, the application of LiFePO₄ is hindered by its low conductivity.¹ Efforts have been made to increase its conductivity by carbon coating,² aliovalent doping³ and reducing particle size.⁴ In March 2009, Kang and Ceder⁵ reported that the formation of a Li₄P₂O₇-like “fast ion-conducting surface phase” in “off-stoichiometric” LiFePO₄ could help to achieve ultrafast discharging of a full battery in 10–20 s. Although this study⁵ led to a great excitement, it also resulted in a hot debate.^{6,7} A technical comment⁶ noted: “There is no reason to believe that Li₄P₂O₇ impurity will coat the (LiFePO₄) particles. Instead, impurities usually form nanoparticles that stick on the surfaces.”

Thermodynamically, a β phase may spontaneously coat on an α particle if replacing a “clean” α surface (γ_α⁽⁰⁾) with a β surface (γ_β) and an α-β interface (γ_{αβ}) lowers the total interfacial energies

$$\Delta\gamma \equiv \gamma_{\beta} + \gamma_{\alpha\beta} - \gamma_{\alpha}^{(0)} < 0. \quad (1)$$

Several relevant nanoscale wetting phenomena should be recognized.^{8,9} First, a nanoscale metastable β-like phase of thickness *h* can be thermodynamically stabilized on the α surface if

$$-\Delta\gamma > \Delta G_{\text{vol}} \cdot h, \quad (2)$$

where Δ*G*_{vol} is the volumetric free energy penalty to form the metastable β phase. Second, if the surface β film is nanometer-thick, short-range, vdW dispersion, electrostatic and other interfacial interactions may arise.^{8,9} In a phenomenological model, the excess surface free energy can be written as^{8,9}

$$G^x(h) = \gamma_{\beta} + \gamma_{\alpha\beta} + \Delta G_{\text{vol}} \cdot h + \sigma_{\text{short-range}}(h) + \sigma_{\text{vdW}}(h) + \sigma_{\text{elec}}(h) + \dots \quad (3)$$

Consequently, this β-like film will adopt an “equilibrium” thickness (*h*_{EQ}) that minimizes Eq. (3) [producing γ_α

≡ *G*^{*x*}(*h*_{EQ}) < γ_α⁽⁰⁾]. Finally, the adjacent α phase can significantly modify the structure and properties of this nanoscale β-like film.

The above nanoscale wetting phenomena are well known for aqueous, organic and low-temperature systems.¹⁰ Recently, analogous phenomena have been discovered for oxide surfaces at high temperatures. Specifically, “equilibrium-thickness” surficial amorphous films (SAFs) (multilayer adsorbates) have been observed for Bi₂O₃ on ZnO, V₂O₅ (VO_{*x*}) on TiO₂ and other binary oxides.^{8,11–13} The thermodynamic stability of these liquidlike SAFs can be markedly different from the bulk liquid or glass phase, and their presence often enhances surface transport. Most recently, Tang *et al.*¹⁴ modeled LiMPO₄ (*M*=Fe, Mn, Co, and Ni) olivines and suggested that SAFs can form and affect battery properties. In this letter, we demonstrate that the fast ion-conducting surface phase reported by Kang and Ceder are indeed equilibrium-thickness SAFs, and we further discuss the significant opportunities of utilizing these nanoscale interfacial phenomena to tailor battery materials.

Following Kang and Ceder’s recipe,⁵ we synthesized LiFe_{1–2*y*}P_{1–*y*}O_{4–δ} (*y*=0, 0.05, 0.1, and 0.2) by ball milling appropriate amounts of Li₂CO₃, FeC₂O₄·2H₂O, and NH₄H₂PO₄ using acetone as a medium. The mixtures were calcined at 350 °C for 10 h and then isothermally annealed at desired temperatures in flowing argon. X-ray diffraction (XRD) analysis (using a Scintag diffractometer) identified a secondary crystalline Li₄P₂O₇ phase in specimens with *y* = 0.1 and 0.2 (but not in those with *y* = 0 and 0.05), supporting that LiFe_{1–2*y*}P_{1–*y*}O_{4–δ} is broken into a two-phase mixture of (1–2*y*)LiFePO₄ and (0.5*y*)Li₄P₂O₇ (Ref. 6) and some Li₄P₂O₇ may be present as a (bulk or surface) glass phase. The particle surfaces were characterized by high-resolution transmission electron microscopy (HRTEM) using a Hitachi 9500 microscope. Minimum exposure was used during HRTEM to avoid beam damage. Water-free solvents were used in the synthesis, and specimens were kept in a desiccator and characterized in <48 h to minimize the moisture attacks of particle surfaces.

In stoichiometric LiFePO₄ equilibrated at 600 °C, 0.6–1 nm thick SAFs were observed on seven out of ten sur-

^{a)}Author to whom correspondence should be addressed. Electronic addresses: jl原因@alum.mit.edu and jianluo@clemson.edu.

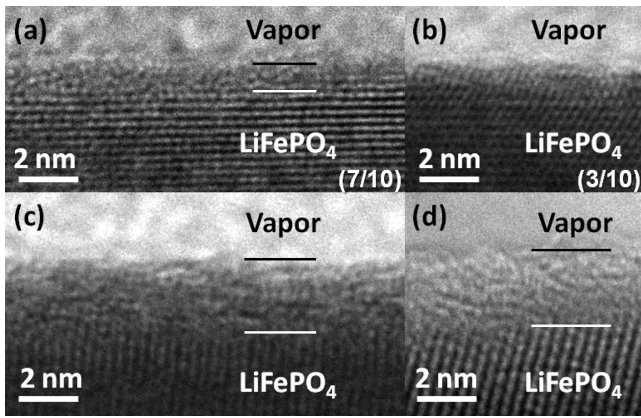


FIG. 1. Representative HRTEM images of the surfaces of [(a) and (b)] LiFePO_4 and [(c) and (d)] $\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$ specimens (annealed at 600°C for 10 h). All nanoparticles were placed on carbon coated TEM grids.

faces that could be clearly imaged [Fig. 1(a)]. The other three surfaces appeared to be clean and crystalline [with $< \sim 0.3$ nm films; Fig. 1(b)]. In the $\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$ specimen (with nominally 5.2 vol % $\text{Li}_4\text{P}_2\text{O}_7$), nanoscale SAFs were observed on all 16 surfaces where clear HRTEM images could be taken [Figs. 1(c) and 1(d)]; the average film thickness is 2.37 nm, being significantly greater than that for stoichiometric LiFePO_4 (Fig. 2). When the nominal $\text{Li}_4\text{P}_2\text{O}_7$ volume fraction was further increased, the film thickness appeared to level off (Fig. 2); this indicates that these SAFs exhibit self-limiting (equilibrium) thickness, whereas some kinetic limitations to equilibration must exist.

Figure 3 demonstrates reversible temperature dependence to film thickness. In a specimen annealed at 400°C , the average film thickness was found to be 1.12 nm. When the annealing temperature was increased to 600°C , the measured average thickness was more than doubled to 2.37 nm. The third specimen was first equilibrated at 600°C ; subsequently, the temperature was lowered to 400°C for another 10 h annealing to approach equilibration from a higher temperature; consequently, the average thickness reduced to 1.69 nm

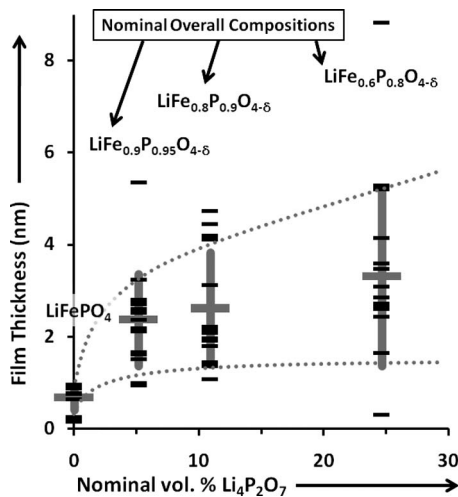


FIG. 2. Measured film thickness versus the nominal vol % of the secondary $\text{Li}_4\text{P}_2\text{O}_7$ phase. Each black bar represents one measurement of an independent surface (which is an average thickness along that specific surface). The wider gray bars are the mean thicknesses for films on multiple independent surfaces of different particles, and the error bars represent \pm one standard deviations. These specimens were annealed at 600°C for 10 h.

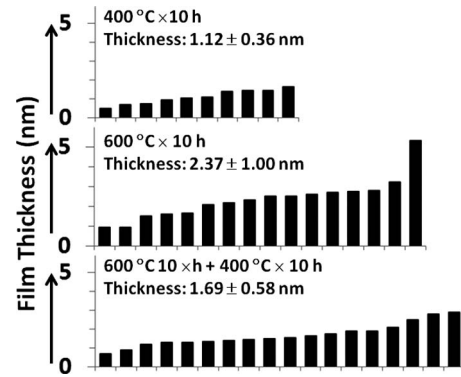


FIG. 3. Reversible temperature dependence to film thickness for specimens with a nominal composition of $\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$. Each bar represents one measured film thickness. The heat treatment conditions are labeled.

nm. Furthermore, nanodrops were observed in $\sim 10\%$ of (3 out of 25) surfaces, which may form from “bead up” of the initially thicker SAFs. One example is shown in Fig. 4(b). Such nanodrops appear to be characteristic for specimens where equilibration was approached from a higher temperature. While hysteresis effects clearly exist, Fig. 3 further supports that these SAFs exhibit an equilibrium (thermodynamically determined) thickness.

The observation of relatively uniform SAFs on virtually all surfaces resolves the controversy about whether $\text{Li}_4\text{P}_2\text{O}_7$ phase can coat the LiFePO_4 particles,^{6,7} and it implies that Eq. (1) holds ($\Delta\gamma < 0$). The existence of an equilibrium (self-limiting) thickness further indicates that this is not a case of complete wetting. Since the crystalline $\text{Li}_4\text{P}_2\text{O}_7$ phase was detected by XRD, the film thickness is likely limited by the volumetric free energy term $\Delta G_{\text{vol}} \cdot h$ in Eq. (3).⁸ This is further supported by the observation (Fig. 3) that the film is thinner at a lower temperature with a greater ΔG_{vol} .^{8,15}

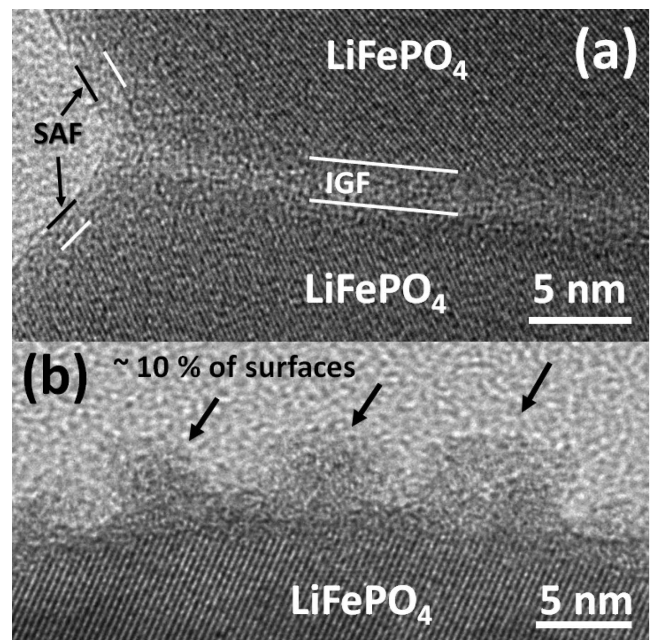


FIG. 4. Two selected HRTEM images of particle surfaces in a specimen with a nominal composition of $\text{LiFe}_{0.9}\text{P}_{0.95}\text{O}_{4-\delta}$ that was annealed at 600°C for 10 h and then 400°C for 10 h. The backgrounds are from the carbon-coated TEM grids.

These $\text{Li}_4\text{P}_2\text{O}_7$ -like SAFs were also found in the stoichiometric LiFePO_4 specimen without the presence of a bulk $\text{Li}_4\text{P}_2\text{O}_7$ phase [Fig. 1(a)]. This provokes an analogy to the phenomenon of prewetting,¹⁶ which refers to nanoscale wetting occurring when the phase that does the wetting ($\text{Li}_4\text{P}_2\text{O}_7$) is not yet a stable bulk phase [if Eq. (2) holds]. The film thickness increases with reducing Fe activity, but it levels off after a secondary bulk $\text{Li}_4\text{P}_2\text{O}_7$ phase precipitates (Fig. 2), showing that the equilibrium thickness depends on the chemical potential instead of the overall phase composition. These observations can be explained as a case of coupled surface prewetting and premelting from a generalized Cahn model.¹⁵

These $\text{Li}_4\text{P}_2\text{O}_7$ -like SAFs on LiFePO_4 (a complex oxide system) are akin to those observed in simpler binary oxides such as Bi_2O_3 on ZnO and V_2O_5 on TiO_2 ,^{8,11–13} whereas some subtle differences exist. In simple binary oxides, SAFs generally do not form without the presence of the “impurity,” and they are alternatively interpreted as a class of multilayer adsorbates.^{8,9} Multilayer adsorption of $\text{Li}_4\text{P}_2\text{O}_7$ on LiFePO_4 can be regarded as “negative” adsorption (or depletion) of the Fe, P, and O species. Furthermore, these $\text{Li}_4\text{P}_2\text{O}_7$ -like SAFs must contain some Fe;⁵ in general, the average composition of liquidlike SAFs is markedly different from that of the associated bulk liquid or glass.^{8,12}

Finally, we also found nanoscale intergranular films (IGFs, which are the grain-boundary counterparts to SAFs) between LiFePO_4 particles [Fig. 4(a)], which can serve as an additional fast ion-conducting “interfacial phase.” Similar IGFs have been widely observed in ceramics⁹ as well as some metals,^{9,17} where they often control the transport kinetics and properties.⁹ A prior work also showed that the formation of metal phosphide intergranular networks can enhance the LiFePO_4 conductivity.¹⁸

To conclude, we have demonstrated that the fast ion-conducting surface phase on LiFePO_4 particles observed by Kang and Ceder⁵ are SAFs of self-selecting thickness. Similar IGFs have also been observed. Although this result cannot fully prove that ultrafast charging and discharging can be commercially realized (because several other technical issues are still in debate^{6,7}), the presence of nanoscale SAFs (and IGFs) of self-selecting thickness does offer great opportunities to tailor LiFePO_4 and other battery materials. First, it is well known that $\text{Li}_4\text{P}_2\text{O}_7$ glass is a good Li^+ ion conductor⁵ and the anticipated layering structures in SAFs may further increase the surface transport rates. Second, these SAFs and IGFs should control the sintering and coarsening of nanoparticles during heat treatments,^{8,9} which are also of importance for optimizing battery cathode fabrication.¹⁹ Third, the thickness, structure and physical properties of these nanoscale SAFs and IGFs can be systematically tailored by changing the processing temperature and using additional metal

dopants,^{8,9,11–13} thereby offering great opportunities for further optimization. Finally, Dillon *et al.* recently identified multiple “interface phases” (termed as “complexions”).^{20–22} These SAFs may be considered as the free-surface counterparts to the Dillon–Harmer complexion V (and complete wetting surface films will be complexion VI).^{20,21} Other surface complexions may also exist and critically affect the properties of battery materials. Moreover, first-order surface transitions may occur and result in drastic changes in transport rates and properties.^{13,15,21,23} All these nanoscale interfacial phenomena can be intentionally utilized to tailor the (electronic, ionic and other) properties, thermodynamic stability and fabrication protocols of oxide nanoparticles for battery (and many other) applications.²²

This work is supported by an NSF CAREER award (Contract No. DMR-0448879).

¹J. B. Goodenough, *J. Power Sources* **174**, 996 (2007).

²N. Ravet, Y. Chouinard, J. F. Magnan, S. Besner, M. Gauthier, and M. Armand, *J. Power Sources* **97–98**, 503 (2001).

³S. Y. Chung, J. T. Bloking, and Y. M. Chiang, *Nature Mater.* **1**, 123 (2002).

⁴M. Gaberscek, R. Dominko, and J. Jamnik, *Electrochem. Commun.* **9**, 2778 (2007).

⁵B. Kang and G. Ceder, *Nature (London)* **458**, 190 (2009).

⁶K. Zaghib, J. B. Goodenough, A. Mauger, and C. Julien, *J. Power Sources* **194**, 1021 (2009).

⁷G. Ceder and B. Kang, *J. Power Sources* **194**, 1024 (2009).

⁸J. Luo and Y.-M. Chiang, *Annu. Rev. Mater. Res.* **38**, 227 (2008).

⁹J. Luo, *Crit. Rev. Solid State Mater. Sci.* **32**, 67 (2007).

¹⁰D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley, *Rev. Mod. Phys.* **81**, 739 (2009).

¹¹J. Luo and Y.-M. Chiang, *J. Eur. Ceram. Soc.* **19**, 697 (1999); J. Luo, Y.-M. Chiang, and R. M. Cannon, *Langmuir* **21**, 7358 (2005); H. J. Qian and J. Luo, *Appl. Phys. Lett.* **91**, 061909 (2007); H. J. Qian, J. Luo, and Y. M. Chiang, *Acta Mater.* **56**, 862 (2008).

¹²J. Luo and Y.-M. Chiang, *Acta Mater.* **48**, 4501 (2000).

¹³H. Qian and J. Luo, *Acta Mater.* **56**, 4702 (2008).

¹⁴M. Tang, H. Y. Huang, N. Meethong, Y. H. Kao, W. C. Carter, and Y. M. Chiang, *Chem. Mater.* **21**, 1557 (2009).

¹⁵J. Luo, M. Tang, R. M. Cannon, W. C. Carter, and Y.-M. Chiang, *Mater. Sci. Eng., A* **422**, 19 (2006).

¹⁶J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977).

¹⁷V. K. Gupta, D. H. Yoon, H. M. Meyer III, and J. Luo, *Acta Mater.* **55**, 3131 (2007); X. Shi and J. Luo, *Appl. Phys. Lett.* **94**, 251908 (2009).

¹⁸P. S. Herle, B. Ellis, N. Coombs, and L. F. Nazar, *Nature Mater.* **3**, 147 (2004).

¹⁹A. Yamada, S. C. Chung, and K. Hinokuma, *J. Electrochem. Soc.* **148**, A224 (2001).

²⁰S. J. Dillon, M. Tang, W. C. Carter, and M. P. Harmer, *Acta Mater.* **55**, 6208 (2007); S. J. Dillon and M. P. Harmer, *J. Eur. Ceram. Soc.* **28**, 1485 (2008); *J. Am. Ceram. Soc.* **91**, 2314 (2008); **91**, 2304 (2008); S. J. Dillon, M. P. Harmer, and J. Luo, *JOM* **61**(12), 38 (2009).

²¹J. Luo, *Appl. Phys. Lett.* **95**, 071911 (2009).

²²J. Luo, *Curr. Opin. Solid State Mater. Sci.* **12**, 81 (2008).

²³M. Tang, W. C. Carter, and R. M. Cannon, *Phys. Rev. Lett.* **97**, 075502 (2006).