Fast interfaces

Ganapathy, Swapna; Wagemaker, Marnix

DOI
10.1038/s41560-020-0631-8

Publication date
2020

Document Version
Accepted author manuscript

Published in
Nature Energy

Citation (APA)
Ganapathy, S., & Wagemaker, M. (2020). Fast interfaces. *Nature Energy*, *5*(6), 424-425.
https://doi.org/10.1038/s41560-020-0631-8

Li-ion Batteries

Fast Interfaces

$Li_4Ti_5O_{12}$ is a commonly used negative electrode material, but the origin of its fast rate capability has puzzled scientists for decades. Now, a facile Li-ion transport route featuring metastable intermediates is revealed to rationalize the fast-charging kinetics.

Swapna Ganapathy and Marnix Wagemaker*

*m.wagemaker@tudelft.nl

Spurred by unrelenting demand, Li-ion batteries face the challenge of how to get more energy and power in combination with a high efficiency and a long cycle life. A higher energy density would allow a longer driving range per charge and a higher power density would allow a faster re-charge. The defective spinel $Li_4Ti_5O_{12}$ is a fast-charging negative electrode material, already used in commercial Li-ion batteries. Upon Li-ion insertion it transforms to the rocksalt $Li_7Ti_5O_{12}$ phase with almost no volume change. In general, the maximum rate at which an electrode material can be charged largely depends on Li mobility and phase transformation mechanisms in the electrode[1]. The $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ end member phases, however, both possess poor ionic conductivity, which makes the high rate performance exhibited by this material counterintuitive. Despite much effort to understand the fast-rate capability, the secret to its excellent performance – especially under non-equilibrium operating conditions – has remained elusive. Writing in *Science*, Feng Wang, Gerbrand Ceder and co-workers[2] now report that the facile Li-ion transport in $L_4Ti_5O_{12}$ is mediated by metastable intermediates, with low energy-barriers for Li-ion transport, explaining the high-rate performance..

In the defective spinel $Li_4Ti_5O_{12}$, the tetrahedral 8a sites are fully occupied with Li, and the octahedral 16d sites are occupied with Li and Ti (Fig. 1a). On charge, Li-ions are inserted on the octahedral 16c sites, accompanied by a migration of Li-ions from the 8a to 16c sites, resulting in the rocksalt $Li_7Ti_5O_{12}$ (Fig. 1b). This transition from 8a occupied to 16c occupied domains represents a two-phase transformation, which is expected to result in sluggish Li-ion transport because of the poor ion conductivity of the end-member phases. In contrast, a solid solution transformation that entails a homogeneous change in Li-ion occupancy is generally observed for fast-charging materials as the abundance of unoccupied sites allows facile ion transport.

It has been suggested that on (dis)charge, intermediate interfacial $Li_{4+x}Ti_5O_{12}$ ($0 \geq x \geq 3$) states (Fig. 1d) are formed, where Li occupies adjacent face-sharing 8a and 16c polyhedra (Fig. 1e), either as a homogenous solid-solution[3] or as a mixture of phase-separated nano-domains[4,5], explaining its surprising performance. However, experimental verification of these hypotheses by monitoring the interface states at non-equilibrium conditions has been very challenging. Wang, Ceder and co-workers use a combinatorial experimental and computational approach to unambiguously determine the nature of these intermediate Li states, , both at low and high rates under non-equilibrium conditions in working batteries. This determination overcomes what is perhaps the last big challenge for this material.

Wang, Ceder and team find that these intermediate $Li_{4+x}Ti_5O_{12}$ metastable configurations manifest as an additional peak in the Li-electron energy loss spectrum (Li-EELS) only visible under non-equilibrium conditions, and that the intensity of this peak is rate dependent. Using first principles calculations, they can assign this peak to Li-ions present in distorted face-sharing 16c polyhedra at low rates and to Li-ions present in both distorted face-sharing 16c and 8a polyhedra at high rates at the reaction front. At high rates, the overpotentials drive the formation of $Li_{4+x}Ti_5O_{12}$ configurations with higher formation energies, leading to more distorted face-sharing 16c and 8a polyhedra, as reflected by the higher peak intensity in the Li-EELS spectra.

Wang and team also use first principles calculations to predict a low energy barrier for Li-ion transport across these distorted face-sharing polyhedra. They attribute the low diffusion barrier to the smaller number of face sharing occupied polyhedra in the transition state than that in $Li_{4+x}Ti_5O_{12}$, and to the minimal change in Li-coordination which is already reduced due to local distortion in $Li_{4+x}Ti_5O_{12}$. This result is consistent with earlier work that predicted low energy barriers for interfacial Li-ion transport with molecular dynamics[5] resulting in very mobile, almost liquid-like, moving interfaces under equilibrium conditions, as well as the low energy barriers for Li transport obtained from NMR[3]. The formation of a large number of face sharing polyhedra with low Li diffusion batteries across the boundaries means that Li-transport through the particles can take place mainly through these polyhedral interfaces. This bypasses the poorly-conducting $Li_4Ti_5O_{12}$/$Li_7Ti_5O_{12}$ end-member phases (Fig. 1d), explaining the excellent kinetics exhibited by this material at high rates.

Such excellent Li-ion mobility translates in a low internal resistance for Li-ion transport through the electrode material. What process dominates the internal resistance of the full battery depends on the mobility of the charge carriers in both electrodes and the electrolyte as well as the battery and electrode dimensions (e.g. electrode thickness, morphology, particle size, etc.).[6,7] A lower battery internal resistance enables faster charging, hence raising the power density, however within practical limitations (including effects from current, connectors, cables and cooling). Because the performance parameters in a battery are coupled and typically competing, a lower internal resistance can alternatively be invested in a larger practical energy density or in a longer cycle life. This may be achieved by increasing the electrode loading, and for the same loading by virtue of the lower overpotentials that will lead to less irreversible degradation processes, respectively. If Li-ion diffusion in the electrode particles is limiting, thus dominating the internal resistance, a conceptually simple strategy is to reduce the diffusion path length by nano-sizing the electrode particles. However, smaller particles generally also have disadvantages, including lower practical electrode densities that compromise the practical energy density, and larger electrode-electrolyte contact areas that increase the electrolyte decomposition reactions and consequently shorten the battery cycle life. It is therefore desirable to have large electrode particles with excellent charge transport properties. The findings of Wang, Ceder and co-workers are highly relevant in this context. If design strategies could be realized for appealing electrode materials to enable similar metastable states where fast charge kinetics could be accessed, this would enable larger electrode particles, circumventing interfacial challenges currently associated with several promising electrode materials. Similarly, it may offer an approach to enhance the Li-ion kinetics in solid-state electrolytes to enable the development of all-solid-state batteries, especially in materials that are electrochemically stable, which typically possess mediocre conductivities.

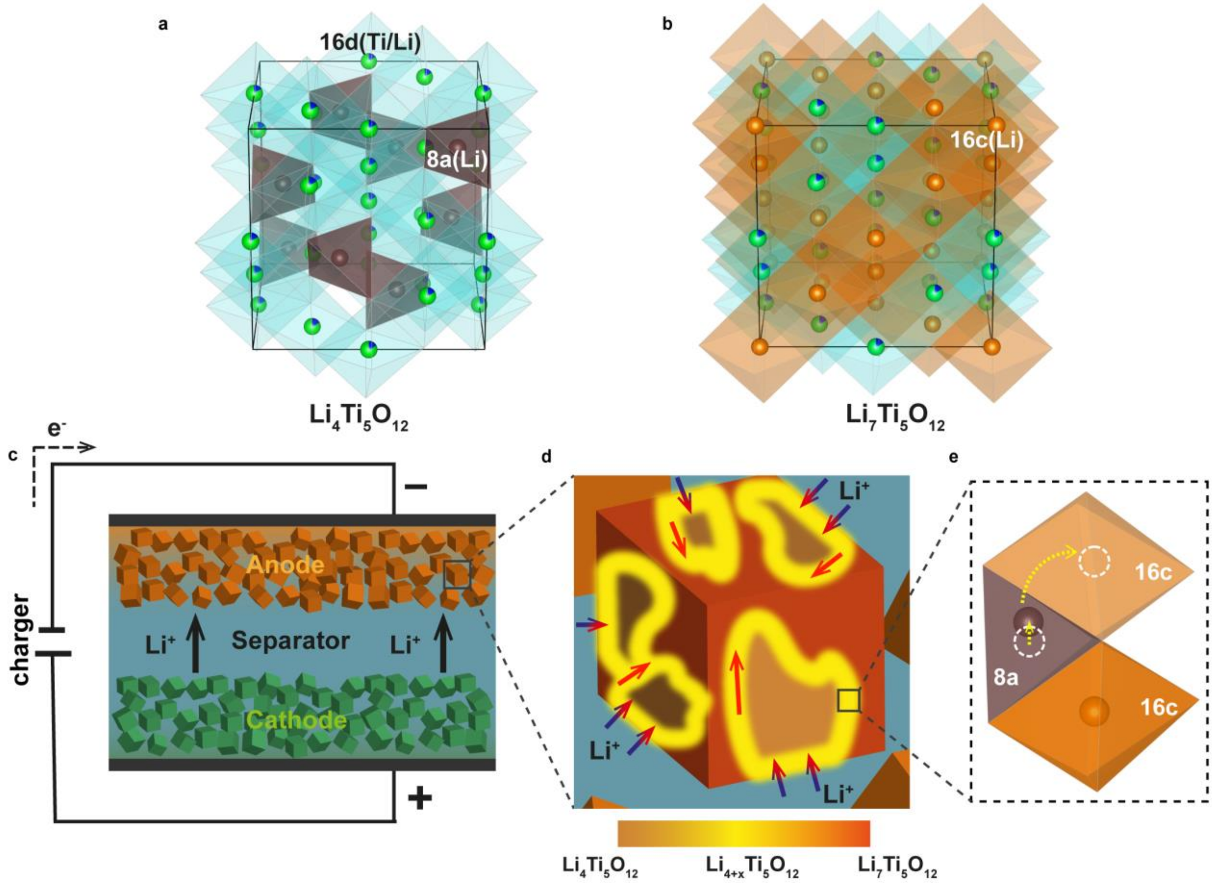

Fig. 1 Looking deep into a $Li_{4+x}Ti_5O_{12}$ ($0 \geq x \geq 3$) electrode particle during charge (a,b) Crystal structures of the (a) $Li_4Ti_5O_{12}$ and (b) $Li_7Ti_5O_{12}$ end member phases. The turquoise polyhedra represent octahedral 16d(Ti,Li) sites, brown, the tetrahedral 8a(Li) sites and orange, the octahedral 16c(Li) sites. (c) Schematic of a Li-ion battery during the charge process depicting its various components; (d) Magnified section of the negative electrode from (c) where the $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ end member domains with low Li-ion mobility and the metastable $Li_{4+x}Ti_5O_{12}$ ($0 \geq x \geq 3$) interfacial regions with high Li-ion mobility are visible. (e) Magnified section of the metastable intermediate, with a low energy barrier for Li-transport where distorted face-sharing 8a and 16c polyhedra are depicted.

References

1. Van der Ven, A., Bhattacharya, J. & Belak, A. A. *Acc. Chem. Res.* **46**, 1216–1225 (2013).
2. Zhang, W. *et al. Science* **367**, 1030–1034 (2020).
3. Schmidt, W. *et al. Chem. Mater.* **27**, 1740–1750 (2015).
4. Zhang, W. *et al. J. Am. Chem. Soc.* **139**, 16591–16603 (2017).
5. Ganapathy, S., Vasileiadis, A., Heringa, J. R. & Wagemaker, M. *Adv. Energy Mater.* **7**, 1601781 (2017).
6. Vasileiadis, A. *et al. Adv. Funct. Mater.* **28**, 1705992 (2018).
7. Bazant, M. Z. *Acc. Chem. Res.* **46**, 1144–1160 (2013).