

Understanding Li-ion thermodynamic and kinetic behaviors in concentrated electrolyte for the development of aqueous lithium-ion batteries

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ABSTRACT

High-concentration aqueous electrolytes are attractive for deployments in future lithium-ion batteries due to high safety, environmental friendliness, and wide voltage window. It is of great significance to understand the Li-ion behaviors in high concentration conditions for both mechanistic studies and commercial applications. Herein, by analyzing cyclic voltammetry and voltage profiles using a customized single-particle model, we clarify the Li-ion thermodynamic and kinetic behaviors in aqueous electrolytes at various concentrations using LiFePO₄ as the active electrode. With the increase of the electrolyte concentration, the equilibrium potentials of LiFePO₄ shift to higher values, which is attributed to the increased Li-ion activity and activity coefficient induced by the formation of polymeric solution structure ((Li⁺(H₂O)₂)_n) at high concentrations. To further quantify the interface reaction constants (k^0) and the activation energy (E_a), theoretical simulations based upon experimental data are carried out, identifying that the sluggish Li-ion desolvation process is the main contributor to the slower interface kinetics in high concentration electrolytes. Other factors affecting the Li-ion interface process, including temperature, scan rate, and type of anion, are also evaluated here. These fundamental understandings are of great value to the development of high-concentration aqueous electrolyte, in a cost-effective, sustainable and efficient way.

1. Introduction

Aqueous Li-ion batteries (LIBs) with high-concentration electrolytes have been extensively studied in the past few years, especially after the groundbreaking work of “water-in-salt” pioneered by Suo et al. [1] Aqueous high-concentration electrolyte is a tempting alternative towards the traditional organic electrolyte for next generation LIBs, owing to its non-flammable property, low toxicity, and low cost [2,3]. Compared to the low concentration electrolyte with a narrow electrochemical stability window of 1.23 V dictated by water, the electrochemical stability window of high-concentration electrolyte can be raised to >4.0 V, which not only enables the application of high voltage cathodes, such as LiCoO₂ [4], LiMn₂O₄ [1], LiVPO₄F [5], and

LiNi_{0.5}Mn_{1.5}O₄ [6], but also broadens the application of LIB chemistries. The causes for the widened stability window in high-concentration aqueous electrolyte were considered to be the reduced activity of H₂O and the formation of solid-electrolyte interphase (SEI) on the anode surface by the decomposition of solvent and salt [1,5,7]. Thereafter, Pan et al. proposed the kinetic factor, i.e., the high energy barrier to free water molecules from the formed (Li⁺(H₂O)₂)_n polymer-like cluster, as the main contributor that widens the stability window [8]. However, since the first report of aqueous rechargeable Li batteries in 1994 by Dahn et al., [9] almost all the attention has been focused on the role of water molecule and/or the SEI layer rather than the Li-ion behaviors, and many fundamental questions related to high concentration aqueous electrolytes remain unclear. These questions include but are not limited

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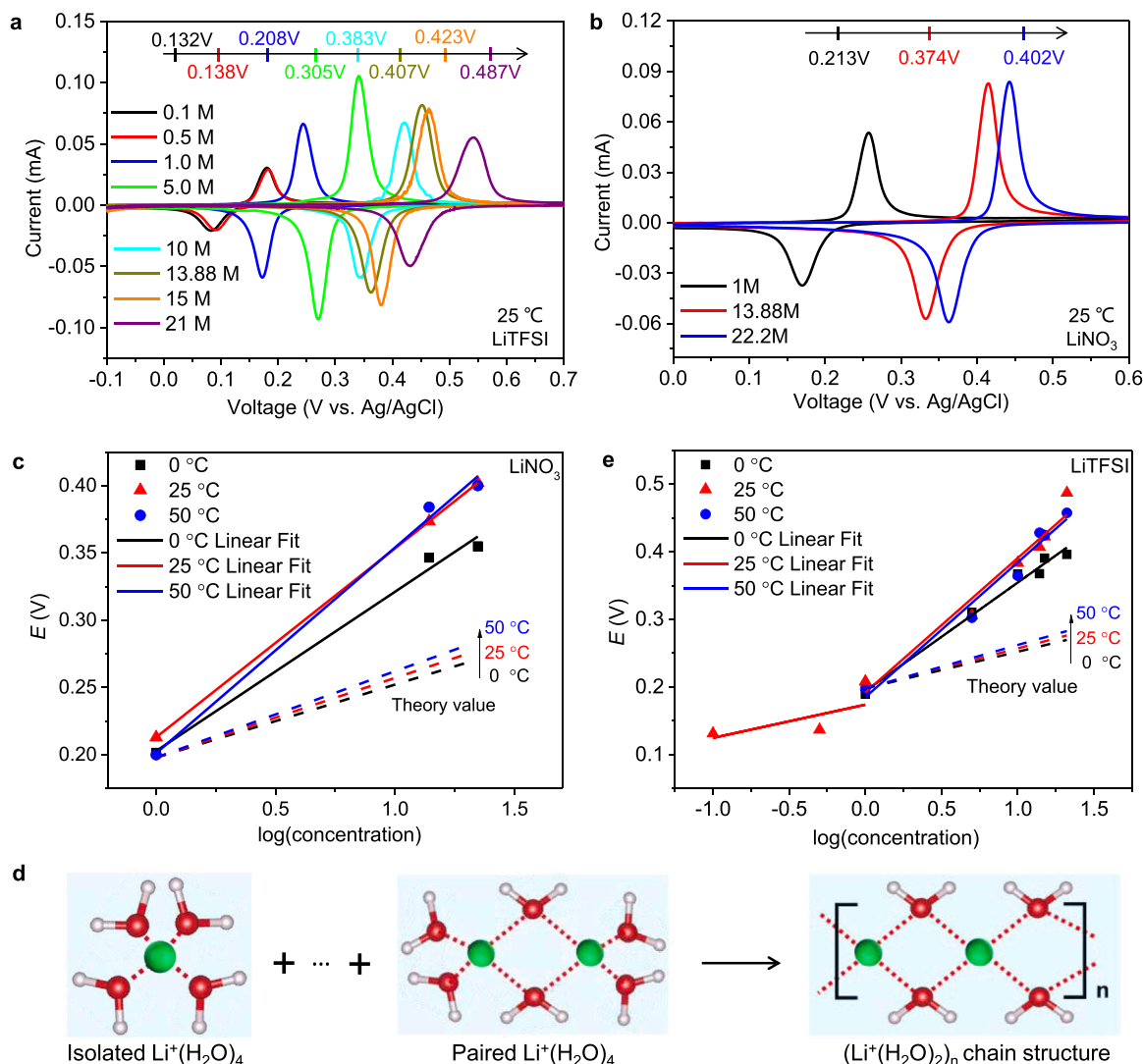


Fig. 1. CV curves of LFP SP electrode measured in (a) LiTFSI and (b) LiNO₃ solutions at different concentrations, the corresponding scan rate and testing temperature are 1 mV s⁻¹ and 25 °C. The axis above identifies the equilibrium potentials. (c) Redox potential difference vs. logarithm of LiNO₃ concentration as a function of temperature. The dotted lines are obtained by Nernst equation in ideal solutions, where there are no aggregated ions. (d) The evolution of Li-ion solvation sheath for LiNO₃ solution from diluted to highly concentrated electrolytes. (e) Redox potential difference vs. logarithm of LiTFSI concentration as a function of temperature. The dotted lines are obtained by Nernst equation in ideal solutions. Moreover, the linear relationship under low concentration conditions (0.1 M, 0.5 M, 1.0 M) is also built, which obeys the Nernst equation.

to: (1) Will the concentration of the aqueous electrolyte affect the thermodynamic equilibrium states of the electrode materials, and how? (2) What is the effect of solution concentration on the interfacial kinetics of Li-ion? (3) Is the higher the electrolyte concentration, the better for practical applications?

Herein, olivine-type LiFePO₄ (LFP) with a stable structure [10], clean surface, and perfect two-phase transition behavior during electrochemical reaction [11–13], was applied as the reference material to clarify the above unexplored secrets. LFP single particle (SP) electrode [14,15] was firstly designed to decrease the agglomeration and minimize the inter-particle interaction of the active nanoparticles. In the study of thermodynamics, the cyclic voltammetry (CV) curves with SP electrode under different electrolyte concentrations reveal that the equilibrium potential gradually shifts to a higher voltage with the increase of the electrolyte concentration, which is attributed to the increase of Li-ion activity in the polymeric (Li⁺(H₂O)₂)_n solution. In the study of kinetics, the sluggish Li-ion desolvation process from the polymeric (Li⁺(H₂O)₂)_n structure of the high concentration electrolyte is responsible for a low interface rate constant (k^0) and a high activation

energy (E_a) during the interface reaction. Moreover, this slowed Li-ion interfacial kinetics at high concentrations is also observed at different temperatures and scan rates, and the lower temperature and higher scan rate lead to a more sluggish process. The type of anion in the electrolyte is another considerable factor, as a smaller anion size is more conducive to the interface reaction. The fundamental understandings on Li-ion behaviors (thermodynamics and kinetics) in high-concentration electrolyte are useful for the selection of suitable electrolytes and working conditions for specific battery applications.

2. Results and Discussions

The as-prepared LFP particles are well dispersed by carbon nanotube (CNT) network in the SP electrode to minimize concentration polarization, electrochemical polarization, and other internal interferences, and thus the real electrochemical behavior of LFP particles could be well reflected. (Fig. S1) CV curves of LFP SP electrode in lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) solutions with different concentrations are shown in Fig. 1a (25 °C) and Fig. S2 (0 °C and 50 °C). The

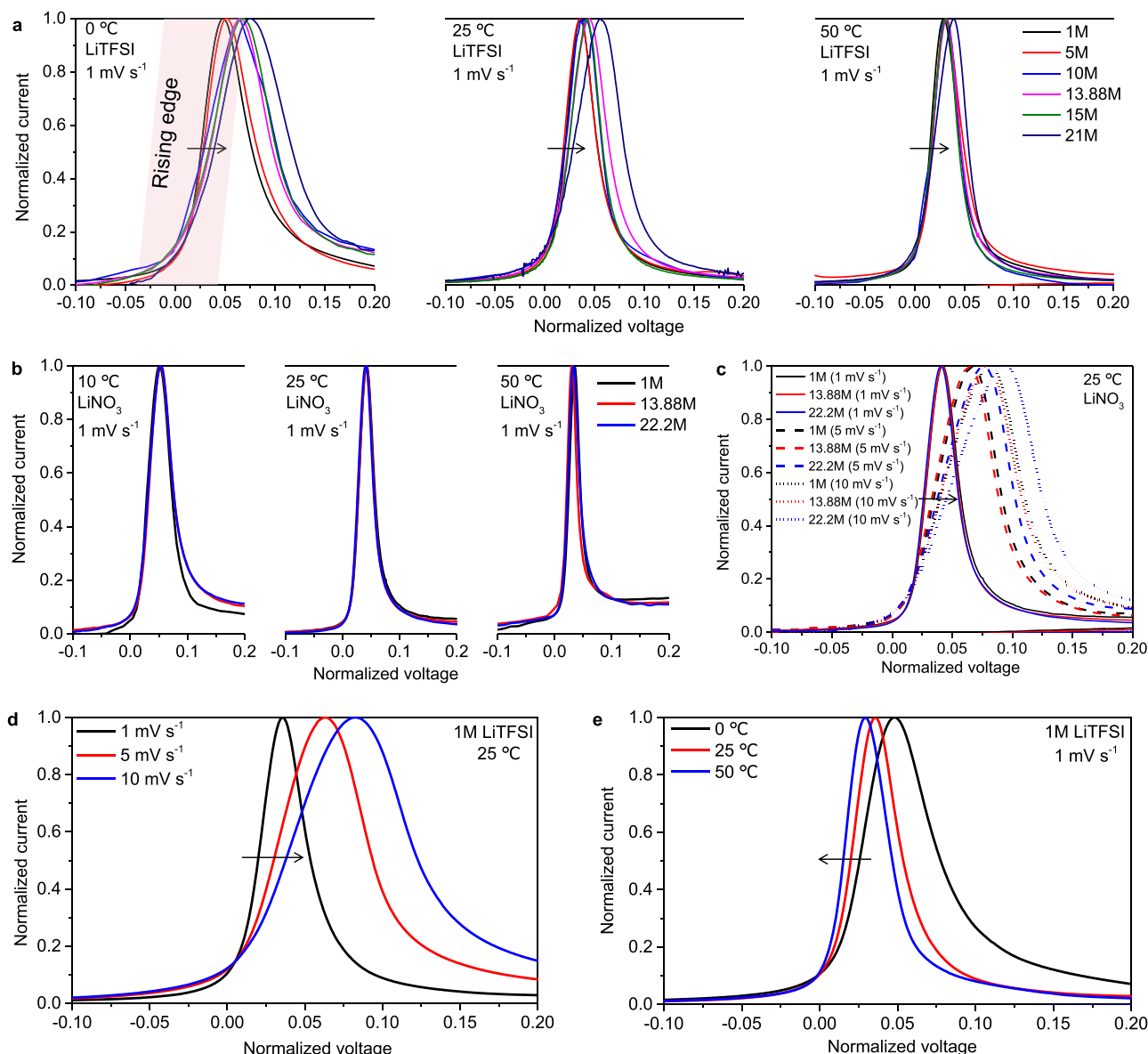


Fig. 2. (a) Normalized CV curves measured at 0 °C, 25 °C, and 50 °C in LiTFSI based electrolytes at different concentrations. The scan rate is 1 mV s⁻¹. (b) Normalized CV curves measured at 10 °C, 25 °C and 50 °C in LiNO₃ based electrolytes at different concentrations. (c) Normalized CV curves tested in LiNO₃ aqueous with different concentrations at 25 °C, the corresponding scan rates are 1 mV s⁻¹, 5 mV s⁻¹ and 10 mV s⁻¹. (d) Normalized CV curves in 1 M LiTFSI at different scan rates, the corresponding test temperature is 25 °C. (e) Normalized CV curves in 1 M LiTFSI at different temperatures, the corresponding scan rate is 1 mV s⁻¹.

oxidation and reduction peaks gradually migrate to the higher potentials with the electrolyte concentration increasing from 0.1 to 21 M, corresponding to the shift of the equilibrium potential from 0.132 to 0.487 V at 25 °C. The LiTFSI salt was then substituted by LiNO₃, and the electrolyte concentrations were reselected to be 1.0, 13.88, and 22.2 M. Similarly, the redox peaks of LFP shift to higher potentials with the increase of solution concentrations (Fig. 1b (25 °C) and Fig. S3 (10 °C and 50 °C)), corresponding to the equilibrium potentials of 0.213, 0.374, and 0.402 V at 25 °C, respectively. Therefore, it can be concluded that the equilibrium potential will increase to a higher value when the electrolyte concentration increases regardless of the testing temperature and the type of anion.

The shift of the oxidation and reduction peaks is related to thermodynamics, which could be evaluated using the Nernst equation. The Nernstian relationship between the equilibrium potential and the concentration of the LiNO₃ electrolyte is shown in Fig. 1c. The dotted lines are based on ideal solutions at different temperatures calculated using the Nernst equation, and they deviate from the experimental data (solid

curves). Nernst equation seems not suitable to describe the relationship between the electrode potential and Li-ion activity when the electrolyte concentration is higher than 1 M. According to our previous work on high concentration LiNO₃ [8], isolated Li⁺(H₂O)₄ tends to be paired to form (Li⁺(H₂O)₂)_n chain (Fig. 1d) with the increase of electrolyte concentration, which results in the increase of (Li⁺(H₂O)₂)_n percentage and decrease of free water (Fig. S4). With the increase of electrolyte concentration, the electrolyte structure changes and the Li-ion activity coefficient increases [16–18]. Based on the relationship of $\alpha = \gamma \cdot c$ (where α is ion activity, γ is activity coefficient, and c is ion concentration), clearly, the increase of activity coefficient will lead to higher ion activity in high concentration conditions. According to Nernst equation $E = E^0 + (RT)/(nF) \ln \alpha$ (where E is cell potential, E^0 is standard potential, R is molar gas constant, T is the absolute temperature, n is ion charge, and F is Faraday constant), that the higher of α contributes to the larger cell potential (E). Hence, the shift of redox peaks to the high potentials in CV curves at a high concentration is attributed to the high Li-ion activity caused by the formation of (Li⁺(H₂O)₂)_n chain. As for LiTFSI-based

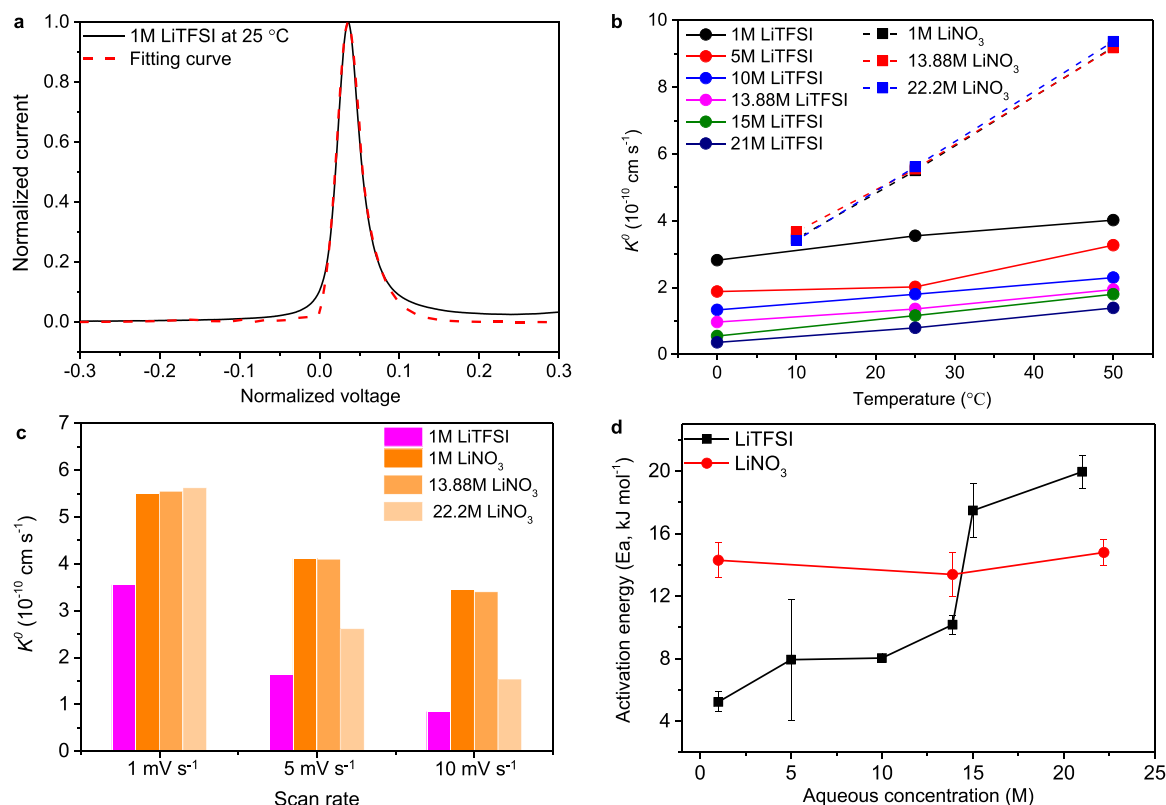


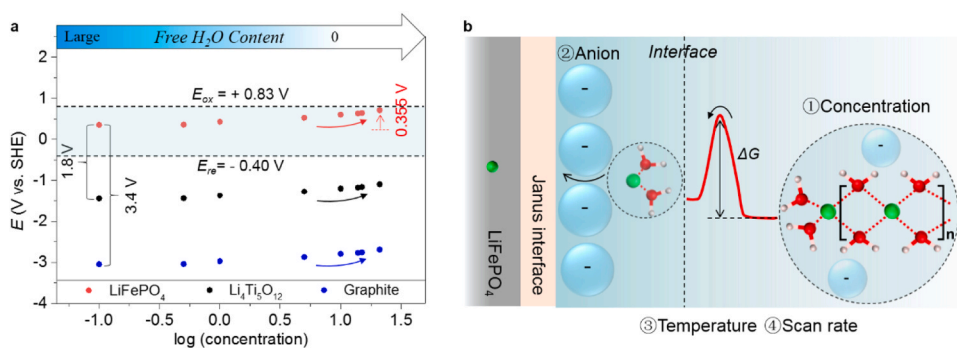
Fig. 3. (a) Sample of simulation result by analyzing CV and charge/discharge curves, corresponding to 1 M LiTFSI at 25 °C. (b) Interfacial reaction constant (k^0) vs. operation temperature (T) as a function of solution concentrations, the corresponding scan rate is 1 mV s^{-1} . (c) k^0 vs. scan rate as a function of solution concentrations at 25 °C. (d) Evolution of activation energy (E_a) with the increase of electrolyte concentrations in both LiTFSI and LiNO₃ solutions.

electrolytes, the similar trend in the equilibrium potential can also be explained by the above theory, and the relationship between the equilibrium potential and the logarithm of LiTFSI electrolyte concentration was also plotted to compare with the Nernst equation (Fig. 1e). When the electrolyte concentrations are higher than 1 M, the experimental potentials (solid lines) deviate from the theoretical values (dotted lines), consistent with the result for LiNO₃-based electrolytes. However, at low concentrations (0.1 M, 0.5 M and 1 M, red solid line), the experimental data are well consistent with the theory values, meaning that the electrolytes with low Li-ion concentrations are close to the ideal solution full of isolated Li ions. In addition, between LiTFSI and LiNO₃ system, the equilibrium potential position at certain concentration and the shift contents from low to high concentration are different (Fig. 1a and b), which should be the affection of anion on solution structure [19].

To investigate the effect of electrolyte concentration on the Li-ion kinetic behavior at the interface between LFP and electrolyte, the CV curves collected were normalized, and the medium potentials of the redox peaks were set as normalized zero. In LiTFSI electrolytes, the normalized CV curves follow a constant trend with the increase of the electrolyte concentration, and the rising edge of the normalized oxidation peaks shifts to a higher potential. (Fig. 2a) On the basis of our previous work [14], the rising edge of CV curve is related to the interfacial kinetic process. The right-shifted CV rising edges shown in Fig. 2a suggest that the Li-ion interfacial kinetic process slows down gradually as the electrolyte concentration increases. In LiNO₃ electrolytes, the normalized CV curves at different concentrations almost overlap (Fig. 2b) when the scan rate was set as 1 mV s^{-1} , which means there is enough time for Li-ion to achieve interface activation process and the dynamic-determining step at low scan rate is not the interface activation. However, when the scan rate was raised up to 5 mV s^{-1} and 10 mV s^{-1} , the rising edges migrate noticeably to high potentials at high LiNO₃ concentrations (Fig. 2c). Hence, in LiNO₃ electrolyte system, the

effect of electrolyte concentration on the interface kinetics is not prominent at low scan rates, but becomes apparent at high scan rates. In LiNO₃, it is also true that a higher electrolyte concentration leads to slower Li-ion interface kinetics. At a given concentration, a higher scan rate leads to a more significant shift of the CV rising edge toward a higher voltage, occurring in both LiTFSI and LiNO₃ electrolyte systems (Fig. 2c and d). In addition, the normalized CV curves at different temperatures demonstrate that a high temperature is beneficial to interfacial kinetics, owing to an enhanced molecular thermal motion (Fig. 2e, S5 and S6) [14].

SP model was built to analyze the CV curves and the state of charge (SOC) profiles, and then to quantify the Li-ion interface kinetics. The detailed simulation process is described in the experimental section. The charge/discharge profiles of LFP SP electrode tested in LiTFSI and LiNO₃ electrolytes at different temperatures are shown in Figs. S7 and S8. With the temperature increasing, the gap between the charging and discharging plateaus becomes smaller, typically 22.5, 21.9, and 15.3 mV at 0, 25, and 50 °C in 1 M LiTFSI (Fig. S7a). The CV curve of LFP SP electrode in 1 M LiTFSI at 25 °C was simulated based on the SP model (Fig. 3a), and it (dotted line) is well consistent with the experimental one. The interface rate constants (k^0) in LiTFSI and LiNO₃ electrolytes with different concentrations were obtained by simulation (Fig. 3b and c). As shown in Fig. 3b, there is an upward trend of k^0 with the increase of temperature at a certain concentration in both LiTFSI and LiNO₃ electrolytes, consistent with the results shown in Fig. 2e, S4 and S5. In LiTFSI electrolyte, k^0 becomes smaller gradually with the increase of electrolyte concentration (Fig. 3b) at low scan rate (1 mV s^{-1}), suggesting a slower interfacial kinetic process, well consistent with the right-shifted CV rising edges shown in Fig. 2a. However, in LiNO₃ system, with the increase of electrolyte concentration, the downward trend of k^0 is apparent only at high scan rates (5 mV s^{-1} and 10 mV s^{-1}). k^0 is almost a constant value against the electrolyte concentration at



electrolyte concentration, anion type, temperature, and scan rate.

1 mV s^{-1} scan rate (Fig. 3b and c), because k^0 is obtained from the fitting curve, which is determined by the undifferentiated raw normalized curves (Fig. S9). Moreover, at equal scan rate and temperature, the simulated k^0 values in LiNO_3 electrolyte are larger than those in LiTFSI electrolyte, which can be attributed to the difference in the anion adsorption layer that the larger of anion size, the slower of Li^+ interface dynamics (Fig. 3b and c) [15]. Based on the simulated k^0 and the testing temperature in LiTFSI electrolyte (Fig. 3b), activation energy (E_a) was calculated using Arrhenius equation. The activation energy increases as the concentration increases, meaning that more energy is needed to drive interface reaction in high concentration solutions (Fig. 3d). As for LiNO_3 system, E_a is almost independent of the concentration at 1 mV s^{-1} scan rate, and it is much lower than that in LiTFSI system under high concentration conditions. Fig. S10 illustrates the possible Li-ion diffusion process from electrolyte to LFP bulk, including situations in low concentration and high concentration electrolytes. Since the cathode is the same material, the different values of k^0 in low and high concentration electrolytes should be attributed to the different Li-ion diffusion processes in the Helmholtz layer, where the Li-ions desolvate to the ionic adsorption layers, and then move to the Janus interface. The H_2O molecule has a stronger binding energy with Fe and Li to achieve interface reconstruction and form a Janus interface on the surface of LFP. It was previously prove that the barrier energies for Li-ion to cross the Janus layer should be the same [15]. Moreover, it is well known that more energy is needed to overcome the desolvation barrier than to cross the SEI layer [20,21], so the effect of Li-ion desolvation process on interfacial kinetics is more significant compared to that of the ionic adsorption layer, which is a much looser structure than the SEI layer. Hence, the difference in the interfacial kinetics under different concentrations can be attributed to the diversity in the Li-ion desolvation processes ($\Delta G_1 < \Delta G_2$) in the formed Helmholtz layer [8].

In summary, the effects of aqueous high-concentration electrolyte on Li-ion electrochemical behaviors have been studied, in terms of both thermodynamics and kinetics. Relevant factors are summarized and illustrated in Fig. 4. The thermodynamic effect is mainly manifested by the change in the equilibrium potential with the electrolyte concentration, and this effect is attributed to the increase of effective Li ions concentration induced by the formed $(\text{Li}^+(\text{H}_2\text{O})_2)_n$ polymeric structure. In a high concentration electrolyte, positive shift of the equilibrium potential will increase the possibility of electrolyte oxidation, which poses additional challenges at the cathode side. In contrast, at the anode side, such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$, graphite or other anodes, positive shift of the equilibrium potential can delay the decomposition of H_2O or the dissolved salt (Fig. 4a). Hence, finding the shifted potential is conducive to accurately determine the working voltage range to maximize the capacity of the cathode material without affecting the stability of the electrolyte. For the Li-ion kinetic process, temperature, scan rate, type of anion, and Li-ion concentration (solvation structure) all have an effect. A high temperature and a slow scan rate both belong to external driving

Fig. 4. Effect of electrolyte concentration on Li-ion thermodynamic and kinetic behaviors. (a) Change of LiFePO_4 equilibrium potential with the increase of electrolyte concentration coupled with reference electrodes. In $\text{Li}_4\text{Ti}_5\text{O}_{12}||\text{LiFePO}_4$ and Graphite $||\text{LiFePO}_4$ full cells, the working voltages are close to 1.8 V [22] and 3.4 V [23], respectively. Therefore, with the constant voltage windows and gradually increased potentials at the cathode side, the potentials at the anode sides will simultaneously shift to a higher value. 0.83 V and -0.40 V are the oxidation potential (E_{ox}) and reduction potential (E_{re}) of free H_2O molecule in neutral solutions ($\text{pH} = 7$). (b) Collection of factors on interface kinetic process, including

forces, which facilitate Li-ion kinetics and contribute to a larger k^0 . The effect of anion size on interface kinetics has been studied in our previous work, showing that the smaller the anion is, the larger the k^0 becomes. As to the electrolyte concentration, there are more $(\text{Li}^+(\text{H}_2\text{O})_2)_n$ polymeric structures in high concentration electrolytes than those in dilute electrolytes, resulting in higher Li^+ desolvation energy (ΔG) and lower k^0 , and thus slower interface diffusion (Fig. 4b).

3. Conclusions

In conclusion, a systematic study on the Li-ion thermodynamics and kinetics behaviors in aqueous electrolyte of a series of concentrations was performed. With the increase of the electrolyte concentration, the voltage stability window was expanded and the equilibrium potentials shift to a higher potential indicating the less favorable thermodynamics, owing to the increase of Li-ion activity in $(\text{Li}^+(\text{H}_2\text{O})_2)_n$ structure, which results in additional challenges at the cathode side and suppressed hydrogen evolution at the anode side. As for Li-ion kinetics, the temperature, scan rate, and type of anion all play a role, in addition to the electrolyte concentration. Typically, a low concentration, a high temperature, a slow scan rate, and anions with a small size contribute to a high interface reaction constant (k^0), thus showing a fast interfacial kinetic process. This all-embracing fundamental study is of great significance to getting insights into high-concentration aqueous Li-ion batteries and selecting optimal working conditions to achieve high performances.

Author declaration

We confirm that the manuscript has been read and approved by all named authors and there is no interest conflict among the authors.

Supporting Information

Supporting information provides, simulation model, SEM images, normalized CV curves, charge/discharge curves and definition of used parameters.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2021.106413](https://doi.org/10.1016/j.nanoen.2021.106413).

References

- [1] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, "Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries, *Science* 350 (2015) 938–943.
- [2] M. Pasta, C.D. Wessells, R.A. Huggins, Y. Cui, A high-rate and long cycle life aqueous electrolyte battery for grid-scale energy storage, *Nat. Commun.* 3 (2012) 1149.
- [3] Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama, A. Yamada, Hydrate-melt electrolytes for high-energy-density aqueous batteries, *Nat. Energy* 1 (2016) 16129.
- [4] G. Wang, L. Fu, N. Zhao, L. Yang, Y. Wu, H. Wu, An Aqueous Rechargeable Lithium Battery with Good Cycling Performance, *Angew. Chem.* 119 (2007) 299–301.
- [5] C. Yang, J. Chen, T. Qing, X. Fan, W. Sun, A. von Cresce, M.S. Ding, O. Borodin, J. Vatamanu, M.A. Schroeder, N. Eidson, C. Wang, K. Xu, 4.0 V Aqueous Li-Ion Batteries, *Joule* 1 (2017) 122–132.
- [6] F. Wang, L. Suo, Y. Liang, C. Yang, F. Han, T. Gao, W. Sun, C. Wang, Spinell $\text{LiNi}_0.5\text{Mn}_{1.5}\text{O}_4$ Cathode for High-Energy Aqueous Lithium-Ion Batteries, *Adv. Energy Mater.* 7 (2017), 160922.
- [7] N. Dubouis, P. Lemaire, B. Mirvaux, Elodie Salager, M. Deschamps and A. Grimaud, *Energy Environ. Sci.*, 11 (2018) 3491–3499.
- [8] J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, Y. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, J.C. Neufeld, Y. Ren, K. Amine, L.-W. Wang, K. Xu, F. Pan, Understanding Thermodynamic and Kinetic Contributions in Expanding the Stability Window of Aqueous Electrolytes, *Chem* 4 (2018) 2872–2882.
- [9] W. Li, J.R. Dahn, D.S. Wainwright, Rechargeable lithium batteries with aqueous electrolytes, *Science* 264 (1994) 1115–1118.
- [10] L.-X. Yuan, Z.-H. Wang, W.-X. Zhang, X.-L. Hu, J.-T. Chen, Y.-H. Huang, J. B. Goodenough, Development and challenges of LiFePO_4 cathode material for lithium-ion batteries, *Energy Environ. Sci.* 4 (2011) 269–284.
- [11] J. Zheng, Y. Hou, Y. Duan, X. Song, Y. Wei, T. Liu, J. Hu, H. Guo, Z. Zhuo, L. Liu, Z. Chang, X. Wang, D. Zhrebetskyy, Y. Fang, Y. Lin, K. Xu, L.W. Wang, Y. Wu, F. Pan, Janus Solid-Liquid Interface Enabling Ultrahigh Charging and Discharging Rate for Advanced Lithium-Ion Batteries, *Nano Lett.* 15 (2015) 6102–6109.
- [12] L. Laffont, C. Delacourt, P. Gibot, M.Y. Wu, P. Kooyman, C. Masquelier, J. M. Tarascon, Study of the $\text{LiFePO}_4/\text{FePO}_4$ Two-Phase System by High-Resolution Electron Energy Loss Spectroscopy, *Chem. Mater.* 18 (2006) 5520–5529.
- [13] G. Oyama, Y. Yamada, R.-i Natsui, S.-i Nishimura, A. Yamada, Kinetics of Nucleation and Growth in Two-Phase Electrochemical Reaction of Li_xFePO_4 , *J. Phys. Chem. C* 116 (2012) 7306–7311.
- [14] J. Hu, W. Li, Y. Duan, S. Cui, X. Song, Y. Liu, J. Zheng, Y. Lin, F. Pan, Single-Particle Performances and Properties of LiFePO_4 Nanocrystals for Li-Ion Batteries, *Adv. Energy Mater.* 7 (2016), 1601894.
- [15] J. Hu, W. Ren, X. Chen, Y. Li, W. Huang, K. Yang, L. Yang, Y. Lin, J. Zheng, F. Pan, The role of anions on the Helmholtz Plane for the solid-liquid interface in aqueous rechargeable lithium batteries, *Nano Energy* 74 (2020), 104864.
- [16] E. Gluckauf, The influence of ionic hydration on activity coefficients in concentrated electrolyte solutions, *Trans. Faraday Soc.* 51 (1955) 1235–1244.
- [17] Z. Abbas, E. Ahlberg, Activity Coefficients of Concentrated Salt Solutions: A Monte Carlo Investigation, *J. Solut. Chem.* 48 (2019) 1222–1243.
- [18] A. Levy, M. Bazant, A. Kornyshev, Ionic activity in concentrated electrolytes: Solvent structure effect revisited, *Chem. Phys. Lett.* 738 (2020), 136915.
- [19] Y. Marcus, Ionic radii in aqueous solutions, *Chem. Rev.* 88 (1988) 1475–1498.
- [20] K. Xu, A. von Cresce, U. Lee, Differentiating contributions to "ion transfer" barrier from interphasial resistance and Li^+ desolvation at electrolyte/graphite interface, *Langmuir* 26 (2010) 11538–11543.
- [21] Q. Li, D. Lu, J. Zheng, S. Jiao, L. Luo, C.M. Wang, K. Xu, J.G. Zhang, W. Xu, Li^+ Desolvation Dictating Lithium-Ion Battery's Low-Temperature Performances, *ACS Appl. Mater. Interfaces* 9 (2017) 42761–42768.
- [22] C.-C. Yang, H.-C. Hu, S.-J. Lin, W.-C. Chien, Electrochemical performance of V-doped spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ composite anode in Li-half and $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$ -full cell, *J. Power Sources* 258 (2014) 424–433.
- [23] L. Tan, L. Zhang, Q. Sun, M. Shen, Q. Qu, H. Zheng, Long-term outcome of a metal-on-polyethylene cementless hip resurfacing, *J. Arthroplast.* 29 (2014) 802–807.



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