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## Inhibiting Solvent Co-Intercalation in a Graphite Anode by a Localized High-Concentration Electrolyte in Fast-Charging Batteries

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Abstract: Lithium-ion batteries with routine carbonate electrolytes cannot exhibit satisfactory fast-charging performance and lithium plating is widely observed at low temperatures. Herein we demonstrate that a localized high-concentration electrolyte consisting of 1.5 M lithium bis(fluorosulfonyl)imide in dimethoxyethane with bis(2,2,2-trifluoroethyl) ether as the diluent, enables fast-charging of working batteries. A uniform and robust solid electrolyte interphase (SEI) can be achieved on graphite surface through the preferential decomposition of anions. The established SEI can significantly inhibit ether solvent co-intercalation into graphite and achieve highly reversible Li<sup>+</sup> intercalation/de-intercalation. The graphite | Li cells exhibit fast-charging potential (340 mAhg<sup>-1</sup> at 0.2 C and 220 mAhg<sup>-1</sup> at 4 C), excellent cycling stability (ca. 85.5 % initial capacity retention for 200 cycles at 4 C), and impressive low-temperature performance.

 $\mathbf{R}$  echargeable lithium-ion batteries (LIBs) have been widely applied in portable electronics, electric vehicles, and grid storage owing to their high energy density, low self-discharge, long lifetimes, and reasonable costs.<sup>[1]</sup> The requirement for fast-charging battery is more urgent than ever. However, current LIBs with graphite anodes are unable to reach the desired fast-charging target with 80% capacity acquired in 15 minutes charging time.<sup>[2]</sup> Among all factors that affect fastcharging of a battery, electrolyte dominates the operating voltage, rate and cycle performance, temperature range as well as safety.<sup>[3]</sup> Importantly, the formation of solid electrolyte interphase (SEI) is highly dependent on the reductive reactions of electrolyte on the electrode surface.<sup>[4]</sup> A stable SEI prevents direct contacts between the graphite anode and the electrolyte to inhibit the reductive decomposition of electrolyte.<sup>[5]</sup> Otherwise, the continuous decomposition of the

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the author(s) of this article can be found under: https://doi.org/10.1002/anie.202009738. electrolyte induces low Coulombic efficiency, and the accompanying solvent co-intercalation reaction leads to the destruction of the graphite structure.<sup>[6]</sup>

Li<sup>+</sup> is solvated by a plenty of solvents to form a Li<sup>+</sup> solvation sheath in routine low-concentration ether electrolytes (LCEs).<sup>[7]</sup> When Li<sup>+</sup> is embedded in the graphite anode, the co-intercalation of ether solvent molecule occurs into the graphite interlayers. The subsequent decomposition easily induces the structural exfoliation of graphite (Figure 1a), leading to capacity degradation and cycle instability. The strong chemical coordination between the ether solvent and Li<sup>+</sup> makes it hard to be de-solvated, which easily give rise to co-intercalation. The co-intercalation reaction can be effectively suppressed by adjusting the solvation structure of the electrolyte. It is well known that after introducing ethylene carbonate (EC) into the non-aqueous electrolyte, graphite can be protected from irreversible exfoliation induced by propylene carbonate (PC) co-intercalation.<sup>[8]</sup> Recently, the adopting high-concentration electrolytes (HCEs) is proposed to adjust Li<sup>+</sup> solvation structure.<sup>[9,10]</sup> Since anions can be squeezed into the Li<sup>+</sup> solvation sheath in HCEs, an anionderived SEI layer dominated by inorganic components is generated, thereby rendering uniform and rapid Li<sup>+</sup> transportation. Nevertheless, HCEs tend to bring high viscosity, inferior wettability, low ionic conductivity, poor low temperature performance, and high costs.<sup>[11]</sup> The introduction of a low-polarity diluent that does not dissolve lithium salts to dilute HCEs achieve localized high-concentration electrolvtes (LHCEs).<sup>[12,13]</sup> The special solvation structure of the LHCEs system is shown in Figure 1b, the free solvent molecules disappear to form contact ion pairs (CIPs, anion coordinating to a single Li<sup>+</sup> cation) and aggregates (AGGs,



Localized high-concentration electrolyte (LHCE) • Li\* SFSI STA DME BTFE KLow temperature

Figure 1. Illustrations of the solution structures and the process of  $\rm Li^+$  intercalation graphite layer in a) LCE and b) LHCE based on LiFSI in DME without/with BTFE.

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anion coordinating to two or more Li<sup>+</sup> cations) in the LHCEs with a large number of diluents.<sup>[12]</sup> It has been reported that LHCEs demonstrate unique advantages in stabling the Li metal/electrolyte interfaces and improving the Coulombic efficiency of a Li metal battery.<sup>[11,14]</sup> However, less attention has been paid to the investigation of fast-charging graphite anode in LHCEs.<sup>[15]</sup> The rational design of compatible electrolytes that promotes ionic transportation and inhibits solvent co-intercalation is simultaneously considered for fast-charging LIBs.

Herein, an emerging ether-based LHCE was proposed to suppress solvent co-intercalation into the graphite anodes and exhibit fast-charging potential in LIBs. A fluorinated ether of bis(2,2,2-trifluoroethyl) ether (BTFE) diluent was mixed with dimethoxyethane (DME) in a volume ratio of 2:1 to prepare a LHCE with 1.5 M lithium bis(fluorosulfonyl)imide (LiFSI). In contrast to organic solvents, the anions preferentially get decomposed and form a stable SEI mainly composed of inorganic components on graphite surface after initial cycle. The LHCE leads to the formation of a uniform and robust SEI film with inorganic components, inhibiting the cointercalation of ether solvent into the graphite anode and rendering good rate performance (340 mAhg<sup>-1</sup> at 0.2 C and  $220 \text{ mAh g}^{-1}$  at 4 C), excellent cycling stability (ca. 85.5%) capacity retention for 200 cycles at 4 C), and impressive low temperature performance.

To explore the solvation structures, Raman spectra were obtained for LHCE (1.5 M LiFSI in DME:BTFE), HCE (4.5 M LiFSI in DME), and LCE (1.5 M LiFSI in DME) (Figure 2a). Free DME molecules demonstrate vibration peaks at 820 and 847 cm<sup>-1</sup>, which correspond to the CH<sub>2</sub> rocking and C-O stretching vibration of DME, respectively.<sup>[12]</sup> The gradual reduction of free DME molecules with increasing salt concentration is confirmed by the weakening peaks between 810-860 cm<sup>-1</sup>, especially for HCE. An extra vibration peak at about 875 cm<sup>-1</sup> is assigned to the Li<sup>+</sup>coordinated DME and the peak intensity also increased with the rise of salt concentration. Additionally, the LCE also exhibits a vibration peak at 717 cm<sup>-1</sup>, indicating the presence of abundant free FSI<sup>-</sup> anions.<sup>[16]</sup> The FSI<sup>-</sup> Raman band is significantly blue-shifted to about 730 cm<sup>-1</sup> because the FSI<sup>-</sup> mainly exists in the modes of CIPs and AGGs. Notably, except for the vibration band of BTFE at  $820-870 \text{ cm}^{-1}$ ,<sup>[17]</sup> the LHCE obtained by adding BTFE diluent illustrates almost the same Raman absorption peaks as the HCE. This confirms the fact that the CIPs, AGGs, and Li<sup>+</sup>-coordinated DME



*Figure 2.* a) Raman spectra of LHCE, HCE, LCE, solvent, and diluent. b) The first capacity–voltage profiles of LHCE, HCE, LCE, and RCE in graphite | Li cells at 0.2 C.

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solvation structures are well preserved. BTFE does not engage in the  $\rm Li^+$  solvation structure.  $^{[13]}$ 

The first-cycle capacity-voltage profiles of LHCE, HCE, LCE, and routine electrolyte (RCE, 1.0 M LiPF<sub>6</sub> in EC:DMC) were explored and compared in graphite | Li cells at 0.2 C. Except for RCE, all the first capacity-voltage curves of the lithiation process exhibit a unique peak between 0.95-1.25 V (Figure 2b). According to the results of peak position in cyclic voltammetry (CV), it can be concluded that the reduction potentials are 1.18, 1.20, and 1.05 V for LHCE, HCE, and LCE (Supporting Information, Figure S1), respectively. The anions in the LHCE system are more likely to reach their decomposition voltages and preferentially decompose over solvent molecules to form inorganic compounds dominated SEI. This can be explained by the fact that the anion driven by AGGs and CIPs can quickly migrate to the graphite surface in the dilute LHCE and undergo reductive decomposition. The decomposition of anions is also happened in LCE system. However, the decomposition and co-intercalation of solvent molecules have been accompanied with the reduction of potential (Supporting Information, Figure S1b) and caused subsequent exfoliation of graphite. As a result, a rapid decay is observed on the cell capacity in LCE (Figure 2b). Furthermore, these peaks represent the decomposition of anions disappear in the subsequent lithiation process (Supporting Information, Figure S2), indicating that the as-formed SEI is complete enough to prevent the additional consumption of anions.

X-ray photoelectric spectroscopy (XPS) was applied to identify the specific composition of the SEI on the graphite anodes surface (Figure 3). To determine whether the decom-



**Figure 3.** a)–f) The XPS characterization of the SEI components on the graphite anodes disassembled from the graphite | Li cells with LHCE, HCE, and LCE in the first cycle, respectively. a) C 1s and b) F 1s spectra of the SEI film on graphite anodes surface with LHCE, HCE, and LCE. c) N 1s, d) O 1s, e) S 2p, and f) Li 1s spectra of the SEI film on graphite anodes surface with LHCE. g) The proposed mechanism of FSI<sup>-</sup> decomposition.

position of anions occurred at the initial lithiation process and confirm the corresponding decomposition products, a graphite anode surface after washing with DME obtained by disassembling the graphite | Li cell. The interface was formed at 1.12, 1.05, and 0.98 V in LCHE, HCE, and LCE, respectively. There are similar element peaks on the XPS survey spectra of graphite surface in the LHCE, HCE, and LCE systems (Supporting Information, Figure S3). In the C 1s spectra of all electrolytes studied, the relative contents of compounds containing C–O bonds (284.5 eV) is low (Figure 3a).<sup>[18]</sup> The graphite surface contains less organic components. It indicates that the decomposition of DME has not yet proceeded. Therefore, the F, N, and S elements detected on the graphite surface can be concluded from the decomposition of anions. Whereas, the relative content of LiF in SEI induced by LHCE is relatively high in the F1s spectra (Figure 3b), indicating that the anions driven by AGG can quickly reach the graphite surface in the dilute electrolyte to decompose to form a large amount of LiF. A LiF-rich SEI layer can be highly valuable for enhancing the stability of the electrode interfaces.<sup>[7,13,19]</sup> The N 1s peak at about 398.8 eV is most likely from N-SO<sub>x</sub> species generated by incomplete decomposition of FSI-,<sup>[14]</sup> while the peak at about 397.5 eV is attributed to Li<sub>3</sub>N species (Figure 3 c). In the O 1s and S 2p spectra (Figure 3 d, e), there are also apparent signals of S– $O_x$  species at about 531.3 and 165-170 eV, respectively, from further anion decomposition and inorganic species Li<sub>2</sub>O and Li<sub>2</sub>S at about 528.0 and about 161.1 eV, respectively. Simultaneously, the elemental mapping images demonstrate that C, O, N, S, and F atoms are uniformly distributed on the graphite surface (Supporting Information, Figure S4). Furthermore, these inorganic species are also detected in the Li 1s spectrum (Figure 3 f). Based on the aforementioned analysis, the possible mechanisms of the decomposition of FSI- anions in the electrolyte are inferred as Figure 3 g.<sup>[20]</sup>

To further determine the composition of SEI induced by LHCE at 1.12 V in the first cycle, the surface chemistry of the graphite anodes was characterized by transmission electron microscope (TEM). The graphite anode surface is covered by SEI with different lattice fringes of LiF, Li<sub>2</sub>O, Li<sub>3</sub>N, Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Figure 4a), which is consistent with the XPS analysis results. Additionally, the TEM images indicated that no SEI is formed on the surface of the conductive agent carbon black



**Figure 4.** TEM images of a graphite anode disassembled from a graphite | Li cell with LHCE at 1.12 V in the first cycle. a) The inorganic compounds on graphite anode. b) The SEI attached on graphite layer.

(Supporting Information, Figure S5), whereas the SEI layer with a thickness of about 2.5 nm is observed on graphite surface (Figure 4b). Combined with the results of XPS and TEM, we conclude that the species mainly interacted with the graphite anode surface are anions rather than diluent molecules (BTFE) in the SEI formation. The BTFE does not engage in the Li<sup>+</sup> solvation structure, and the large steric hindrance makes it difficult to participate in the preferential formation of the interfaces. The additional electrochemical impedance spectroscopy (EIS) measurement illustrates that the SEI resistance and charge transfer resistance in LHCE are the lowest (Supporting Information, Figure S6), indicating the SEI formed in LHCE is more conductive than that formed in other control electrolytes. Consequently, the SEI layer with an inorganic component initially established on the graphite anode surface, which is favorable for constructing a more stable electrode/electrolyte interface and inhibiting co-intercalation of solvent molecules during lithiation process.

To evaluate the fast-charging and long cycle performance of graphite anodes under different SEI, typical galvanostatic discharge/charge tests were performed for the graphite | Li cells. Figure 5a exhibits capacity-voltage curves of the batteries using LHCE, HCE, and RCE  $(1.0 \text{ M LiPF}_6 \text{ in }$ EC:DMC) at 1 C and 4 C. Among them, several voltage plateaus appear below about 0.2 V at 1 C, which are characteristic of the continuous formation of multi-stage structures of LiC<sub>r</sub>.<sup>[10]</sup> Obviously, the reversible capacity obtained with LHCE is the highest ( $322 \text{ mAh g}^{-1}$  at 1 C). However, as the rate is increased to 4 C, the voltage plateaus of the cells using HCE and RCE disappeared, while those of the cell using LHCE remained prominent, indicating that the LHCE system can adequately supply Li<sup>+</sup> in the ratedetermining step of intercalation. As depicted in Figure 5b, the graphite | Li cell with LHCE exhibits good rate potential for lithiation of graphite, especially they can deliver a high capacity of 220 mAhg<sup>-1</sup> at 4 C and the capacity retention



**Figure 5.** The electrochemical performance of graphite | Li cells using LHCE, HCE, and RCE after activation. a) Capacity-voltage curves at 1 C and 4 C. b) Rate capability for lithiation of graphite. c) Cycling performance and Coulombic efficiency with different electrolytes at 4 C. d) Capacity-voltage curves of the fifth cycle of graphite | Li cells with different electrolytes at 0.1 C under -20 °C.

reaches 64% of that at 0.2 C (340 mAh g<sup>-1</sup>). Unfortunately, the battery using HCE and RCE possess poor rate performance and only deliver a capacity of  $\approx 50 \text{ mAh g}^{-1}$  at 4 C. Although their reversible capacity is almost the same at low rates, the gap becomes obvious as the rate increases to 1 C.

Compared to HCE, the significantly improved rate capability employing LHCE can be attributed to the slow interface reaction kinetics caused by reduced viscosity and improved electrode/separator wettability.<sup>[13]</sup> The graphite | Li cell with LHCE is also highlighted with superior cycling stability at a high rate of 4 C, maintaining 85.5% capacity retention with an average Coulombic efficiency of about 99.8% even after 200 cycles (Figure 5c). The cell with RCE holds poor capacity at high rates. Therefore, the LHCE that inhibits the solvent co-intercalation into the graphite anode is conducive to the fast-charging and long cycle performance of LIBs.

Graphite with a high areal capacity loading  $(3.0 \text{ mAh cm}^{-2})$  is also used to evaluate the transportation behavior of Li ions through the electrode/electrolyte interface. The SEI induced by LHCE has better potential at high rate than that of RCE (Supporting Information, Figure S7).

After cycling at 2 C (Supporting Information, Figure S7) in cells, we found serious Li plating occurred in a RCE cell, island shaped spherical particles were covered on the surface of graphite (Supporting Information, Figure S8). However, in LHCE system, only the smooth morphology was appeared on graphite surface without plating of Li metal. This confirms that the anion-derived SEI can effectively inhibit the occurrence of Li plating.

Based on the low melting point and viscosity of the solvent DME and diluent BTFE as well as the robust inorganic-rich SEI, the LHCE system is expected to enable LIBs to operate at a low temperature range. As exhibited in Figure 5d, the graphite | Li cell of LHCE yields a high capacity of  $90 \text{ mAh g}^{-1}$  at 0.1 C rate at -20 °C, while the capacity of a battery in the HCE or RCE is close to  $0 \text{ mAh g}^{-1}$ . Moreover, the charge/discharge curve still maintains a clear voltage plateaus for the LHCE system, rather than a cliff-like decline due to the generation of extreme polarization for HCE and RCE systems.<sup>[21]</sup> Unfortunately, the cells using HCE cannot be cycled at low temperatures after 5 cycles due to severe deformities (Supporting Information, Figure S9). The cell with RCE also exhibits extremely low capacity with nonbattery behavior and maintains only 18 cycles (Supporting Information, Figure S10). In a graphite | Li cell with a high areal loading of  $3.0 \text{ mAh cm}^{-2}$ , the capacity of the cell with LHCE can maintain 90 mAh  $g^{-1}$  at 0.1 C, while the capacity in RCE is 12 mAh g<sup>-1</sup> (Supporting Information, Figures S11 and S12). The result is well consisting with the thin graphite anode. In contrast, the cell without any additive in RCE exhibits poor electrochemical performance at -20°C due to the extreme large charge-transfer resistance (Supporting Information, Figure S11). The charge-transfer resistance in a LHCE cell is 1/10 of that in a RCE cell, both before and after cycling (Supporting Information, Figure S11 and S13), indicating the de-solvation barrier of Li ions in a LHCE cell is significantly reduced.

Even as the rate increases, the LHCE cell can also maintain the efficient cycles (Supporting Information, Figure S14). The improvement in rate capabilities at a low temperature is mainly due to the fact that the LHCE system increases the ionic conductivity of the electrolyte at low temperatures to alleviate the concentration polarization, and the SEI layer derived from LHCE mainly composed of inorganic components can decrease the de-solvation barrier of the coordinated group.<sup>[22]</sup>

The linear sweep voltammetry (LSV) curve of LHCE was given to estimate the electrochemical anti-oxidant ability (Supporting Information, Figure S15). The anodic limit of LHCE was 4.3 V, which was 0.2 V lower than that of RCE, meaning the LHCE tends to decompose while the working voltage of a cell is over 4.3 V. When applied in  $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$  (NCM 523) | graphite full cells with the charge cut-off voltage at 4.2 V, the decomposition of electrolyte in the cell with LHCE was not observed and the specific capacity of LHCE cell owned apparent advantages over the RCE cell at 0.5 C (Supporting Information, Figure S16). Note that the higher salt-to-solvent molar ratio in the electrolyte results in less free solvent molecules and higher oxidation potential, if the anodic limit of ether-based LHCE wants to reach 4.5 V or more, the molar ratio of salt-to-solvent should be above 1:1.2.<sup>[14]</sup>

In summary, we probed the energy chemistry of unique solvation structure in LHCE to sufficiently suppress cointercalation of ether solvent into the graphite anode and exhibit fast-charging potential of LIBs. Herein the preferential decomposition of anions induced an integral SEI composed of inorganic components mainly including LiF, Li<sub>2</sub>O, Li<sub>2</sub>S, Li<sub>3</sub>N, and Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, which is highly conducive to inhibiting the co-intercalation of solvents and optimizing the rapid charging of LIBs. The graphite | Li cell using the LHCE system exhibits good rate performance (340 mAh g<sup>-1</sup> at 0.2 C and 220 mAh  $g^{-1}$  at 4 C), excellent cycling stability (ca. 85.5 % capacity retention for 200 cycles at 4 C) and impressive low temperature performance. The strategy herein extends the applications of the localized high-concentration electrolytes to LIBs with fast-charging and affords an effective method to inhibit the co-intercalation of solvent for next-generation LIBs.

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## Conflict of interest

The authors declare no conflict of interest.

Keywords: fast-charging · graphite anodes ·

lithium ion batteries  $\cdot$  localized high-concentration electrolyte  $\cdot$  solvent co-intercalation

- a) M. Li, J. Lu, Z. Chen, K. Amine, Adv. Mater. 2018, 30, 1800561; b) R. Mo, F. Li, X. Tan, P. Xu, R. Tao, G. Shen, X. Lu, F. Liu, L. Shen, B. Xu, Q. Xiao, X. Wang, C. Wang, J. Li, G. Wang, Y. Lu, Nat. Commun. 2019, 10, 1474; c) X.-Q. Zhang, C.-Z. Zhao, J.-Q. Huang, Q. Zhang, Engineering 2018, 4, 831–847; d) L. Jiang, X.-B. Cheng, H.-J. Peng, J.-Q. Huang, Q. Zhang, eTransportation 2019, 2, 100033.
- [2] a) W. Cai, Y.-X. Yao, G.-L. Zhu, C. Yan, L.-L. Jiang, C. He, J.-Q. Huang, Q. Zhang, *Chem. Soc. Rev.* 2020, *49*, 3806–3833; b) Y. Liu, Y. Zhu, Y. Cui, *Nat. Energy* 2019, *4*, 540–550; c) A. Tomaszewska, Z. Chu, X. Feng, S. O'Kane, X. Liu, J. Chen, C. Ji, E. Endler, R. Li, L. Liu, Y. Li, S. Zheng, S. Vetterlein, M. Gao, J. Du, M. Parkes, M. Ouyang, M. Marinescu, G. Offer, B. Wu, *eTransportation* 2019, *1*, 100011; d) G.-L. Zhu, C.-Z. Zhao, J.-Q. Huang, C. He, J. Zhang, S. Chen, L. Xu, H. Yuan, Q. Zhang, *Small* 2019, *15*, 1805389.
- [3] a) E. R. Logan, J. R. Dahn, *Trends Chem.* 2020, 2, 354–366; b) J. Kalhoff, G. G. Eshetu, D. Bresser, S. Passerini, *ChemSusChem* 2015, 8, 2154–2175.
- [4] a) J. Shi, N. Ehteshami, J. Ma, H. Zhang, H. Liu, X. Zhang, J. Li, E. Paillard, *J. Power Sources* **2019**, *429*, 67–74; b) C. Yan, Y.-X. Yao, W.-L. Cai, L. Xu, S. Kaskel, H. S. Park, J.-Q. Huang, *J. Energy Chem.* **2020**, *49*, 335–338; c) C.-Z. Zhao, B.-C. Zhao, C. Yan, X.-Q. Zhang, J.-Q. Huang, Y. Mo, X. Xu, H. Li, Q. Zhang, *Energy Storage Mater.* **2020**, *24*, 75–84.
- [5] a) L. Wang, A. Menakath, F. Han, Y. Wang, P. Y. Zavalij, K. J. Gaskell, O. Borodin, D. Iuga, S. P. Brown, C. Wang, K. Xu, B. W. Eichhorn, *Nat. Chem.* **2019**, *11*, 789–796; b) C. Yan, R. Xu, Y. Xiao, J.-F. Ding, L. Xu, B.-Q. Li, J.-Q. Huang, *Adv. Funct. Mater.* **2020**, *30*, 1909887.
- [6] S. Maruyama, T. Fukutsuka, K. Miyazaki, T. Abe, J. Appl. Electrochem. 2019, 49, 639–646.
- [7] Z. Wang, F. Qi, L. Yin, Y. Shi, C. Sun, B. An, H. M. Cheng, F. Li, Adv. Energy Mater. 2020, 10, 1903843.
- [8] a) K. Xu, Chem. Rev. 2004, 104, 4303-4417; b) H. Li, Z. Wang, L. Chen, X. Huang, Adv. Mater. 2009, 21, 4593-4607; c) H.-Y. Song, S.-K. Jeong, J. Power Sources 2018, 373, 110-118; d) L. Xing, X. Zheng, M. Schroeder, J. Alvarado, A. von Wald Cresce, K. Xu, Q. Li, W. Li, Acc. Chem. Res. 2018, 51, 282-289.

- [9] a) T. Liu, X. Han, Z. Zhang, Z. Chen, P. Wang, P. Han, N. Ding, G. Cui, *J. Power Sources* 2019, *437*, 226942; b) J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, J. G. Zhang, *Nat. Commun.* 2015, *6*, 6362; c) Y. Yamada, J. Wang, S. Ko, E. Watanabe, A. Yamada, *Nat. Energy* 2019, *4*, 269–280.
- [10] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, A. Yamada, J. Am. Chem. Soc. 2014, 136, 5039-5046.
- [11] L. Yu, S. Chen, H. Lee, L. Zhang, M. H. Engelhard, Q. Li, S. Jiao, J. Liu, W. Xu, J.-G. Zhang, ACS Energy Lett. 2018, 3, 2059–2067.
- [12] L. Qin, N. Xiao, J. Zheng, Y. Lei, D. Zhai, Y. Wu, Adv. Energy Mater. 2019, 9, 1902618.
- [13] S. Chen, J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, J. G. Zhang, *Adv. Mater.* **2018**, *30*, 1706102.
- [14] a) X. Ren, S. Chen, H. Lee, D. Mei, M. H. Engelhard, S. D. Burton, W. Zhao, J. Zheng, Q. Li, M. S. Ding, M. Schroeder, J. Alvarado, K. Xu, Y. S. Meng, J. Liu, J.-G. Zhang, W. Xu, *Chem* **2018**, *4*, 1877–1892; b) X. Ren, L. Zou, X. Cao, M. H. Engelhard, W. Liu, S. D. Burton, H. Lee, C. Niu, B. E. Matthews, Z. Zhu, C. Wang, B. W. Arey, J. Xiao, J. Liu, J.-G. Zhang, W. Xu, *Joule* **2019**, *3*, 1662–1676.
- [15] X. Zhang, L. Zou, Y. Xu, X. Cao, M. H. Engelhard, B. E. Matthews, L. Zhong, H. Wu, H. Jia, X. Ren, P. Gao, Z. Chen, Y. Qin, C. Kompella, B. W. Arey, J. Li, D. Wang, C. Wang, J. G. Zhang, W. Xu, Adv. Energy Mater. 2020, 10, 2000368.
- [16] P. Zeng, Y. Han, X. Duan, G. Jia, L. Huang, Y. Chen, *Mater. Res. Bull.* 2017, 95, 61–70.
- [17] J. Zheng, S. Chen, W. Zhao, J. Song, M. H. Engelhard, J.-G. Zhang, ACS Energy Lett. 2018, 3, 315–321.
- [18] Y. Zhao, C. Dong, L. Sheng, Z. Xiao, L. Jiang, X. Li, M. Jiang, J. Shi, ACS Sustainable Chem. Eng. 2020, 8, 8664–8674.
- [19] X. Fan, L. Chen, X. Ji, T. Deng, S. Hou, J. Chen, J. Zheng, F. Wang, J. Jiang, K. Xu, C. Wang, *Chem* **2018**, *4*, 174–185.
- [20] G. G. Eshetu, X. Judez, C. Li, M. Martinez-Ibanez, I. Gracia, O. Bondarchuk, J. Carrasco, L. M. Rodriguez-Martinez, H. Zhang, M. Armand, J. Am. Chem. Soc. 2018, 140, 9921 – 9933.
- [21] Y. Li, K. W. Wong, Q. Dou, W. Zhang, K. M. Ng, ACS Appl. Energy Mater. 2018, 1, 2664–2670.
- [22] a) J. Hou, M. Yang, D. Wang, J. Zhang, *Adv. Energy Mater.* 2020, *10*, 1904152; b) J. Holoubek, M. Yu, S. Yu, M. Li, Z. Wu, D. Xia, P. Bhaladhare, M. S. Gonzalez, T. A. Pascal, P. Liu, Z. Chen, *ACS Energy Lett.* 2020, *5*, 1438–1447.

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