Model-based Design of Stable Electrolytes for Potassium Ion Batteries

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ABSTRACT: Rechargeable potassium (ion) batteries (KIBs) are an emerging energy storage system with many potential advantages over existing battery systems (e.g., Li-ion, Na-ion battery). However, the electrolyte design for KIBs remains challenging because of serious electrolyte decomposition. Particularly, this problem is aggravated when using metal potassium anodes. Herein, we report that the cation-solvent (i.e., K^+ -solvent) solvation structure which is determined by the electrolyte composition plays a dominant role in the failure of KIBs. We present an analysis of the reaction pathway to understand the behavior of the cation-solvent structure at the surface of metal electrodes (e.g., metal plating or M^+ -solvent decomposition). The electronegativity change of cation-solvent structure was studied and correlated to the stability of the electrolytes. We find that the electrolyte decomposition can be induced when the K^+ -solvent structure accepts one electron from the electrode; however, this process can be suppressed by tuning the electronegativity through varying the solvent chemistry, anions type, and salt concentrations. Our results explain the high stability of existing high-concentration electrolytes, and present a general guideline to design stable electrolytes for KIBs. This approach can pave the way for the realization of high-performance K-ion batteries.

TOC

Potassium (ion) batteries (KIBs) have become a promising candidate for next-generation energy storage systems owing to the abundance of potassium.¹⁻³ Another key benefit of KIBs is the exceptionally negative potential of the K^+/K redox couple (i.e., -2.936 V vs. standard hydrogen electrode (SHE)), which is close to -3.040 V of Li^+/Li .⁴ This value is more negative in nonaqueous solutions (e.g., -0.09 V in propylene carbonate (PC)⁴ and -0.15 V in ethylene carbonate/diethyl carbonate (EC/DEC, v/v 1:1) vs. Li^+/Li reference⁵), which is attractive for pursuing higher energy density. For example, the K-S battery demonstrates a high theoretical specific energy density of 1023 Wh/kg.^{6, 7} However, the electrolyte choice for KIBs is rather limited compared to those of lithium and sodium-ion batteries due to the side-effects caused by electrolyte decomposition, thereby leading to inferior performance. These problems become more aggravated when K metal is used due to the high reactivity of K metal with the electrolyte. Although many problems are faced in the development of potassium ion batteries, such as instability, unsafety, low Coulombic efficiency (CE), and poor cycling performance,^{3, 8-10} the mechanism causing these performance issues remains unclear.

Herein, we present a new analysis about the root cause for failure of KIBs, and present new guidelines to design compatible electrolytes for the first time. Our approach considers the interactions and effects of solvent, anions, and concentration. A new competitive reaction pathway is presented to understand the reaction of the cation-solvent structure on the electrode surface (e.g., metal plating or M^+ -solvent decomposition to form solid electrolyte interphase (SEI)). We show that we can predict the stability of electrolytes through calculating the LUMO/HOMO energy of the cation-solvent structure and studying the electronegativity change of the solvent. We find that solvent decomposition (i.e., electrolyte decomposition) can be induced when the K^+ -solvent structure accepts one electron at the electrode surface, while this process can be suppressed through

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3 tuning the electronegativity of solvent (e.g., by changing the solvent, anions, and concentration).
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5 Our results not only provide the reason for the high stability of concentrated electrolytes but also
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7 present a new guideline to design stable electrolytes for KIBs, paving the way for designing the
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9 high-performance K-ion batteries.
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14 RESULTS AND DISCUSSIONS

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16 **Electrolyte stability in potassium batteries.** We present a new model to understand the behavior
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18 of the cation-solvent solvation structure (i.e., M^+ -solvent, where $M^+ = Li^+, K^+$) on the electrode
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20 interface, where two competitive reaction paths can be expected (**Figure 1a, b**). The first is where
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22 the M^+ -solvent unit could be de-solvated when the M^+ -solvent accepts one electron from the
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24 electrode, resulting in free M^+ which then gets plated on the electrode (e.g., copper foil or metal
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26 anode). The de-solvated M^+ can be also intercalated into the carbon or react with the alloying
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28 compound if the carbon or alloy anode is used as the anode. In this way, the electrolyte could be
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30 stabilized and the battery can work reversibly with high Coulombic efficiency (CE) because there
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32 are no side-reactions. Alternatively, the electron could also preferably transfer from M^+ to solvent
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34 in the M^+ -solvent unit and induce the solvent/anions decomposition for cases where the M^+ -solvent
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36 is not stable. The latter pathway is the well-known electrolyte decomposition process, where the
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38 solid electrolyte interphase could be formed at the electrode interface.¹¹⁻¹⁵ Note that these two
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40 pathways can both exist, while the latter (transfer from M^+ to solvent) could be suppressed once
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42 the SEI was formed on the electrode surface.¹⁶⁻¹⁹ This is because the electron-donating capacity
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44 and activities of the electrode can be reduced after the first or initial few cycles. However, the high
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46 stability of M^+ -solvent unit is required, otherwise, the electrolyte decomposition would occur
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48 continually on the electrode. Thus, the evaluation of M^+ -solvent unit stability becomes ever more
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50 important if we want to predict the electrolyte stability. Note that we exclude the chemical
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3 reactions between the electrode (i.e., copper foil or metal anode) and electrolyte in this model. This
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5 is because the electrolyte is not practical if the electrode could react with the electrolyte directly.
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8 Herein, we have tested the viability of our model by evaluating the M^+ -solvent stability at the
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10 electrode interface (**Figure 1c**, **Figure S1a**). In this model, the lowest unoccupied molecular
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12 orbitals (LUMO) are used to designate the critical orbitals for the M^+ -solvent-anion complex,²⁰
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14 where the corresponding orbitals become HOMO' when one extra electron is obtained from the
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16 electrode during the discharge. We designate the complex (after electron capture) as M^0 -solvent-
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18 anion, as we consider that both LUMO and HOMO' are mainly located on the metal. The energy
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20 difference (i.e., ΔE) between two pairs of orbitals (i.e., HOMO' - LUMO) can be used to evaluate
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22 the electron transfer efficiency from the metal M^0 to the solvent molecule. A smaller energy
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24 difference (HOMO' - LUMO) indicates the similarity between the orbitals, leading to smoother
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26 electron transfer and weaker stability of solvent molecules. In this case, we find that K^+ is more
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28 efficient at capturing electrons than Li^+ from the electrode surface, and donating them toward the
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30 solvent molecules since it has higher ΔE than that of Li^+ -solvent pair (**Figure 1d**, **Figure S1b**,
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32 **Table S1**). Therefore, the electrolyte in KIBs can more easily decompose and form an SEI on the
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34 electrode surface, giving rise to low CE and inferior cycle performance. Our simulations agree
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36 well with the experimental observations, where a much lower CE is obtained for potassium battery
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38 compared to that in lithium battery (**Figure S2**).
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46 **Solvent effect.** The above results suggest that a key factor for designing stable KIB electrolytes is
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48 to stabilize the K^+ -solvent structure. Thus, we investigated the solvent effect in potassium batteries
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50 using K | Cu half-cells. We find that a low CE of 41% and 12.5% are obtained in the classic
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52 carbonate-based electrolyte (e.g., EC/DEC, PC) when KPF_6 is used. However, the value of CE can
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54 increase to 72% and the polarization can be reduced when DME solvent is used instead of
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carbonate solvent (**Figure 1e**, **Figure S3-S4**). This comparative result shows that the solvent plays an important role in electrolyte stability, which is consistent with our simulations. Besides the solvent effect, we also studied the SEI effect on battery performance, since SEI has been believed to be effective for suppressing electrolyte decomposition and/or reducing side-reactions.²¹⁻²³

We prepared SEI-coated copper foil (i.e., Cu@SEI) electrode by discharging the K | Cu half-cell in 1.0 M KPF₆ in PC and then assembling a new K | Cu@SEI cell using 1.0 M KPF₆ in DME electrolyte. We find that the CE increases from 16.5% to 78.8% (**Figure 1f**). This result confirms that the CE can increase significantly when DME is used instead of PC solvent. In contrast, we prepared the Cu@SEI electrode by discharging the K | Cu half-cells in 1.0 M KPF₆ in DME, then we assembled a new K | Cu@SEI using the 1.0 M KPF₆ in PC electrolyte. We find that the CE decreases from 76.5% to 10.2%, demonstrating poor CE when DME is replaced by the PC solvent. Note that similar results were obtained when we increase the areal loading of K (from 0.15 to 0.5 mAh cm⁻²) and cycle numbers to 10 cycles (i.e., forming a more stable SEI²⁴) (**Figure S5**). These comparative results hint us that the solvent plays a critical role in determining battery performance. They also indicate that the formed SEI does not necessarily suppress electrolyte decomposition if the K⁺-solvent unit is not sufficiently stable. Our simulations do support these experimental results. The corresponding orbitals of K⁺-solvent-PF₆⁻ and K⁰-solvent-PF₆⁻ complexes are presented in **Figure 1g**. We find that the ΔE between the HOMO' of the K⁰-DME-PF₆⁻ and the LUMO of the K⁺-DME-PF₆⁻ is higher than those of other K-solvent-PF₆ complexes (**Figure 1h**, **Table S2**). The higher value indicates a weaker capacity of the K-solvent complex at transferring electron to the solvent, which means the lower possibility of solvent decomposition. Therefore, our simulation results confirm the relatively higher stability of DME, which is consistent with the experimental results. The electrochemical impedance spectroscopy (EIS) analysis of the cycled cell in different

electrolyte also corroborates with the variation trend of CE (i.e., degree of side-reactions) when we change the EC/DEC or PC solvent to DME (**Figure S6**).

In addition, the configurational structure of K^+ -solvent at the electrode-electrolyte interface was considered. This feature strongly depends on the type of solvent used and on the location of its anions. The location of anions might also affect K^+ -solvent stability. The PF_6^- anion is located closer to the K^+ -DME unit when compared with the K^+ -EC/DEC and K^+ -PC solvents, as shown in **Figure 2a-f**. This is because the carbonate solvent has a higher dielectric constant (i.e., $\epsilon_{EC}=89.78$; $\epsilon_{PC}=64.92$) compared to DME (i.e., $\epsilon_{DME}=7.2$).^{25,26} The stability of the K^+ -solvent might be increased if the anions were closer to the K^+ on the electrode interface. This is because the anion can reduce the electronegativity change of solvent when the K^+ -solvent unit accepts one electron. This viewpoint is consistent with our experimental results and will be discussed later. Our conjecture was further proved by the Raman and FTIR analysis (**Figure 2g-j**, **Figure S7**). First, the DME solvated PF_6^- can keep a close distance with the K^+ after the dissolution of KPF_6 salt in DME (**Figure 2h₁**, **2i₁**). This is because the dielectric constant of DME is lower, particularly the formed symmetrical five-ring structured $K^+[DME]_2$ by bidentate chelation is small (**Figure S8**). But, the solvated PF_6^- has weak Coulomb interaction with the K^+ due to the barriers of DME solvent (**Figure 2h₁**), especially for the PF_6^- that with a low coordination capability. It means that the PF_6^- and K^+ is hard to form the $K^+PF_6^-$ ionic pairs (**Figure 2h₁**). This was further confirmed by the FTIR analysis.²⁷ We find that the proportion of the $K^+-PF_6^-$ pairs in DME-based electrolyte is about 4.7%, which is much lower 8.8% and 9.5% in EC/DEC and PC-based electrolyte (**Figure 2h₂-h₃**, **Figure 2j**). This result demonstrates that the PF_6^- and K^+ in DME-based electrolyte was quarantined completely by DME (**Figure S8**). As a result, the redshift of PF_6^- peak in Raman is the most obvious in DME-based electrolyte compared to that in EC/DEC and PC-based electrolyte

(**Figure 2g**). In contrast, the completely solvated PF_6^- can keep a far distance with the K^+ in the EC/DEC or PC-based electrolyte due to the higher dielectric constant (**Figure 2h₂-h₃, 2i₂-i₃, Figure S8**).

Our theory was further proved when we change inorganic KPF_6 salt to organic potassium salt, such as potassium bis(fluorosulfonyl)amide (KFSI) (**Figure 2k-l**). The FSI^- can coordinate with the K^+ through the bridged oxygen, and then demonstrate higher coordination capability with K^+ in solution compared to that of PF_6^- (**Figure 2l₁**). Under such conditions, the solvated FSI^- can also interact with K^+ strongly even the FSI^- was solvated by the solvent. Thus, the solvated FSI^- can overcome the barrier effect of DME and interact with K^+ in DME-based electrolyte (**Figure 2l₁**). In this way, the FSI^- has the lower redshift in DME-based electrolyte compared to that in EC/DEC and PC-based electrolyte under the effect of the lower dielectric constant of DME (**Figure 2k, Figure 2l₂-l₃**). Our model can reflect the interaction and location of anions with K^+ in the electrolyte vividly, including the KFSI salt in the electrolyte (**Figure S9**), as discussed later. Besides, our model in **Figure 2h** can also interpret the reason for the limited solubility of KPF_6 salt in most ester (e.g., EC/DEC) and ether-based solvent (e.g., DME), in which sufficient solvent needs to solvate the K^+ and PF_6^- . In contrast, the FSI^- can be like a solvent to coordinate with the K^+ (**Figure 2l₁**), then the KFSI salt could be dissolved in most solvents with a high concentration. Finally, note that although the $\text{K} \mid \text{Cu}$ half-cells work better in the electrolyte of 1.0 M KPF_6 in DME than those in the carbonate-based electrolyte, the value of CE is only about 75.5%, which means there is plenty of room for improvement.

Anion Effect. The value of CE can be much improved when another potassium salt, such as KFSI, is used instead of KPF_6 . Specifically, the CE can increase from 41% and 12.5% to 81% and 67% in the EC/DEC or PC-based electrolyte, respectively (**Figure 3a**). Particularly, the value of CE can

increase from 75.5% to 92%, and also the polarization voltage can decrease from 0.32 V to 0.24 V in the DME-based electrolyte when the 1.0 M KFSI salt is used (**Figure 3a**, **Figure S4**). This result demonstrates that the anions also play a critical role in electrolyte stability (i.e., K^+ -solvent stability). We speculate that the FSI⁻ is located closer to the K^+ on the electrode interface according to our solvation structure and interfacial model. This is because the FSI⁻ has a stronger interaction with the K^+ and locates closely around the K^+ , even though the steric hindrance of FSI⁻ might be slightly higher than PF₆⁻ (**Figure 3b**). The higher binding energy of K^+ -FSI⁻ (i.e., 4.23 Kcal mol⁻¹) than 4.07 Kcal mol⁻¹ of the K^+ -PF₆⁻ pair can support this viewpoint. The K^+ solvation structure in the electrolyte and the interfacial model of the K^+ -DME and K^+ -PC on the Cu foils are shown in **Figure 3c-f**. Our simulation results in **Figure 3g-i** also demonstrate that the FSI⁻ can remain closer to K^+ than PF₆⁻ due to the higher binding energy of K^+ -FSI⁻. In other words, besides the effect of anions to reduce the electronegativity on solvent, the solvent can be excluded by the anions if the anions are located close enough to the K^+ ; under such conditions, the K^+ -solvent decomposition could be suppressed because the solvent can stay far from the K^+ . We believe that these are the main reasons causing the different battery performances observed when different potassium salts are used.

Concentration effect. The value of CE can be further improved various types of solvents when the KFSI salt concentration is increased to 5.0 M. Particularly, the value of CE can increase up to 98% in 5.0 M KFSI in DME (**Figure 4a**), in which improved potassium plating and suppressed dendrite formation can be observed clearly (**Figure S10**). The improved performance can be ascribed to the reduced number of solvent molecules used in the electrolyte. We find that the number of solvent molecules decreases from 9.616 to 1.92 (i.e., stoichiometrically calculated by the molar concentration) when the concentrated electrolyte was used, in which an aggregation of

solvent and anions can be formed (**Figure 4b**). Only about one DME molecule appears around the K^+ on the electrode surface according to our interfacial model, where the FSI^- is located closer to the K^+ (**Figure 4c**, **Figure S11**). This interfacial situation is different from that in dilute electrolytes, such as 1.0 M KFSI in DME, where more than 2DME molecules appear around the K^+ . Thus, together with the effect of the anion, the K^+ -DME becomes more stable than the K^+ -2DME during the process when the K^+ -solvent accepts one electron from the electrode. Note that the effect solvent, anion, and concentration are the main factors driving the electrode performance, while the SEI effect is minor. This is because the CE of $K | Cu@SEI$ decreases immediately to 90% when the KFSI concentration is reduced to 1.0 M in a new cell (**Figure S12-S13**). In addition, the higher stability of K^+ -DME compared to K^+ -EC/DEC and K^+ -PC pairs in concentrated electrolyte further confirm the validity of our model (**Figure S3c**). These simulations further support our results. We find that the ΔE (i.e., HOMO'-LUMO) of K^+ -DME under the high salt concentration is 0.074 Hartree, which is higher than 0.061 Hartree calculated for K^+ -2DME at low concentration (**Figure 4d**, **Table S3**). This trend is the same when we consider other anions. For example, ΔE of the K^+ -DME- FSI^- is 0.046 Hartree at high concentration, which is higher than 0.040 Hartree of K^+ -2DME- FSI^- at a low concentration. In addition, the HOMO'-LUMO value of the cation-solvent increased in the presence of FSI^- anions. This result further confirms the positive effect of anions in suppressing solvent reduction, which is consistent with the experimental results, particularly at high concentration.

The EIS analysis of the cell upon cycling also corroborates with the results when we compare the anions' concentration, or when change the EC/DEC or PC solvent to DME (**Figure S14**). Besides a reasonable interpretation for the reversible K plating/stripping behaviors on the current collector (e.g., Cu foil),^{9, 28} our model is applicable to interpret the reversible K^+ (de-)intercalation

within graphite and the mitigated electrolyte decomposition when the concentrated electrolyte was used.²⁹⁻³¹ One of the main reasons is the higher thermodynamic stability of K^+ -solvent and K^+ -solvent-anion, such as in the concentrated electrolyte of 4.0 M KFSI in EMC (i.e., $K^+[EMC]_{2.5}[FSI^-]$)²⁹ and 4.0 M KFSI in DME (i.e., $K^+[DME]_{2.4}[FSI^-]$)³¹ (**Figure S15**). This is because the solvent number around the K^+ on the electrode surface becomes less, while the frequency of FSI^- appeared around the K^+ -solvent becomes higher, which can reduce the K^+ -solvent polarization significantly and then enhance the electrolyte stability. Thus, we can conclude that increasing the concentration of electrolytes (i.e., reducing the average number of solvent molecules around K^+) also improves electrolyte stability, suggesting that the concentrated KFSI in DME should be an appropriate electrolyte for KIBs.

Application in K-S Battery. The advantages of 5.0 M KFSI in DME electrolytes were verified by a new high-performance K-S battery, in which the plated K anode and sulfurized polyacrylonitrile (SPAN) cathode were used (**Figure 5a**). The activation process of SPAN cathode (i.e., breaking of S-S bond)³²⁻³⁴ and the high reversibility of the K-S battery can be observed from the CV curves (**Figure 5b**). As a result, an extremely high average capacity up to 333.72 mAh g⁻¹ could be obtained at a current density of 200 mA g⁻¹ in the initial 300 cycles (**Figure 5c**). Particularly, a capacity of around 283.2 mAh g⁻¹ was retained after 300 cycles, meaning a capacity retention as high as 98.4% was achieved (**Figure 5d**). In addition, a robust rate capability was confirmed, where high capacities of 360, 340, 299, 242 and 172 mAh g⁻¹ were delivered at the rates of 0.1C, 0.2C, 0.5C, 1C and 2C (1C = 1000 mAh g⁻¹), respectively (**Figure 5e**). The capacity, cycle performance, and rate capabilities of our K-S battery are summarized and compared in **Figure 5f**.^{6, 7, 35-37} One of the reasons for the high performance of this K-S battery is our methodical approach to design the appropriate electrolyte, which can guarantee a high CE of 99.6%

and good cycle performance. In contrast, the lower capacity and CE of K-S battery in EC/DEC and PC-based electrolyte further confirms the advantages of DME-based electrolyte (**Figure S16**).

CONCLUSION

We have presented a new model for understanding electrolyte decomposition behavior in K-ion batteries by analyzing the competitive reaction pathways for the K^+ -solvent pairs on the metal anode surface. We experimentally investigated the effect of solvent chemistry, anion type, and electrolyte concentration on electrolyte decomposition behavior in KIBs. By using molecular orbital, cation-solvation structure, and interfacial model calculations, a compatible electrolyte was predicted and tested in KIBs. Our experimental and theoretical analysis presents a new point of view for understanding electrolyte decomposition in KIBs and offers a new guideline to design stable electrolytes for KIBs (e.g., K-S batteries). Although we have specifically explained the main electrolyte failure mechanism in potassium (ion) batteries, we believe our results are applicable in other battery systems.

Figure 1. A model of the competitive reaction paths for cation-solvent structure, geometrical simulation, and solvent effect for K plating/stripping behaviors. The model for the (a) lithium and (b) potassium (ion) batteries. (c) HOMO-LUMO simulation figures of K-solvents before (K^+) or after (K^0) accepting one extra electron obtained from the electrode. (d) Comparative HOMO'-LUMO energy (ΔE s) of cation-solvent. (e) Typical voltage vs. capacity profiles during the K plating/stripping process in K | Cu cell using different solvent (e.g., PC, EC/DEC, DME) in KPF_6 -based electrolyte. Insets are a schematic illustration of K | Cu cell and optical micrographs of the plated K on Cu in 1.0 M KPF_6 in PC (left) and 0.8 M KPF_6 in DME (right), respectively. (f) Revisiting the SEI effect to suppress electrolyte decomposition. (g) HOMO-LUMO simulation figures of K-solvents- PF_6^- before (K^+) and after (K^0) accepting one extra electron from the electrode. (h) HOMO'-LUMO energy (ΔE s) of K^+ -solvents- PF_6^- .

Figure 2. Schematic illustration of molecular interaction between solvent and solute in different systems. The K^+ solvation structure and interfacial behaviors in the different electrolytes of (a, b) 0.8 M KPF_6 in DME, (c, d) 0.8 M KPF_6 in EC/DEC, and (e, f) 1.0 M KPF_6 in PC. (g) Comparative Raman spectrum, (h, h_1 - h_3) schematic interaction of ions (K^+ , PF_6^-) and solvent, (i, i_1 - i_3) simulated cation solvation structure and proposed interaction with the PF_6^- anions in different kinds of solvents, and (j) FTIR analysis of KPF_6 -based electrolyte. (k) Comparative Raman spectrum and (l, l_1 - l_3) schematic interaction of ions (K^+ , FSI^-) and solvent in $KFSI$ -based electrolyte.

Figure 3. Anion effect for K plating/stripping behaviors. (a) Typical voltage vs. capacity profiles during the K plating/stripping process in K | Cu cell using different solvents in KFSI-based electrolyte. Inset is the molecular structure of FSI⁻. (b) Binding energy of K⁺-anion (L) and the stack form of solvent (B). Insets are buried volume (%V Buried) calculations of PF₆⁻ and FSI⁻. The K⁺ solvation structure and interfacial behaviors in the electrolyte of 1.0 M K-salt (e.g., KPF₆, or KFSI) in (c, d) DME, and in (e, f) PC. Simulated interfacial behavior of the electrolyte of (g) 1.0 M KFSI in DME, (h) 1.0 M KPF₆ in DME, and (i) 1.0 M KFSI in PC electrolytes on the Cu foil, respectively.

Figure 4. Concentration effect for K plating/stripping behaviors. (a) Typical voltage vs. capacity profiles during the K plating/stripping process in K | Cu cells using different solvent (e.g., PC, EC/DEC, DME) in 5.0 M KFSI-based electrolyte. (b, c) The K^+ solvation structure and interfacial behaviors in 5.0 M KFSI in DME. (d) HOMO-LUMO and HOMO'-LUMO' energy (ΔEs) of K^+-2DME (low concentration) and K^+-DME (high concentration) with or without FSI^- before (K^+) or after (K^0) one extra electron obtained from the electrode. Insets are LUMO and HOMO' simulation figures.

Figure 5. High-performance K-SPAN Batteries. (a) Schematic configuration of K-SAN full battery. (b) CV curve under the scan rate of 0.1 mV s^{-1} . (c) Typical voltage vs. capacity profiles and (d) cycle performance in the initial 300 cycles. (e) Rate capability. (f) Comparison of capacity vs. other kinds of K-S batteries.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Experimental and simulation sections, **Figures S1-S9** and **Table S1-S3** are included.

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Notes

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Author Contribution

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. †J. Zhang and Z. Cao contributed equally.

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