Lithium carboxylate: Effectively suppressing hydrogen evolution by self-introducing CO\(_2\) in aqueous electrolyte

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**HIGHLIGHTS**

- Both Li\(_2\)CO\(_3\)CH\(_3\) and Li\(_2\)CO\(_3\)CF\(_3\) aqueous electrolytes can self-introduce CO\(_2\).
- CO\(_2\) is introduced as a film-forming additive via the decarboxylation reaction.
- The Li\(_2\)CO\(_3\) SEI film can effectively suppress hydrogen evolution.
- 28 M Li\(_2\)CO\(_3\)CF\(_3\) aqueous electrolyte widens the electrochemical window to ~3.0 V.

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**ABSTRACT**

We have found that the formation of passivation film plays a major role in the negative shift of the decomposition voltage in the hydrogen-generating process. Both the hydrolysis of weak acid ions and the decarboxylation reaction of carboxylate can make the Li\(_2\)CO\(_3\)CH\(_3\) produce a passivation film to inhibit the water decomposition to a certain extent. As for the Li\(_2\)CO\(_3\)CF\(_3\) without hydrolysis of weak acid ion, it can be highly possible to facilitate the introduction of CO\(_2\) via its carboxylate specific decarboxylation reaction, and further produce lithium carbonate passivation film as well. However, the water decomposition voltage in the oxygen-producing process is more dependent on the properties of lithium salt anions. Those with strong electron-absorbing groups such as the trifluoromethyl are more likely to effectively endure the aqueous electrolyte with a high oxidative decomposition potential. Moreover, the concentration of Li\(_2\)CO\(_3\)CF\(_3\) aqueous electrolyte can reach up to 28 mol kg\(^{-1}\), and hence the electrochemical stability window of this water-base electrolyte can be expanded to about 3.0 V. This work provides a new idea for the selection of high concentration lithium salt.

1. Introduction

With the rapid development of electrochemical energy technology, lithium-ion batteries with high energy density \([1]\), excellent cycle performance \([2]\) and good rate performance \([3]\) have been widely used in the small and medium electrical equipment, such as mobile telephones, laptops and electrical cars. They are also considered as one of the most promising energy supplies for the electric vehicles, smart grids and so on \([4]\). However, it has been greatly limited the applications in large-scale power energy fields \([5]\) owing to its intrinsic disadvantages such as safety problems and toxicity from organic electrolytes \([6]\), severe demand for waterless and oxygen-free operation environment, and high cost of equipment requirements. Compared with nonaqueous lithium-ion batteries, aqueous ones \([7-9]\) have the advantage of two orders of magnitude higher than the organic ones in terms of ionic conductivity \([10]\). What’s more, they are also low-cost \([11,12]\), and have no the harsh environmental requirements \([13]\), therefore, they are undoubtedly more competitive than the former \([14]\). However, due to the presence of hydrogen evolution \([15]\) and oxygen evolution side reactions, the stable electrochemical window of aqueous electrolyte is only about 1.23 V \([16]\), which also makes the aqueous lithium-ion battery a big challenge for the application in large-scale energy storage equipment \([17]\). In order to solve the problem of narrow electrochemical window of aqueous lithium-ion batteries, Suo et al. \([18]\) have...
first proposed the concept of “water-in-salt” [19] in a high-concentration aqueous electrolyte. In their work, 21 mol kg\(^{-1}\) lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) water-base electrolyte was prepared, its stable electrochemical stability window was first broadened to 3.0 V. The new electrolyte electrochemical performance was studied with Mo\(_6\)S\(_8\) anode material, which showed completely different performances from the traditional lithium salts such as lithium nitrate (LiNO\(_3\)) and lithium sulfate (Li\(_2\)SO\(_4\)). It can normally appear two redox peaks, which were not possible in the case of traditional dilute aqueous electrolytes. In addition, they also obtained 28 mol kg\(^{-1}\) water-in-bisalt higher concentration aqueous electrolyte by adding 7 mol kg\(^{-1}\) lithium bis(pentafluoroethanesulfonyl)imide (LiBTFI) to the 21 mol kg\(^{-1}\) LiTFSI water-base electrolyte, and its electrochemical window was further expanded to about 3.1 V [20]. It can be seen that the strategy of using ultra-concentration lithium salt can effectively solve the problem of much too narrow electrochemical window. In the reported studies of high-concentration aqueous electrolytes [21], except for the lithium sulfonimide salts such as LiTFSI [22], [13,20,23] or LiNO\(_3\) [24–26], there are also reports about the lithium acetate (LiCO\(_2\)CH\(_3\)). For example, Wu et al. [27] used a saturate LiCO\(_2\)CH\(_3\) aqueous electrolyte in the Li–S battery system, but their work only focused on the modification of sulfur electrode without analyzing the properties of the electrolyte. Lukatskaya et al. [28] also reported a mixed 40 mol kg\(^{-1}\) ultra-high concentration acetate aqueous electrolyte prepared by mixing 8 mol kg\(^{-1}\) LiCO\(_2\)CH\(_3\) and 32 mol kg\(^{-1}\) potassium acetate (KCO\(_2\)CH\(_3\)). And the electrolyte made the batteries with a variety of material systems obtain excellent electrochemical performance. However, the nature of this kind of water-base electrolyte has been still not clear enough.

In our work, the properties of lithium carboxylate aqueous electrolyte have been studied deeply. We have found that both the hydrolysis of weak acid ion (−COO\(^-\)) and decarboxylation reaction of LiCO\(_2\)CH\(_3\) make the electrolyte have unique electrochemical properties. That is to say, the passivation film mainly composed of lithium carbonate (Li\(_2\)CO\(_3\)) formed by the dissolution of CO\(_2\) can inhibit water decomposition to a certain extent. Although lithium trifluoroacetate (LiCO\(_2\)CF\(_3\)) is just one kind of strong acid and strong base lithium salt without hydrolysis of weak acid ion, it can be quite likely to facilitate the introduction of CO\(_2\) through its decarboxylation reaction specific to carboxylate, and further produce Li\(_2\)CO\(_3\) passivation film as well. Meanwhile, due to the strong electron absorption effect of trifluoromethyl (−CF\(_3\)), its solubility in water can be further improved to 28 mol kg\(^{-1}\), so that the
The electrochemical window of the electrolyte can be expanded to about 3.0 V. Therefore, this work provides a new idea for the selection of high concentration lithium salt. In addition, we have also proposed an opinion that the main factors of affecting the stable electrochemical window should be considered separately. We think the passivation film plays a very important role in the negative shift of the decomposition voltage during the hydrogen-generating process. On the other hand, the water decomposition voltage in the oxygen evolution process depends much on the properties of anions that have strong electron-withdrawing groups such as nitrate or trifluoromethyl. If they have a strong interaction with water, or to say, have a certain destructive ability to hydrogen bond, can effectively expand the electrochemical window. We have used some characterizations like nuclear magnetic resonance (NMR) and Raman spectroscopy to conduct preliminary verification. The result is also consistent with the mechanism explanation about the high-concentration 21 M LiTFSI water electrolyte proposed by Lim et al. [29] based on the femtosecond infrared radiation (IR) spectroscopy and molecular dynamics simulation.

2. Experiment section

2.1. Material preparation

The lithium acetate (99.9%), D₂O (99.9 atom % D), lithium nitrate (99.9%) were purchased from the Energy Chemical, China. The lithium trifluoroacetate (97%), lithium formate (99%), LiTFSI(99%), MoS₂ (99%), CuS (99%), and concentrated dispersion of polytetrafluoroethylene (PTFE, 60%) were all bought from Aladdin, China. The LiMn₂O₄ was from Xiya Reagent Co., Ltd., China. All the aqueous electrolytes were prepared at the molality (mol-salt in kg-solvent) according to the required concentration. The deuterium solvent was used for the ¹⁷O NMR tests to lock fields. The binder of PTFE was diluted ten times from the concentrated dispersion.

The activated carbon working electrode was obtained by mixing up with activated carbon and PTFE at a mass ratio of 9 : 1. The mixture was adjusted with deionized water, followed by coating on a nickel foal, and then dried in a vacuum oven at 60 °C overnight.

The Chevrel phase Mo₆S₈ was prepared by removing Cu from Cu₂Mo₆S₈ with the molten salt synthesis method reported before [30]. The first step was grinding the mixture of CuS, Mo powder and MoS₂ for at least 2 h, followed by calcining at 80 °C for 1 h, and gradually heating to 850 °C for 60 h at 2 min⁻¹ in the Argon atmosphere. The next step was stirring the product calcined before in a 6 mol L⁻¹ HCl solution for about 2 days. Finally, the product was washed with deionized water three times, and then dried at 80 °C overnight under vacuum.

2.2. Material characterization

The X-ray diffraction (XRD) data were got by using the Rigaku miniflex 600 X-ray diffractometer with Cu Kα radiation from 10° to 90° at 2° min⁻¹. The scanning electron microscopy (SEM) pictures were picked by the field-emission scanning electron microscopy (FESEM, HITCHI 4800). The transmission electron emission (TEM) images were collected by using the TECANI G2 F30 device. The X-ray photoelectron spectroscopy (XPS) analysis was examined on the PHI Quantum 2000 equipment. The Raman spectra results were acquired on the Xplora Raman microscopy system with 532 nm Ar-ion laser. All the electrolytes of ¹⁷O NMR spectra on solvent were conducted on the Bruker AV400 spectrometer at the constant temperature of 25 °C.

2.3. Electrochemical measurement

The electrodes were both fabricated by mixing active material powder (Mo₆S₈ or LiMn₂O₄), Super P and poly(vinylidene difluoride) (PTFE) at a mass ratio of 8 : 1 : 1, and the mass ratio of cathode and anode was about 2 : 1. The cyclic voltammetry (CV) tests were performed on the three-electrode system composed of stainless steel grid working/counter electrode and Ag/AgCl reference electrode at 10 mV s⁻¹.
scanning rate on an electrochemical work station (CHI 600D). The samples were equilibrated in a 25 °C thermostat water-bath, and each sample was passed nitrogen for at least 1 h to remove dissolved oxygen from the electrolyte before testing. The active material electrode (Mo₆S₈ or LiMn₂O₄) was also used as a working electrode, together with the active carbon counter electrode and Ag/AgCl reference electrode, at a scanning rate of 0.1 mV s⁻¹ to investigate the electrochemical performance. The aqueous full batteries composed of LiMn₂O₄ cathode (about 16 mg cm⁻²), glass fiber and Mo₆S₈ anode (about 8 mg cm⁻²) were assembled in the 2016-type coin cells in the atmosphere, and then carried out the galvanostatic charge-discharge tests on a Land BT2000 battery test system (Wuhan, China) at 25 °C. The ionic conductivity was measured in the way mentioned before [22].

3. Results and discussion

First of all, to ensure the concentration diversity of aqueous electrolyte experimental investigations, we selected 1 mol kg⁻¹ dilute solution as a representative of low concentration, and the 5 mol kg⁻¹ one as a representative of high concentration. In addition, LiTFSI and LiNO₃ were used to compare with the LiCO₂CH₃ and LiCO₂CF₃. Then the cyclic voltammetry (CV) tests were performed, and the electrochemical windows of four different aqueous electrolytes in two concentrations were compared, respectively (Fig. 1, e and f). We have found that whatever at 1 mol kg⁻¹ or 5 mol kg⁻¹, the water decomposition voltage sequence of the four electrolytes at the hydrogen evolution basically satisfies such an arrangement order: LiCO₂CH₃ < LiCO₂CF₃ < LiTFSI < LiNO₃, but the oxygen evolution zone is LiTFSI > LiNO₃ > LiCO₂CF₃ > LiCO₂CH₃. According to the above phenomena, we propose a conjecture, namely, the water decomposition voltage during the hydrogen evolution process depends largely on the formation of passivation film. The lithium carboxylate is most likely to introduce CO₂ via the characteristic Kolbe [31] decarboxylation reaction [32] and then form a passivation film with main component of Li₂CO₃ even in a dilute aqueous solution. As we all know, the decarboxylation can produce CO₂ and free radicals, and the reaction formula is as follows:
RCOO$^-$ → RCOO$^-$ + e$^-$
RCOO$^-$ → R + CO$_2$

2R → \[	ext{R-R} \]

For specific electrochemical decarboxylation reaction, taking LiCO$_2$CH$_3$ as an example, the reaction mechanism can be expressed as follows:

\[2\text{CH}_3\text{COO}^- \rightarrow \text{electrolysis} \rightarrow \text{CH}_3\text{CH}_3^- + 2\text{CO}_2 \]

What's more, LiCO$_2$CF$_3$ is easier to introduce CO$_2$ in a similar reaction due to the electron absorption of –CF$_3$ (more details are shown in the supporting information), so as to form a passivation to inhibit water decomposition, which is also consistent with the experimental phenomenon.

Of course, in addition to the unique decarboxylation reaction, LiCO$_2$CH$_3$ can also promote the dissolution of CO$_2$ in the air by hydrolysis of weak acid ions. To prove this point, we have tested the pH values of the electrolytes before and after the CV tests (Supporting information, Table 1), and found that they did have a significant change. Besides, the importance of passivation film to affect hydrogen evolution decomposition potential can also be further illustrated by both the LiNO$_3$ and LiTFSI water-base electrolytes. The LiNO$_3$ aqueous electrolyte is completely unable to generate the passivation film from beginning to end, and the LiTFSI one can only obtain a little layer by absorbing a small amount of CO$_2$ in the air by weak hydrolysis under the condition of at least 5 mol kg$^{-1}$ [33]. In this way, the importance of passivation film and the reasonableness of our conjecture can be said with more certainty. The existence of the passivation film will be demonstrated in the subsequent characterization. As for the water decomposition voltage in the oxygen evolution area, it is more dependent on the nature of lithium salt anions, which are embodied in the close interaction with water molecules. If they have strong electron withdrawing groups such as nitrate or trifluoromethyl, or to say, they can cause some damages to the hydrogen bond, the oxygen evolution potential of the electrolyte will undergo a significant positive shift.

As a rough verification of this viewpoint, the electrochemical windows of two carboxylates (LiCO$_2$CH$_3$ and LiCO$_2$CF$_3$) aqueous electrolytes with different concentrations were tested at 25°C. From the result, we can see the stable electrochemical window of LiCO$_2$CH$_3$ aqueous electrolyte (Fig. 1 g) is only about 2.3 V even under the saturated condition (less than 9.0 mol kg$^{-1}$). On the other hand, the LiCO$_2$CF$_3$ one (Fig. 1 h) surprisingly increases the electrochemical stability window to nearly 3.0 V, almost comparable to the 21 mol kg$^{-1}$ LiTFSI [22]. That can benefit from the strong electron-withdrawing effect of fluorine atoms, which greatly improves its solubility in water, thus obtaining a 28 mol kg$^{-1}$ ultra-high concentration aqueous electrolyte. To be more convincing, both $^{17}$O NMR spectra and Raman vibrational spectroscopy of the solvent had been applied to further verify the prediction.
Firstly, we define the chemical shift of D$_2$O oxygen nucleus as a baseline of 0 ppm. As shown in the comparison of NMR spectra of different electrolytes (Fig. 2 a and b), we can find the large difference between dilute and concentrated solutions, which means that the environment around oxygen atoms in water molecules has changed dramatically. Under the condition of low concentration, water molecules mainly interact closely with Li$^+$, which is generally accepted as a solvation layer model, where about four solvent molecules locate around Li$^+$ to form a solvation sheath. In this case, the oxygen atoms of water are mainly attracted by the electrostatic attraction of Li$^+$. It leads to the decrease of electron cloud density, and then the chemical shift moves to a positive direction. When the concentration increases to a certain degree, the anions may enter into the solvation sheath or come closer to Li$^+$, so as to break the initial balance. As a result, the electron cloud density belonging to H$_2$O oxygen atom is determined by both cation and anion. In such a condition, the electrostatic attraction of Li$^+$ reduces the electron cloud density and the anions also weaken the deshielding effect of water molecules by directly interacting with Li$^+$. What’s more, the excess anions in the vicinity may also indirectly interact with Li$^+$ through the hydrogen-oxygen bond. Therefore, it causes the electron cloud density to drop in no small measure. Finally, the combined effect is that the chemical shift of the solvent oxygen moves from a low field to a high field with a significant negative shift. To be specific, as we can see, the chemical shift of the solvent in LiCO$_2$CH$_3$ aqueous electrolyte is up to about 2.7 ppm in a dilute solution, but no more than −0.4 ppm in a high concentration solution, which should be related to the slight interaction between the anion and water molecule. Its deshielding effect on the electron cloud on solvent oxygen is not as strong as that of other lithium salt anions, thus hardly moving to a higher field than others. In contrast to the LiCO$_2$CH$_3$, the LiTFSI moves from 1.8 ppm (1 M) to −3.5 ppm (5 M), which is greatly owing to its bulky trifluoromethylsulfonimide anion group (−N(SO$_2$CF$_3$)$_2$) with strong electron-withdrawing action. It is also noted that the other two electrolytes, LiNO$_3$ and LiCO$_2$CF$_3$ aqueous electrolytes, exhibit almost the same change (2.1 ppm and 2.2 ppm in 1 M, −2.8 ppm and −2.5 ppm in 5 M, respectively), which is attributed to their approximate impact of anions. All in all, the results given above are excellently consistent with the order of decomposition potential of water in the oxygen evolution zone.

In addition, the Raman spectroscopy was also employed to demonstrate the conclusion. Four kinds of electrolytes with two concentrations were observed, mainly focusing on the proportionality differences in five OH stretching sub-bands located at 3041 cm$^{-1}$, 3220 cm$^{-1}$, 3430 cm$^{-1}$, 3572 cm$^{-1}$ and 3600 cm$^{-1}$, (Fig. 2c and d). The different frequencies can be ascribed to be engaged in different types of local hydrogen bonding which can reflect several different states of water molecules [18]. In other words, with the increase of the proportion of high-frequency wavelength, the hydrogen bond in the solution system will be destroyed to a greater extent, and the interaction between water molecules will be weakened as well. In details, we can see from the
Raman spectroscopy data of the four dilute electrolytes in Fig. 2 c. They all show similar results on the whole, but the normalized Raman intensity ratio of LiTFSI electrolyte at two frequencies around 3600 cm$^{-1}$ is slightly higher than that of the other three ones. It means the hydrogen bond network structure of water molecules in the electrolyte is damaged to a greater extent (Fig. S1 a in details). When the concentration increases 5 mol kg$^{-1}$, the existing form of water molecules in LiTFSI electrolyte is obviously different from the dilute solution, especially at 3572 cm$^{-1}$ and 3636 cm$^{-1}$, which are raised from the initial 21.99% and 14.65%–34.14% and 14.65% respectively (more relevant details are presented on Fig. S1, Table 2 and Table 3 in the Supplementary information). It suggests that this kind of lithium salt is excellently advantageous in inhibiting water decomposition to produce oxygen, especially compared with LiTFSI in the same concentration, Chevrel phase Mo$_6$S$_8$ anode materials were also chosen for CV testing. As we know, the LiTFSI aqueous electrolyte makes it function normally under the condition of no less than 10 M [18]. However, the LiCO$_2$CH$_3$ one allows two pairs of redox peaks to reversibly appear under only a matter of 5 M condition, which seems to indicate the existence of passivation film and the superiority of such a kind of lithium salt. Of course, in order to ascertain the existence of passivation film, TEM (Fig. 3 c and d) and XPS (Fig. 3 e-g) characterizations were carried out. The results are shown in the TEM comparison charts of Mo$_6$S$_8$ anode materials cycled 10 times before (Fig. 3 c) and after (Fig. 3 d) in the saturate LiCO$_2$CH$_3$ electrolyte. It can be found that there is indeed a layer of passivation film with about 5 nm thickness. According to the XPS characterization analyses of Li1s, C1s and O1s, the main component can be confirmed to be Li$_2$CO$_3$, which also explains the rationality of our previous conjecture to some extent. By the way, we also applied the LiCO$_2$CH$_3$ aqueous electrolyte to LiMn$_2$O$_4$ cathode material (Fig. 3 b). And it can be reversibly cycled under both dilute solution and saturate concentration conditions, which also shows its practicality of this electrolyte system. As for the passivation film formed in the 28 M LiCO$_2$CF$_3$ aqueous electrolyte, it’s nearly twice as thick as in the LiCO$_2$CH$_3$ one (Fig. 4 c) and the composition is also mainly Li$_2$CO$_3$ (Fig. 4 d-g). It should be noted that the passivation film generated in 21 M LiTFSI aqueous electrolyte is mainly composed of LiF, which also suggests the differences of reaction mechanism between the two electrolytes. Similarly, the CV tests on LiCO$_2$CF$_3$ water-base electrolytes with several different concentrations (5 M, 10 M, 20 M, and 28 M) were performed (Fig. 4 a). The results are in agreement with our expectations, and resemble to the previous report [18].

To further demonstrate the importance of introducing CO$_2$ and the utility of this type of lithium carboxylate, two sets of control experiments were designed. In the first set, we artificially dissolved a certain amount of CO$_2$ into three dilute electrolytes LiCO$_2$CH$_3$, LiCO$_2$CF$_3$ and LiTFSI to prepare these electrolytes with different CO$_2$ concentrations, respectively. In the second set, we added a certain amount of Na$_2$CO$_3$ to the 5 M LiCO$_2$CH$_3$, 10 M LiCO$_2$CF$_3$ and 20 M LiTFSI to prepare these electrolytes with different Na$_2$CO$_3$ concentrations, respectively. Then, we chose the full aqueous Li-ion cells with Mo$_6$S$_8$ and LiMn$_2$O$_4$ as anode and cathode materials in the saturate LiCO$_2$CH$_3$ (c and d) and 28 M LiCO$_2$CF$_3$ (e and f) aqueous electrolytes at the current density of 0.02 A g$^{-1}$, respectively.

![Fig. 6. a, Ionic conductivity at 25°C in different concentrated LiCO$_2$CF$_3$ electrolytes (1 M, 5 M 10 M, 20 M and 28 M); b, Arrhenius plots of Lithium ion conductivity in the temperature range of 10°C-50°C; Electrochemical performance of full aqueous Li-ion cells using Mo$_6$S$_8$ and LiMn$_2$O$_4$ as anode and cathode materials in the saturate LiCO$_2$CH$_3$ (c and d) and 28 M LiCO$_2$CF$_3$ (e and f) aqueous electrolytes at the current density of 0.02 A g$^{-1}$, respectively.](image-url)
amount of CO₂ into the 1 M and 5 M LiNO₃ aqueous electrolytes respectively before the CV tests. During the test, we kept them in a CO₂ atmosphere so as to produce a Li₂CO₃ passivation film. It can be seen from the results (Fig. 5 a and b), compared with the initial two kinds of LiNO₃ electrolytes, the dilute one after appropriate treatment obtains a marked negative shift in the hydrogen evolution potential, so does the concentrated one. These are also what we expected. The results indicate that the introduction of CO₂ to generate a passivation film is favorable to broaden the hydrogen evolution potential. In the second set, four mixed electrolytes were obtained by adding 1 M LiCO₂CF₃ or LiCO₂CF₂ to 4 M LiNO₃ water-base electrolytes and 5 M LiCO₂CF₃ or LiCO₂CF₂ to 10 M LiNO₃ water-base electrolytes respectively, and then the electrochemical windows were tested. The results show that the hydrogen evolution potential of LiNO₃ electrolyte with only 1 M lithium carboxylate salt changes relatively small (Fig. 5 d). However, as the concentration increases to 5 M, it has a significant negative shift, which is quite similar with the effect of artificially introducing CO₂ (Fig. 5 f). This suggests that concentration is also a key factor. Anyway, no doubt about it, these results are quite intuitive and beneficial to prove the uniqueness and availability of the lithium carboxylate represented by these two lithium salts. And it is also believed that more unexpected surprises will be gotten if we carry out more reasonable systematic researches on them.

What’s more, ionic conductivity of LiCO₂CF₂ electrolytes with different concentrations at 25 °C were measured (Fig. 6 a). And LiMnO₂||MoorS full aqueous lithium-ion batteries were also assembled and tested. They were charged and discharged for 100 cycles at a current density of 0.02 A g⁻¹ with saturated LiCO₂CH₂ (Figs. 6 c) and 28 M LiCO₂CF₃ (Fig. 6 e) aqueous electrolytes, respectively. However, due to the harsh reaction conditions and simplicity of leading a residual impurity (mostly MoS₂) in the calcining process, the samples synthesized by us for many times cannot still reach the standard of completely high purity (Supplementary Fig.S2 a). Though it has little impact on the previous characterizations such as CV tests, it still unavoidably leads to low full-battery capacity. Even so, the 28 M LiCO₂CF₂ solution still enables the full-cells to own more outstanding cyclic stability than the saturated LiCO₂CH₃ does, which shows its decent applicability and superiority. This also indicates that the decrease of water molecule numbers, or to say, the reduction of their activity is critical to the performance in a full-battery system.

4. Conclusions

We have investigated the properties of lithium carboxylate (LiCO₂CH₂ and LiCO₂CF₂) water-base electrolytes by using the NMR, Raman spectroscopy and other characterization methods. It is revealed that their unique advantages probably ascribe to the introduction of CO₂ by decarboxylation reaction of this specific carboxylate and in turn to generate passivation film. In addition, it is the effect of strong electron-donating of the trifluoromethyl groups that its solubility in water is improved to 28 mol kg⁻¹, and the stable electrochemical window of this aqueous electrolyte is widened to 3.0 V. Its mechanism is in conformity with that about LiFTSI recent report [29]. Based on the previous results, we are more firmly to believe that this is a kind of novel electrolyte with enormous developmental potential. We also hope that more people can conduct in-depth explorations, and more unique properties of this electrolyte can be gradually unveiled in the near future.

Declaration of competing interests

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.

CRediT authorship contribution statement

Shuangshuang Lin: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Visualization, Investigation, Software, Validation, Writing - review & editing. Haiming Hua: Software, Writing - original draft, Visualization. Jiayang Li: Software, Data curation, Visualization, Investigation, Supervision, Software. Peng Zhang: Conceptualization, Methodology, Supervision. Jinbao Zhao: Conceptualization, Methodology, Supervision.

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Appendix. BSupplementary data

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References
