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Lithium carboxylate: Effectively suppressing hydrogen evolution by self-introducing CO₂ in aqueous electrolyte

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HIGHLIGHTS

• Both LiCO₂CH₃ and LiCO₂CF₃ aqueous electrolytes can self-introduce CO₂.

• CO2 is introduced as a film-forming additive via the decarboxylation reaction.

• The Li₂CO₃ SEI film can effectively suppress hydrogen evolution.

• 28 M LiCO₂CF₃ aqueous electrolyte widens the electrochemical window to \sim 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 $LiCO_2CH_3$ produce a passivation film to inhibit the water decomposition to a certain extent. As for the $LiCO_2CF_3$ 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 endue the aqueous electrolyte with a high oxidative decomposition potential. Moreover, the concentration of $LiCO_2CF_3$ aqueous 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

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Fig. 1. CV results of aqueous electrolytes with different concentrations collected in a three-electrode device including stainless steel grid as working electrodes and Ag/AgCl as reference electrode at the scanning speed of 10 mV s⁻¹ e and f, Electrochemical windows of LiTFSI, LiNO₃, LiCO₂CH₃ and LiCO₂CF₃ electrolytes at 1 M and 5 M, respectively; (a and c) and (b and d) are enlarged views near the extremes of the anode and cathode in e and f, respectively; g, Electrochemical window of LiCO₂CH₃ electrolyte at 1 M, 5 M and saturated concentration; h, Electrochemical window of LiCO₂CF₃ at 1 M, 5 M, 10 M, 20 M and 28 M.

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 Mo₆S₈ anode material, which showed completely different performances from the traditional lithium salts such as lithium nitrate (LiNO₃) and lithium sulfate (Li₂SO₄). 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 LiNO₃ [24-26], there are also reports about the lithium acetate (LiCO₂CH₃). For example, Wu et al. [27] used a saturate LiCO₂CH₃ 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 LiCO₂CH₃ and 32 mol kg⁻¹ potassium acetate (KCO₂CH₃). 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 LiCO₂CH₃ make the electrolyte have unique electrochemical properties. That is to say, the passivation film mainly composed of lithium carbonate (Li₂CO₃) formed by the dissolution of CO₂ can inhibit water decomposition to a certain extent. Although lithium trifluoroacetate (LiCO₂CF₃) 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 CO₂ through its decarboxylation reaction specific to carboxylate, and further produce Li₂CO₃ passivation film as well. Meanwhile, due to the strong electron absorption effect of trifluoromethyl (-CF₃), its solubility in water can be further improved to 28 mol kg⁻¹, so that the



Fig. 2. ¹⁷O NMR and Raman results of different electrolytes. **a** and **b**, ¹⁷O NMR spectra of LiTFSI, LiNO₃, LiCO₂CH₃ and LiCO₂CF₃ aqueous electrolytes at 1 M and 5 M, respectively; **b** and **d**, Raman spectra of OH stretching band located at 3041, 3220, 3430, 3572, and 3636 cm⁻¹ in LiTFSI, LiNO₃, LiCO₂CH₃ and LiCO₂CF₃ aqueous electrolytes at 1 M and 5 M, respectively.

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 highconcentration 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%), Mo (99.9%), 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 foam, and then dried in a vacuum oven at 60 °C overnight.

The Chevrel phase Mo_6S_8 was prepared by removing Cu from $Cu_2Mo_6S_8$ with the molten salt synthesis method reported before [30]. The first step was grinding the mixture of CuS, Mo powder and MoS_2 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 Kr 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 (Mo_6S_8 or $LiMn_2O_4$), 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



Fig. 3. Electrochemical performance of LiCO₂CH₃ aqueous electrolyte. **a** and **b**, CV results of Mo_6S_8 and $LiMn_2O_4$ electrodes at 1 M, 5 M and saturate concentration, respectively; **c** and **d**, TEM images of Mo_6S_8 electrode before and after 10 cycles in saturate $LiCO_2CH_3$ electrolyte; **e**-g, XPS characterization results of Mo_6S_8 anode after 10 cycles in saturate $LiCO_2CH_3$ electrolyte.

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 (Mo_6S_8 or Li Mn_2O_4) 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 Li Mn_2O_4 cathode (about 16 mg cm⁻²), glass fiber and Mo_6S_8 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: LiCO_2CH_3 \approx LiCO_2CF_3 < LiTFSI < LiNO_3, but the oxygen evolution zone is LiTFSI > LiNO_3 \approx LiCO_2CF_3 > LiCO_2CH_3. 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:



Fig. 4. Electrochemical properties of LiCO₂CF₃ aqueous electrolyte. **a**, CV results of Mo₆S₈ electrodes at 5 M, 10 M, 20 M and 28 M, respectively; **b** and **c**, TEM results of Mo₆S₈ electrode before and after 10 cycles at 28 M, respectively; **d**-g, XPS characterization of Mo₆S₈ electrode after 10 cycles at 28 M, respectively.

$$RCOO^{-} \rightarrow RCOO + e^{-}$$
$$RCOO \rightarrow R + CO_{2}$$

 $2R \rightarrow R-R$

For specific electrochemical decarboxylation reaction, taking $LiCO_2CH_3$ as an example, the reaction mechanism can be expressed as follows:

$$2CH_3COO - \leftrightarrow electrolysisCH_3 - CH_3 + 2CO_2$$

What's more, $LiCO_2CF_3$ 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, $LiCO_2CH_3$ 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 LiNO₃ and LiTFSI water-base electrolytes. The LiNO₃ 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 (LiCO₂CH₃ and LiCO₂CF₃) aqueous electrolytes with different concentrations were tested at 25 °C. From the result, we can see the stable electrochemical window of LiCO₂CH₃ aqueous electrolyte (Fig. 1 g) is only about 2.3 V even under the saturate condition (less than 9.0 mol kg⁻¹). On the other hand, the LiCO₂CF₃ 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 ¹⁷O NMR spectra and Raman vibrational spectroscopy of the solvent had been applied to further verify the prediction.



Firstly, we define the chemical shift of D₂O 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 H₂O 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 LiCO₂CH₃ aqueous electrolyte is up to about 2.7 ppm in a dilute solution, but no

Fig. 5. CV test results of LiNO₃ aqueous electrolyte under different conditions at a sweep rate of 10 mV S^{-1} **a** and **b**, Electrochemical windows of 1 M and 5 M LiNO₃ aqueous electrolytes in CO₂ atmosphere, respectively; **d**, Electrochemical window of 5 M double-salt electrolytes containing 1 M LiCO₂CH₃ and LiCO₂CF₃, respectively; **f**, Electrochemical window of 10 M double-salt electrolytes containing 5 M LiCO₂CH₃ and LiCO₂CF₃, respectively. (**c** and **e** are enlarged images near the extremes of the anode in **d** and **f**, respectively).

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 LiCO₂CH₃, 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(SO₂CF₃)₂) with strong electron-withdrawing action. It is also noted that the other two electrolytes, LiNO₃ and LiCO₂CF₃ 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



Fig. 6. a, Ionic conductivity at 25 °C in different concentrated $LiCO_2CF_3$ 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 Mo₆S₈ and LiMn₂O₄ as anode and cathode materials in the saturate LiCO₂CH₃ (**c** and **d**) and 28 M LiCO₂CF₃ (**e** and **f**) aqueous electrolytes at the current density of 0.02 A g⁻¹, respectively.

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 LiCO₂CH₃. On the other hand, LiNO₃ and LiCO₂CF₃ have nearly similar performance in both dilute solution and high concentration solution, which is also in good agreement with the NMR and CV test results.

In order to prove the existence of passivation film, other electrochemical tests and characterizations have been carried out. For example, in view of the better ability of inhibiting water decomposition at the hydrogen evolution area than that of LiTFSI in the same concentration, Chevrel phase Mo_6S_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 LiCO₂CH₃ 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 Mo₆S₈ anode materials cycled 10 times before (Fig. 3 c) and after (Fig. 3 d) in the saturate LiCO₂CH₃ 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 Li₂CO₃, which also explains the rationality of our previous conjecture to some extent. By the way, we also applied the LiCO₂CH₃ aqueous electrolyte to LiMn₂O₄ 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 LiCO₂CF₃ aqueous electrolyte, it's nearly twice as thick as in the LiCO₂CH₃ one (Fig. 4 c) and the composition is also mainly Li₂CO₃ (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 LiCO2CF3 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 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 LiCO₂CH₃ or LiCO₂CF₃ into 4 M LiNO3 water-base electrolytes and 5 M LiCO2CF3 or LiCO2CF3 into 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 LiCO2CF3 electrolytes with different concentrations at 25 °C were measured (Fig. 6 a). And LiMn₂O₄||Mo₆S₈ 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 saturate LiCO₂CH₃ (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 LiCO₂CF₃ solution still enables the full-cells to own more outstanding cyclic stability than the saturate 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 (LiCO₂CH₃ and LiCO₂CF₃) 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-withdrawing 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 LiTFSI 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. **Jiyang 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

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2020.228136.

References

- [1] X. Xu, J. Liu, Z. Liu, J. Shen, R. Hu, J. Liu, L. Ouyang, L. Zhang, M. Zhu, ACS Nano 11 (2017) 9033–9040.
- M. Pasta, C.D. Wessells, R.A. Huggins, Y. Cui, Nat. Commun. 3 (2012) 1149–1155.
 M. Du, Y. Meng, C. Wang, C. Duan, F. Zhu, Y. Zhang, J. Electroanal. Chem. 834 (2019) 17–25.
- [4] M. Armand, J.M. Tarascon, Nature 451 (2008) 652–657.
- [5] J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367.
- [6] Z. Lei, X. Chen, W. Sun, Y. Zhang, Y. Wang, Adv. Energy Mater. (2018) 1801010–1801022.
- [7] H. Kim, J. Hong, K.Y. Park, H. Kim, S.W. Kim, K. Kang, Chem. Rev. 114 (2014) 11788–11827.
- [8] X. Wang, Y. Hou, Y. Zhu, Y. Wu, R. Holze, Sci. Rep. 3 (2013) 1401–1405.
- [9] R.A. Huggins, J. Electrochem. Soc. 164 (2017) A5031–A5036.
- [10] Y. Li, K.W. Wong, Q. Dou, W. Zhang, K.M. Ng, ACS Appl. Energy Mater. 1 (2018) 2664–2670.
- [11] X.L. Wu, L.Y. Jiang, F.F. Cao, Y.G. Guo, L.J. Wan, Adv. Mater. 21 (2009) 2710–2714.
- [12] D. Choi, D. Wang, V.V. Viswanathan, I.-T. Bae, W. Wang, Z. Nie, J.-G. Zhang, G. L. Graff, J. Liu, Z. Yang, T. Duong, Electrochem. Commun. 12 (2010) 378–381.
- [13] L. Suo, F. Han, X. Fan, H. Liu, K. Xu, C. Wang, J. Mater. Chem. A 4 (2016) 6639–6644.
- [14] J. Liu, C. Xu, Z. Chen, S. Ni, Z.X. Shen, Green Energy Environ. 3 (2018) 20–41.
 [15] N. Dubouis, P. Lemaire, B. Mirvaux, E. Salager, M. Deschamps, A. Grimaud, Energy Environ. Sci. 11 (2018) 3491–3499.
- [16] W. Li, J.R. Dahn, D.S. Wainwright, Science 264 (1994) 1115-1118.
- [17] J.W. Choi, D. Aurbach, Nat. Rev. Mater. 1 (2016) 16013–16028.
- [18] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, Science (2015) 938–944.
- [19] M. McEldrew, Z.A.H. Goodwin, A.A. Kornyshev, M.Z. Bazant, J. Phys. Chem. Lett. 9 (2018) 5840–5846.
- [20] L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, S.M. Russell, M. Armand, A. Angell, K. Xu, C. Wang, Angew Chem. Int. Ed. Engl. 55 (2016) 7136–7141.
- [21] S. Han, Sci. Rep. 8 (2018) 9347-9356.
- [22] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, Science 350 (2015) 938–943.
- [23] C. Yang, L. Suo, O. Borodin, F. Wang, W. Sun, T. Gao, X. Fan, S. Hou, Z. Ma,
- K. Amine, K. Xu, C. Wang, Proc. Natl. Acad. Sci. U. S. A. 114 (2017) 6197–6202.
 J. Zheng, G. Tan, P. Shan, T. Liu, J. Hu, Y. Feng, L. Yang, M. Zhang, Z. Chen, Y. Lin, J. Lu, J.C. Neuefeind, Y. Ren, K. Amine, L.-W. Wang, K. Xu, F. Pan, Inside Chem. 4 (2018) 2872–2882.
- [25] J. Liu, L. Yi, L. Liu, P. Peng, Mater, Chem. Phys. 161 (2015) 211-218.
- [26] M. Zhao, W. Zhang, F. Qu, F. Wang, X. Song, Electrochim. Acta 138 (2014) 187–192
- [27] X. Wu, X. Yuan, J. Yu, J. Liu, F. Wang, L. Fu, W. Zhou, Y. Zhu, Q. Zhou, Y. Wu, Nanoscale 9 (2017) 11004–11011.
- [28] M.R. Lukatskaya, J.I. Feldblyum, D.G. Mackanic, F. Lissel, D.L. Michels, Y. Cui, Z. Bao, Energy Environ. Sci. 11 (2018) 2876–2883.
- [29] J. Lim, K. Park, H. Lee, J. Kim, K. Kwak, M. Cho, J. Am. Chem. Soc. 140 (2018) 15661–15667.
- [30] E. Lancry, E. Levi, A. Mitelman, S. Malovany, D. Aurbach, J. Solid State Chem. 179 (2006) 1879–1882.

- [31] A.K. Vijh, B.E. Conway, Chem. Rev. (1967) 623–664.
 [32] T.S. Oakwood, M. Maxine R, J. Am. Chem. Soc. (1950) 1840.
- [33] L. Suo, D. Oh, Y. Lin, Z. Zhuo, O. Borodin, T. Gao, F. Wang, A. Kushima, Z. Wang, H.C. Kim, Y. Qi, W. Yang, F. Pan, J. Li, K. Xu, C. Wang, J. Am. Chem. Soc. 139 (2017) 18670–18680.