Lithium Ion Batteries Operated at −100 ℃

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Enabling lithium-ion batteries (LIBs) to operate in a wider temperature range, e.g., as low or high as possible or capable of both, is an urgent need and shared goal. Here we report, for the first time, a low-temperature electrolyte consisting of traditional ethylene carbonate, methyl acetate, butyronitrile solvents, and 1 M $LiPF_6$ salt, attributed to its very low freezing point ($T_f = -126.3$ ℃) and high ion conductivity at extremely low temperatures (0.21 mS/cm at −100 ℃), successfully extends the service temperature of a practical 9.6 Ah LIB down to −100 ℃ (49.6% capacity retention compared to that at room temperature), which is the lowest temperature reported for practical cells so far as we know, and is lower than the lowest natural temperature (−89.2 ℃) recorded on earth. Meanwhile, the high-temperature performance of lithium-ion batteries is not affected. The capacity retention is 88.2% and 83.4% after 800 cycles at 25 ℃ and 45 ℃, respectively. The progress also makes LIB a proper power supplier for space vehicles in astronautic explorations.

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We have witnessed great success over the past three decades that the employment of lithium-ion batteries (LIBs) in portable devices such as laptop computers, cameras, smartphones, wearable electronic devices, electric tools, electric vehicles (EVs), and static energy storage stations.[1,2] We are still industrious to power many more devices in other emerging fields using LIBs.[1] As the core part of a powering system, a battery has to withstand very harsh conditions in some application scenarios.[3–6] EVs may be exposed to −30 ℃ in high latitude regions, and even down to −90 ℃ (−89.2 ℃, Vostok Station, Antarctica, 1983) in the polar regions in winter. Devices for space exploration will experience much more harsh conditions, e.g., the extremely low temperature is as low as −120 ℃ on the Martian surface.[2,3,7–11] One of the main obstacles for previous LIBs to work under the aforementioned cryogenic conditions is the freezing of non-aqueous electrolytes hindering the transport of Li^+ ions, which are the carriers of energy in the batteries. The freezing point (T_f) of the most commonly used solvent ethylene carbonate is about 36 ℃ (solid at room temperature), which cannot support LIB to service under sub-zero temperature conditions. Most of the LIB and related devices are default settled to shut down when the environmental temperature is lower than 0 ℃ presently. Many of us have encountered the embarrassing circumstance of suddenly auto-switching off mobile phones when going outside in winter. Great efforts in the battery community have been devoted to formulating ideal electrolyte that bears with very low T_f.[5,6,10–25] In order to enable an LIB to operate at sub-zero temperature environment, lowering the freezing point of electrolyte via co-solvents is a conventional and convenient strategic choice for industrial utilization, and solvents with low T_f, low viscosity, and high dielectric constant, such as propylene carbonate, ethyl methyl carbonate, methyl acetate are often the choices, and great progress has been achieved, as shown in Fig. 1.[10,12–15,17,18,24,26–34] The low T_f strategy can support LIBs to work at about −40 ℃ to −30 ℃ (deliver about 50% of the discharge capacity at room temperature).[35] Moreover, with addition of more co-solvents, the high entropy drives the T_f down to as low as −130 ℃.[10] However, the lowest service temperature of co-solvents is −60 ℃, much higher than the T_f reached so far. Liquefied gas was also introduced as an electrolyte to an extremely low-temperature LIB, see Fig. 1.[13,17,34] These facts suggest that ionic conduction in the bulk electrolytes is not the determining factor under extremely low-temperature conditions, though lowering T_f is the first target for most investigations. Li^+ de-solvation process is reported to be the rate-determining step. Tuning the solvation structure of Li^+ in electrolytes is emerging as a promising strategy that can potentially support LIBs to operate at a much lower temperatures.[6,15,18,19,23,25,36] Ionic diffusion in material, electrode level, and total bat-

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tery resistance are other factors that affect or determine the battery performance, besides ionic transport in the bulk electrolyte, interface, and Li^+ solvation structure at low-temperature circumstances. Organic electrode materials were proposed to enable cells to work at −70 ℃.[14]

In this Letter, we report, for the first time, a low-temperature electrolyte (E_{-100}) consistent with traditional ethylene carbonate (EC), methyl acetate (MA), and butyronitrile (BN) solvents and $LiPF_6$ salt, attributed to its extremely low T_f (−126.3 ℃) and high ionic conductivity (0.21 mS/cm at −100 ℃), successfully extends the service temperature of a practical 9.6 Ah LIB down to −100 ℃ (49.6% capacity retention compared to that at room temperature), which is the lowest reported for practical cells so far as we know, and is lower than the lowest natural temperature (−89.2 ℃) recorded on earth. Meanwhile, the high-temperature performance of lithium-ion batteries is not affected. The capacity retention after 800 cycles is 88.2% and 83.4% at 25 ℃ and 45 ℃, respectively. The service temperature range of the LIB is successfully extended, from −100 ℃ to 45 ℃. The progress also makes the LIB a proper power supplier for space vehicles in astronautic explorations.

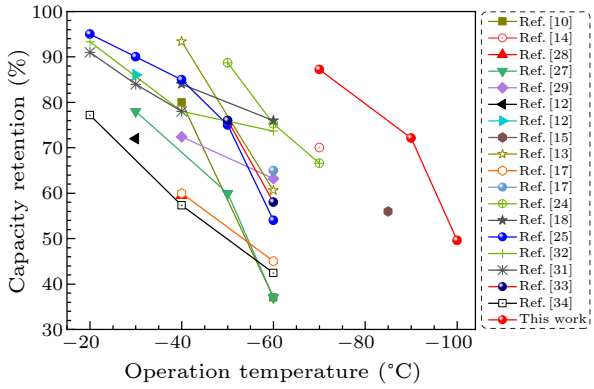

Fig. 1. Comparison of reported LIB performance under extremely low-temperature conditions.[10,12–15,17,18,24,25,27–29,31–34]

Properties of Electrolytes at Low Temperature. The basic function of electrolytes in LIB is to provide the passways for Li^+ ion transportation during charging and discharging. Four basic properties of the solvent including freezing point (T_f), boiling point (T_b), dielectric constant (ε), and viscosity (η) are usually evaluated before being introduced into the electrolyte. Freezing of conventional carbonate ester non-aqueous electrolytes severely limits the limit of low temperature to about −20 ℃ to −40 ℃ at present. To further push the limiting temperature to a much lower limit, much progress has been achieved as a result of extensive efforts. As is commonly known, when two solvents are mixed, their melting points can be lower than the individual melting points, attributed to the effect of entropy increasing, this is called the melting point depression effect. Thus, solvents bear with very low freezing points (T_f) are the preferential candidates. MA and BN as co-solvents were extensively investigated due to their extremely low T_f of −96 ℃ and −112 ℃.[7] In this work, we investigate EC, MA, and BN to work as a low temperature electrolyte (1 M $LiPF_6$ with EC : MA : BN = 1 : 7 : 2 v/v/v, with 2% FEC, 0.5% VC additives, abbreviated as E_{-100} hereafter). As is expected, Fig. 2(a) demonstrates that with the addition of BN, the endothermic peak locates at around −105 ℃ to −111 ℃, very close to the T_f (−112 ℃) of BN. Addition of salt into the solvent has similar effect of decreasing the melting point of the mixture. Then, the melting point of E_{-100} further decreased to −126.3 ℃ when Li salt was added.

As discussed above, butyronitrile introduction would decrease the freezing point of the eutectic solvent system. Li^+ ionic conductivities of the low-temperature electrolyte were measured in the temperature range from −100 ℃ to 25 ℃, as shown in Fig. 2(b), when 20 vol% BN was added to the carbonate-based electrolyte, the ionic conductivity of E_{-100} is much higher than that of conventional carbonate electrolyte (E_{-con}, 1 M $LiPF_6$ in EC : DMC = 1 : 1 v/v) both at 25 ℃ (17.16 mS/cm vs 10.74 mS/cm), and at 0 ℃ (16.32 mS/cm vs 7.5 mS/cm). The ionic conductivities of E_{-con} drastically decrease to 0.001 mS/cm when temperature drops to −40 ℃, and E_{-con} begins to solidify at around −50 ℃, see Fig. S1 in the Supplementary Materials. Noticeably, the ionic conductivities of the electrolyte E_{-100} are still 4.80 mS/cm, 2.88 mS/cm, 1.25 mS/cm, and 0.21 mS/cm at −40 ℃, −60 ℃, −80 ℃, and −100 ℃, respectively. The capability of supporting fast ionic conduction in E_{-100} may support the operation of the LIB at extremely low temperatures.

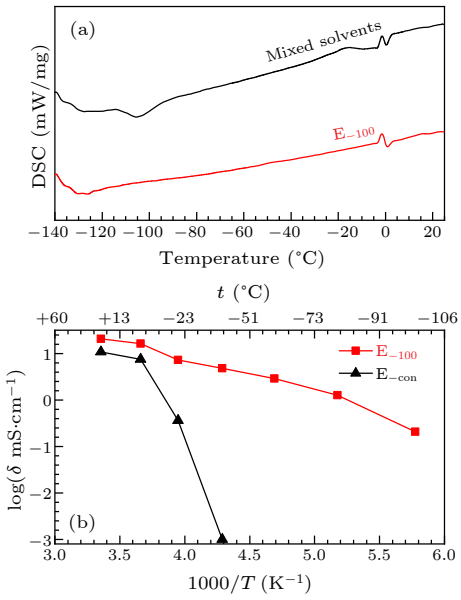

Fig. 2. (a) Differential scanning calorimeter (DSC) measurement for mixed solvents and the low-temperature electrolyte from −150 ℃ to 25 ℃. (b) Ionic conductivity of the low-temperature electrolyte E_{-100} from −100 ℃ to 25 ℃, and conventional electrolyte E_{-con} from −40 ℃ to 25 ℃.

Electrochemical Performance of Lithium-Ion Battery at Extremely Low Temperature. For the LIB working at very low temperatures, sluggish ionic transports in electrolyte, electrolyte-electrode, and electrode result in large

over-potential and early termination of charge and discharge process, thus very low capacity retention. The results get much worse when the temperature further drops. To make it practical for commercial utilization, 9.6 Ah cells are designed, fabricated, and evaluated. Figure 3(a) gives the typical discharging curves of the battery with E_{-100} electrolyte at 0.1 C under −100 ℃, −70 ℃, and −90 ℃. The result demonstrates that the battery with E_{-100} electrolyte delivers 4.75 Ah capacity at −100 ℃. On the other hand, the battery using conventional electrolyte E_{-con} and that without BN can hardly deliver usable discharge capacity, see Fig. S2 in the Supplementary Materials. The result demonstrates that with E_{-100} electrolyte the capacity retentions compared to that at room temperature were 87.2%, 72.1%, and 49.6% at −70 ℃, −90 ℃, and −100 ℃, respectively. Here, −100 ℃ is the lowest temperature reported for practical cells as far as we know, and is also lower than the lowest natural temperature (−89.2 ℃) recorded on Earth. For cycle performance, Fig. 3(b) shows that the capacity retention of the battery adopting E_{-100} electrolyte is 88.2% when cycling at 1 C rate after 800 cycles.

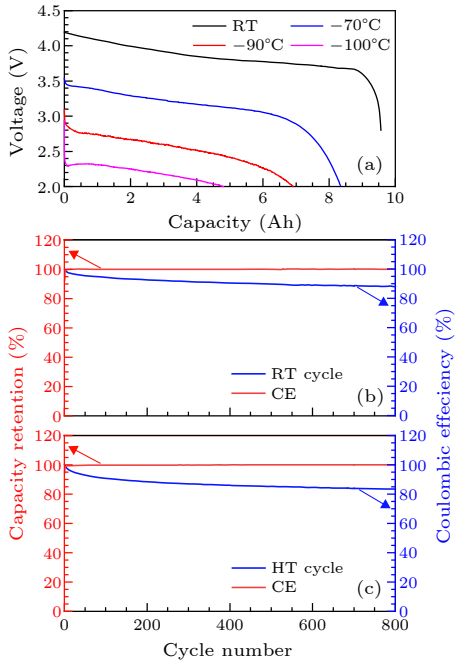

Fig. 3. Performance of the 9.6 Ah $LiCoO_2$/graphite battery. (a) Typical discharging curves of the battery with E_{-100} electrolyte using 0.1 C rate at −100 ℃. [(b), (c)] The capacity retention of the battery using E_{-100} electrolyte cycled (b) at 25 ℃ using 1 C rate in the voltage range of 2.9–4.2 V and (c) at 45 ℃ using 1 C rate in the voltage range of 2.9–4.1 V. RT: room temperature, HT: high temperature, CE: Coulombic efficiency.

Performance in a Wide Temperature Range. Another issue is the compatibility of low-temperature performance and high-temperature (e.g., 45 ℃) performance. Figure 3(c) displays that the capacity retention of battery adopting E_{-100} electrolyte is 83.4% when cycling at 1 C rate after 80 cycles, indicating that BN does not undermine the high-temperature electrochemical performance of conventional carbonate electrolyte besides excellent low-temperature merits.

In summary, we report, for the first time, exploration of the conventional carbonate EC-MA-based electrolyte with butyronitrile addition. An optimized electrolyte E_{-100} with very low T_f and high ionic conductivity is obtained. The T_f of the E_{-100} is as low as −126.3 ℃. The ionic conductivity of E_{-100} is comparable to that of traditional carbonate electrolyte at room temperature, and higher when temperature drops to below −20 ℃. The ionic conductivities of the electrolyte E_{-100} reach 2.88 mS/cm, 1.25 mS/cm, and 0.21 mS/cm at −60 ℃, −80 ℃, and −100 ℃, respectively. Bearing with these merits, E_{-100} successfully extends the service temperature of a practical 9.6 Ah LIB down to −100 ℃ (50% capacity retention compared to that at room temperature), which is the lowest temperature reported for practical cells so far, and is lower than the lowest temperature (−89.2 ℃) recorded on earth. Meanwhile, the high-temperature behavior is not affected, the service temperature range is extended, from −100 ℃ to 45 ℃. These results demonstrate that the LIB with low-temperature electrolytes is a proper power supplier for space vehicles in astronautic explorations.

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