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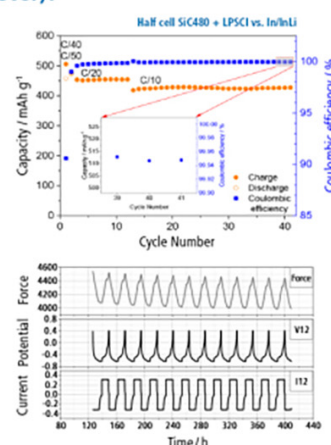
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Fluorine-Free Electrolyte Based on LiBOB and Diethyl Adipate for Lithium-Ion Batteries

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The development of safer and thermally robust electrolytes is essential for improving the reliability of lithium-ion batteries, particularly under demanding operating conditions. In this work, fluorine-free electrolytes based on diethyl adipate (DEA) in combination with lithium bis(oxalato)borate (LiBOB) were developed and evaluated in lithium nickel cobalt manganese oxide (NCM)/graphite lithium-ion cells. An optimal salt concentration of 0.7 molal (m) LiBOB was identified, while the addition of ethylene carbonate (EC) and propylene carbonate (PC) enhances ionic conductivity. Electrochemical testing revealed slightly lower initial capacities at low and moderate temperatures compared to the benchmark electrolyte LP40 (1 molar (M) lithium hexafluorophosphate (LiPF₆) in EC:diethyl carbonate (DEC) (1:1 by weight (wt))), but markedly improved capacity retention during long-term cycling. At 25 °C, the LiBOB–DEA–EC system retained 85.1% of its initial capacity after 965 cycles, compared to 71.4% for LP40, with further improvements at elevated temperatures (40 °C–70 °C), where LiBOB–DEA-based systems showed reduced degradation and no premature cell failure. In addition, the developed electrolytes exhibited substantially improved safety characteristics, including high flash points of 125 °C–132 °C for the DEA-based solvent mixtures and a delayed onset of exothermic reactions in heat-wait-see tests. Overall, the results demonstrate the potential of LiBOB–DEA-based electrolytes as a promising approach toward safer and more thermally stable lithium-ion batteries.

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Lithium-ion batteries (LIBs) have become the dominant technology for electrochemical energy storage in portable electronics, electric vehicles, and stationary applications due to their high energy density, efficiency, and long cycle life.^{1,2} While significant progress has been achieved in electrode materials and cell design, the electrolyte composition has remained largely unchanged and is still predominantly based on mixtures of flammable organic carbonates combined with thermally unstable lithium hexafluorophosphate (LiPF₆) as the conducting salt.^{3–5} Conventional electrolyte systems such as 1 M (mol L^{−1}) LiPF₆ in ethylene carbonate (EC):diethyl carbonate (DEC) (1:1 by weight (wt)), commonly referred to as LP40) exhibit favorable ionic conductivity and compatibility with graphite and layered oxide electrodes, but suffer from limited thermal stability and high flammability, which represent significant safety concerns in real-world applications.^{6–8}

At elevated temperatures, exothermic reactions such as electrolyte decomposition and degradation of interfacial layers can lead to gas evolution, increased internal pressure, and ultimately thermal runaway.^{9–11} A key factor contributing to this behavior is the relatively low flash point and high volatility of carbonate-based electrolytes: for example, EC/DEC based formulations show flash points in the range of 30–50 °C, which is close to typical LIB operating temperatures, increasing the risk of vapor formation and ignition under abusive conditions.^{12–14} Moreover, LiPF₆ is thermally unstable and prone to hydrolysis, producing corrosive species such as HF that can attack cell components and degrade performance.^{15,16}

Because of such safety limitations and to prevent rapid cell degradation, the recommended upper operating temperature for commercial LIBs is typically limited to ≤ 55 °C, and significant research efforts focus on developing electrolyte systems that combine improved safety with adequate electrochemical performance.⁴ High-flash-point solvent alternatives—such as phosphates, or sulfones—can reduce flammability but often exhibit

lower ionic conductivity or unfavorable solid electrolyte interphase (SEI) formation on graphite.³ Likewise, ionic liquids and solid polymer electrolytes can enhance safety but are often associated with increased viscosity, reduced room-temperature conductivity, or processing challenges.^{17–19}

Fluorine-free electrolyte systems have recently attracted increasing attention as alternatives to conventional LiPF₆-based electrolytes due to their potential for reduced environmental impact, improved occupational safety, and the avoidance of HF formation during salt decomposition. In particular, lithium bis(oxalato)borate (LiBOB) has been extensively investigated due to its favorable thermal stability and its ability to form stable interphases on both graphite and positive electrode material.^{20–22} LiBOB has been widely investigated as an electrolyte additive in conventional LiPF₆-based systems, where it can improve interfacial stability and cycling performance.^{23–25} More recently, increasing attention has also been directed toward its use as a stand-alone conducting salt in fluorine-free electrolyte formulations, highlighting its potential for safer lithium-ion battery systems.^{26,27} However, the application of LiBOB as a stand-alone conducting salt remains challenging due to its limited solubility in many organic solvents, which can restrict the achievable salt concentration and consequently the ionic conductivity of the resulting electrolytes.^{28–30} Therefore, the identification of suitable solvent systems that enable sufficient LiBOB dissolution while maintaining favorable electrochemical and safety properties remains a key challenge for the development of fluorine-free liquid electrolytes.

In this work, a new electrolyte concept based on diethyl adipate (DEA) in combination with LiBOB is investigated. DEA is selected as the solvent due to its high flash point, low volatility, and wide electrochemical stability window, which contribute to enhanced intrinsic fire safety compared to conventional linear carbonate solvents. LiBOB is used as the conducting salt because it offers good thermal and chemical stability and forms a stable SEI on graphite while avoiding HF generation associated with LiPF₆ hydrolysis.^{22,31,32} The combination of DEA and LiBOB thus provides a promising route to liquid electrolytes that maintain sufficient ionic

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conductivity while substantially improving safety. The influence of solvent composition and salt concentration on ionic conductivity, electrochemical performance, and cycling stability is systematically analyzed. In addition, safety-relevant properties, including flash point and thermal behavior under abusive conditions, are evaluated and compared to the benchmark LP40 electrolyte.

Experimental

Materials.—In this study, diethyl adipate (DEA), ethylene carbonate (EC), and propylene carbonate (PC) were selected as solvents for the electrolyte preparation. DEA (99% purity, Fisher Scientific, Schwerte, Germany) and PC ($\geq 99.7\%$ purity, Carl Roth, Karlsruhe, Germany) were placed in an argon-atmosphere LABstar glovebox (M. Braun Inertgas-Systeme, Garching, Germany) with a residual water and oxygen content below 0.5 ppm. To further reduce trace moisture, both solvents were left in contact with a molecular sieve (pore diameter 0.3 nm) overnight inside the glovebox. The molecular structure of DEA is depicted in Fig. 1. EC (99% purity, Sigma Aldrich, Taufkirchen, Germany) was introduced into the glovebox and used as received. The lithium salt lithium bis(oxalato)borate (LiBOB, Sigma Aldrich, Taufkirchen, Germany) was likewise handled under the same inert conditions without additional purification. To prepare the test electrolytes the conducting salt was precisely weighed and the solvents were subsequently added. The resulting mixture was then continuously mixed on a magnetic stirrer until full dissolution.

For benchmarking purposes, the commercial electrolyte LP40 (1 M LiPF₆ in EC:DEC 1:1 wt, from E-Lyte Innovations, Kaiserslautern, Germany) was employed.

Table I summarizes the melting point, flash point, and boiling point of the solvents used in this study (DEA, EC and PC). For reference, the same properties for DEC, which appears exclusively in the benchmark electrolyte LP40, are also provided.

Disks of lithium nickel manganese cobalt oxide (NCM 622, 2.0 mAh cm⁻², Münster Electrochemical Energy Technology, Münster, Germany) and graphite (2.9 mAh cm⁻², Varta AG, Ellwangen, Germany) were punched from single-sided coated sheets, with diameters of 15 mm and 16 mm, respectively. The corresponding active material loadings were 11.5 mg cm⁻² for the NCM 622 cathodes and 8.0 mg cm⁻² for the graphite anodes. The resulting negative-to-positive capacity ratio (*N/P* ratio) was 1.45. All electrodes were dried in a vacuum oven (B-585, Büchi Labortechnik AG, Flawil, Switzerland) at 120 °C for 16 h under a pressure below 50 mbar. Separators (FS 2190, Freudenberg, Weinheim, Germany; ≈ 200 μ m thick) were cut into 19 mm disks and subjected to the same drying procedure. The relatively thick nonwoven separator was selected based on preliminary experiments, in which it provided the most reliable electrochemical performance with the newly developed LiBOB–DEA-based electrolytes. Its relatively large thickness may increase the ionic transport distance and contribute to additional internal resistance and polarization. However, the same separator was used for all electrolyte formulations and the LP40 reference cells, ensuring consistent conditions for comparison.

Cell assembly.—All cell assemblies were carried out within the glovebox. For calorimetric experiments, CR2016 casings were used, while CR2032 casings were employed for electrochemical measurements. Both types were made of stainless steel 304 and supplied by PI-KEM Limited (Tamworth, Staffordshire, United Kingdom). Assembly started by placing the graphite electrode in the center of the lower casing, followed by the separator. Next, 70 μ l of the electrolyte was added, and the NCM electrode was positioned on top. A spacer and spring were then inserted above the NCM electrode, and the cell was sealed using a digitally controlled electric crimping machine (MSK-160E, MTI Corporation, Richmond, CA, USA). After cell crimping, the retained electrolyte mass was

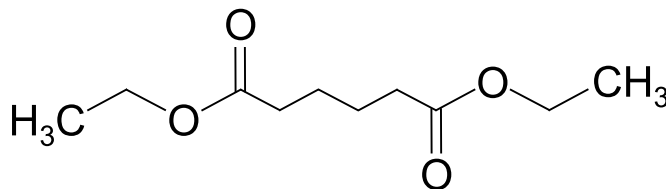


Figure 1. Structural formula of diethyl adipate (DEA).³³

Table I. Melting point (T_{MP}), flash point (T_{FP}) and boiling point (T_{BP}) of the used solvents DEA,³⁴ EC,^{35–37} PC^{35,36,38} and DEC.^{36,39}

	DEA	EC	PC	DEC
T_{MP} (°C)	−20	36	−49	−43
T_{FP} (°C)	113	145	135	>25
T_{BP} (°C)	251	248	242	126

determined gravimetrically to account for electrolyte expelled during sealing. Based on the retained electrolyte mass and the nominal cathode capacity, the resulting electrolyte-to-capacity (E/C) ratio was approximately 16 g Ah⁻¹.

Cell tests.—The performance of the cells containing the new electrolytes was investigated through C-rate testing, aging experiments, and measurements at various temperatures. Electrochemical experiments were conducted using either a CTS battery tester (BaSyTec, Asselfingen, Germany) or an LBT21084uC-5V1A system from Arbin Instruments (College Station, TX, USA). During all tests, the cells were kept at the target temperature inside an IPP 110 climate chamber (Memmert, Schwabach, Germany). Before testing, each cell underwent a formation procedure consisting of three cycles at C/10 followed by three cycles at C/5, employing constant current (CC) for both charging and discharging. Unless otherwise stated, cell formation was performed at the same temperature as the subsequent cycling tests. For the measurements at 70 °C, the cells were formed at 25 °C prior to cycling at 70 °C. The operational voltage window was set from 2.5 V as the lower cut-off to 4.2 V as the upper cut-off.

Differential scanning calorimetry (DSC) measurements.—The low-temperature thermal properties of the electrolyte formulations were characterized by differential scanning calorimetry (DSC) using a DSC 204 instrument (NETZSCH, Selb, Germany). Approximately 35 mg of electrolyte were hermetically sealed in aluminum crucibles inside an argon-filled glovebox to prevent exposure to air and moisture. Measurements were carried out under a continuous flow of high-purity argon using two consecutive cooling and heating cycles over a temperature range from −135 to 70 °C at a heating and cooling rate of 10 °C min⁻¹. Only the second heating cycle was used for data evaluation. The glass transition temperature (T_g) was determined from the inflection point of the baseline shift, while the liquidus temperature (T_{liq}) was obtained from the peak temperature of the corresponding endothermic transition, following the procedures described by Ding et al.⁴⁰ and Höhne et al.⁴¹ A detailed description of the evaluation procedure can be found in.⁴²

Electrochemical stability measurements.—The oxidative and reductive electrochemical stability of the electrolytes was evaluated using three-electrode cells assembled in ECC-Ref housings (EL-Cell, Hamburg, Germany). Lithium metal was used as the counter electrode and a lithium metal reference ring was employed as the reference electrode. Oxidative stability was investigated by linear sweep voltammetry (LSV) using NCM622 as the working electrode in Li/NCM622 cells. Measurements were initiated at the open-circuit

voltage (OCV) and swept to 6.0 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} . Reductive stability was evaluated by cyclic voltammetry (CV) using graphite (C_6) as the working electrode in Li/C_6 cells. One cycle was recorded between the OCV and 0.01 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} . All measurements were performed using a Reference 3000 AE potentiostat (Gamry Instruments, Warminster, PA, USA).

Electrolyte conductivity measurements.—Ionic conductivity measurements were performed using a platinized HTCC conductivity cell (BioLogic, Seyssinet-Pariset, France) coupled to a Reference 3000 AE potentiostat (Gamry, Warminster, PA, USA). For measurements across different temperatures, the conductivity cell was placed in the water bath of a Proline RP845 thermostat (Lauda, Lauda-Königshofen, Germany), and the resistance was recorded at a frequency of 1000 Hz while the temperature was varied from 5°C to 60°C in steps of 5°C . The measured resistances were converted into ionic conductivity using a cell constant that had been previously determined with a standard conductivity solution.

Flash point measurements.—Flash point measurements of the electrolyte formulations were carried out using an NPV Tech flash point tester (Normalab, Valliquerville, France). The device follows the rapid-equilibrium closed-cup method according to ISO 3679 and covers a temperature range from -30°C to 300°C . Ambient pressure is continuously monitored by an integrated barometer, allowing the measured flash points to be automatically corrected to standard pressure. Depending on the expected flash point, either 2 ml of solvent (for temperatures below 100°C) or 4 ml (for higher temperatures) were used for each measurement.

The measurement was carried out in two steps. First, an automated screening run was carried out to estimate the flash point. During this procedure, the sample-filled test cup was heated at a defined rate while the ignition source was triggered at every full-degree temperature increase. The appearance of a flash terminated the scan and provided a preliminary flash point value.

Based on this estimate, the exact flash point was subsequently determined by manual measurements following ISO 3679. According to this method, the test cup is first heated to the selected temperature. A fresh sample is then introduced into the cup and allowed to stabilize for the specified stabilization time before the ignition source is applied to test for ignition. The initial manual test was conducted 2 K below the temperature identified during the automated scan. If no ignition occurred, the procedure was repeated with newly refilled samples while increasing the temperature by 1 K for each attempt until a flash was detected. The temperature at which ignition first occurs is defined as the flash point.

Thermal abuse tests.—The thermal abuse characteristics of the cells are examined using the heat–wait–seek (HWS) technique in an ES-ARC calorimeter (Thermal Hazard Technology, Bletchley, UK). This setup provides sufficient sensitivity to capture the thermal response of low-capacity coin cells (around 5 mAh).^{43,44} To generate a measurable signal with the used low-capacity coin cells, four cells are stacked together, giving a combined capacity of roughly 12 mAh. The stack is held together with heat-resistant tape (3M Industrial Business, Neuss, Germany), and a type E bomb thermocouple is inserted at its center to record the sample temperature accurately. The calorimeter chamber, with an inner diameter of 0.1 m and a height of 0.1 m, has one heater and one thermocouple located in the lid and bottom, respectively, and two heaters and two thermocouples (all type N) in the side wall. The heaters adjust the required temperatures depending on the measurement conditions. Before starting measurements, the calorimeter is calibrated using dummy cells of similar thermal mass, followed by a drift check to verify stable operation. This ensures precise detection of self-heating and uniform heat exposure.

The HWS sequence alternates between heating, equilibration (wait), and monitoring for self-heating (seek). Initially, the stack is brought from ambient temperature to 35°C . Subsequent heating is applied in 5 K increments, with each step followed by a 20 min stabilization period to allow the stack to reach thermal equilibrium. During the monitoring phase, the temperatures recorded by the central thermocouple and the heater thermocouples are continuously compared. When the sample's temperature rise exceeds $0.02^\circ\text{C min}^{-1}$, the onset of self-heating is detected and the system switches to a quasi-adiabatic mode, in which the chamber heaters track the cell temperature to minimize heat loss. Exothermic reactions then dominate the thermal response until either thermal runaway occurs or the reactive energy is exhausted, after which the next 5 K heating step is applied.

Transient events, such as intermediate endothermic processes or gas release, may temporarily suppress self-heating. In such cases, stepwise heating continues until exothermic activity resumes or runaway develops. The methodology is described in detail in.⁴⁵ For safety, all experiments are stopped at 300°C . Measurements for each electrolyte are conducted in triplicate, and the data presented reflect a representative result.

Results and Discussion

The aim of this study is to develop electrolyte formulations with increased thermal robustness by avoiding the use of linear carbonates and replacing LiPF_6 . To achieve this, DEA is explored as an environmentally friendly solvent with favorable physicochemical properties and is combined with the conducting salt LiBOB to improve thermal stability and intrinsic safety. In the following, the electrochemical and thermal properties of the resulting electrolyte systems are presented and compared to those of the benchmark electrolyte LP40.

Optimization of the LiBOB concentration and solvent composition.—LiBOB generally exhibits lower solubility in conventional electrolyte solvents compared to LiPF_6 , which often restricts its application to moderate salt concentrations. In order to identify suitable compositions, the ionic conductivity of LiBOB was investigated in a solvent system based on DEA with the addition of EC, using an 85:15 (wt) mixture. Measurements were carried out for various salt concentrations, and the values represent the mean of three independent measurements, as summarized in Table II. All measurements were conducted at 25°C , where the conductivity exhibits a maximum in the concentration range of 0.7 to $0.8 \text{ m (mol kg}^{-1}\text{)}$.

Although the conductivity reaches a similar maximum at both 0.7 m and 0.8 m LiBOB, a concentration of 0.7 m was selected for further optimization. At this concentration, the ionic conductivity at 25°C was measured for a series of solvent mixtures. All formulations contained 60 wt% DEA, with the remaining fraction composed of varying amounts of EC and PC. The results are summarized in Table III.

The results of the conductivity measurements indicate that incorporating EC or PC into the solvent system increases the ionic conductivity, with both co-solvents producing a similar enhancement. Consequently, C-rate tests ranging from C/10 to 2C were performed in the next step to investigate the behavior of these electrolytes in full cells. The corresponding results are presented in Fig. 2. Up to a C-rate of 1C, the cells exhibit nearly identical capacities for the electrolytes 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), and 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt). At 1.5C and above, clear differences emerge, with cells using EC-containing electrolytes retaining higher capacities at elevated rates.

To further assess the practical applicability of the developed electrolytes, the life cycle performance of all three formulations—0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), and 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt)—was evaluated at different temperatures, with the standard electrolyte LP40 serving

Table II. Ionic conductivity κ of LiBOB at various concentrations m in 85% DEA and 15% EC at 25 °C. Values represent the mean of three independent measurements.

m (mol kg ⁻¹)	0.6	0.7	0.8	1.0
$\kappa_{25\text{ }^{\circ}\text{C}}$ (mS cm ⁻¹)	1.64	1.99	1.99	1.89

Table III. Investigated solvent mixtures by weight (wt) combined with 0.7 m LiBOB and their ionic conductivity at 25 °C. Values represent the mean of three independent measurements.

DEA	EC	PC	$\kappa_{25\text{ }^{\circ}\text{C}}$ (mS cm ⁻¹)
85%	15%	—	1.99
60%	40%	—	2.66
60%	—	40%	2.67
60%	20%	20%	2.65

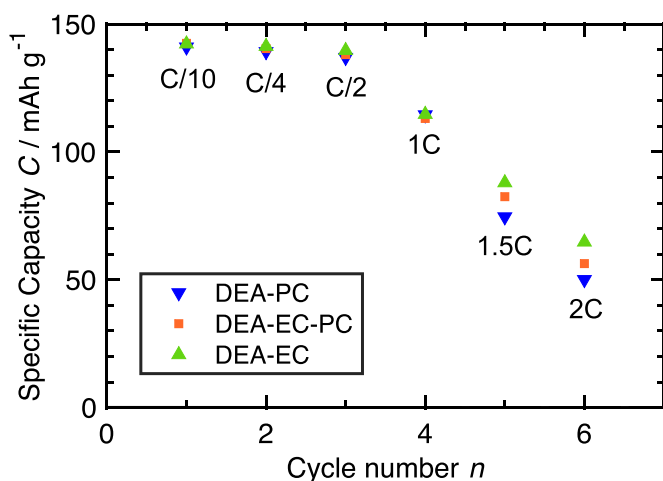


Figure 2. Specific discharge capacity at various C-rates for NCM/graphite cells using a LiBOB concentration of 0.7 m and different solvent compositions (DEA:EC (60:40 wt), DEA:PC (60:40 wt) and DEA:EC:PC (60:20:20 wt)).

as a benchmark. This approach ensures that all three electrolytes are systematically examined, as previous results did not provide a clear indication of which composition might deliver the best overall performance. The following section presents the performance of the cells over extended cycling, highlighting the influence of electrolyte composition and temperature on capacity retention and overall stability in comparison to the standard LP40 electrolyte.

Life cycle performance at different temperatures.—The cycling stability of cells containing the various electrolytes was assessed over 80 to 1000 cycles at different temperatures. After completion of the formation process described in the experimental section, the cells were charged at C/2 under constant current–constant voltage (CCCV) conditions and discharged at C/2 under constant current (CC) conditions, except where noted otherwise.

Ambient temperature (25 °C).—Figure 3 shows the cycling performance of cells containing LiBOB–DEA-based electrolytes compared to cells with LP40 at 25 °C. Due to limited channel capacity, only selected cells were cycled beyond 100 cycles. Additional reference cells containing 0.7 m LiBOB in EC:DEC (50:50 wt) and 1 m LiPF₆ in DEA:EC (60:40 wt) were also investigated to assess the

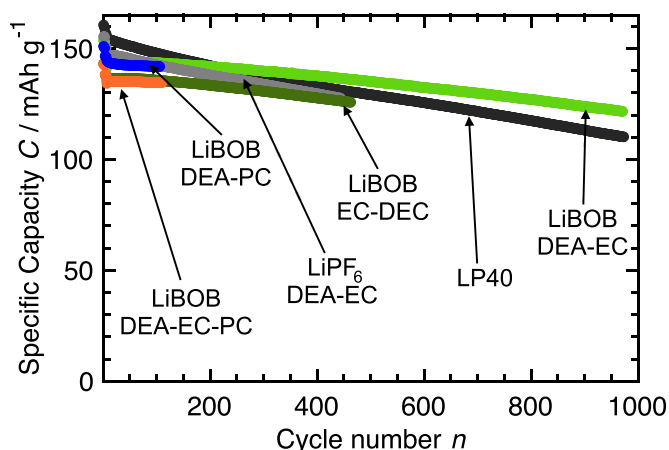


Figure 3. Specific discharge capacity of NCM/graphite cells containing 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt), 0.7 m LiBOB in EC:DEC (50:50 wt), 1 m LiPF₆ in DEA:EC (60:40 wt), and the benchmark electrolyte LP40 at $T_1 = 25\text{ }^{\circ}\text{C}$. The initial three cycles were carried out at C/10, followed by three cycles at C/5 as part of the formation procedure. After formation, the cells were charged at C/2 under CCCV conditions and discharged at C/2 under CC conditions. Cells employing LiBOB-based electrolytes show markedly reduced capacity fade compared to the LiPF₆-based reference electrolytes.

individual influence of the conducting salt (LiBOB) and the novel DEA solvent, respectively.

It can be observed that cells with LiBOB–DEA-based electrolytes exhibit a lower initial specific capacity compared to LP40-based cells. This behavior may be attributed to the lower ionic conductivity of these electrolytes, which can result in increased overpotentials, as well as to the lower coulombic efficiency observed during the first formation cycle, indicating increased formation losses. However, cells containing LiBOB–DEA-based electrolytes show a significantly reduced capacity fade over cycling, indicating improved aging behavior compared to LP40. After 100 cycles, all cells with LiBOB–DEA-based electrolytes retain more than 98% of their initial capacity (referenced to the first cycle after formation). In contrast, cells containing the benchmark electrolyte LP40 retain only 95.6% under the same conditions.

The additional reference cells provide further insight into the individual effects of the conducting salt and solvent. The cell containing 1 m LiPF₆ in DEA:EC (60:40 wt) exhibits a capacity-fade slope similar to that of LP40, but at a lower specific capacity, retaining 97% of its initial capacity after 100 cycles. In contrast, the cell containing 0.7 m LiBOB in EC:DEC (50:50 wt) shows a degradation trend comparable to those of the other LiBOB-based electrolytes, retaining 99% of its initial capacity after 100 cycles. The specific capacity of this cell remains in a similar range to that of the LiBOB–DEA–EC–PC cell. These results suggest that the use of LiBOB contributes to the improved aging behavior, while the electrolyte composition and solvent system additionally affect the accessible specific capacity.

Comparing the three LiBOB–DEA-based electrolytes, a similar aging behavior is observed over the first 100 cycles; however, the cell containing DEA–EC–PC exhibits a lower specific capacity. Among the three systems, the LiBOB–DEA–EC cell shows the highest usable capacity after 100 cycles along with the lowest degree of degradation. Nevertheless, the difference compared to the LiBOB–DEA–PC cell is small and may fall within the range of experimental variability.

To further investigate the long-term performance, the cell with the LiBOB–DEA–EC electrolyte as well as the reference cell with LP40 were further cycled up to nearly 1000 cycles. The specific capacities of both cells intersect at approximately cycle 210; beyond

this point, the LiBOB–DEA–EC cell consistently exhibits higher capacity than the LP40 cell. After 965 cycles, the LiBOB–DEA–EC cell retains about 85.1% of its initial capacity (referenced to the capacity after formation), whereas the LP40 cell retains only 71.4%.

Moderately elevated temperature (40 °C).—To further assess the thermal stability of the investigated electrolyte systems, cycling performance was evaluated at moderately elevated temperature (40 °C). Figure 4 shows the corresponding cycling behavior of NCM/graphite cells. Due to a failure of the cell tester, the measurements were terminated prematurely and could not be meaningfully resumed; therefore, only the first 80 cycles are available for evaluation at this temperature.

At the beginning of cycling, the LiBOB–DEA–EC electrolyte exhibits a specific capacity comparable to that of the LP40 benchmark electrolyte, while the other two LiBOB–DEA-based electrolytes start at slightly lower capacities. Over the course of 80 cycles, all three LiBOB–DEA-based systems show significantly reduced capacity fade compared to LP40. The discharge capacity of the LiBOB–DEA–EC cell surpasses that of the LP40 cell after only a few cycles, while the two other LiBOB–DEA-based electrolytes exceed the LP40 capacity between cycle 40 and 50 and maintain higher capacities thereafter. After 80 cycles, the LiBOB–DEA-based cells retain approximately 99% of their capacity relative to the value measured after formation, whereas the LP40 cell retains only about 91.5% of its post-formation capacity.

Elevated temperature (60 °C).—To assess the effect of elevated temperature on electrochemical performance and degradation behavior, cycling tests were performed at 60 °C. Figure 5 shows the corresponding cycling performance of the investigated cells. The cell containing LP40 exhibits a pronounced, initially exponential capacity decay, which stabilizes at approximately 65 mAh g^{−1} after 120 cycles. In contrast, cells with LiBOB–DEA-based electrolytes display significantly improved stability, showing much lower capacity fade over the entire cycling period.

At the beginning of cycling, the LiBOB–DEA–EC cell delivers a distinctly higher specific capacity than the other two LiBOB–DEA-based systems, which exhibit very similar initial capacities. However, the LiBOB–DEA–EC cell also shows a more pronounced degradation over cycling. In comparison, the LiBOB–DEA–PC and

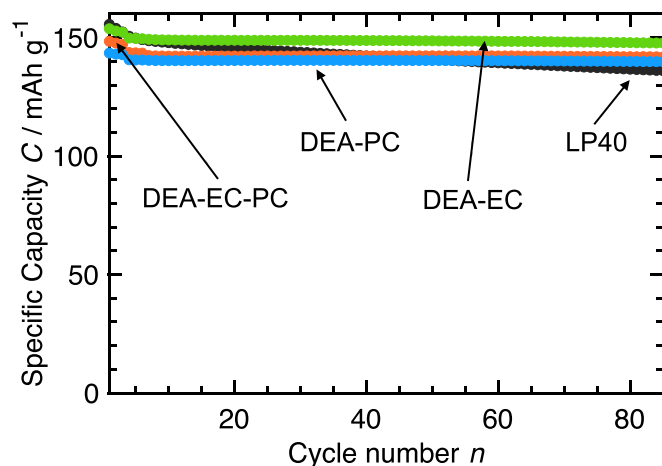


Figure 4. Specific discharge capacity of NCM/graphite cells containing 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt) and the benchmark electrolyte LP40 at $T_2 = 40$ °C. Cycling was carried out at C/2 under CCCV charging and CC discharging after the standard formation procedure. All LiBOB–DEA-based electrolytes show reduced capacity fade compared to LP40.

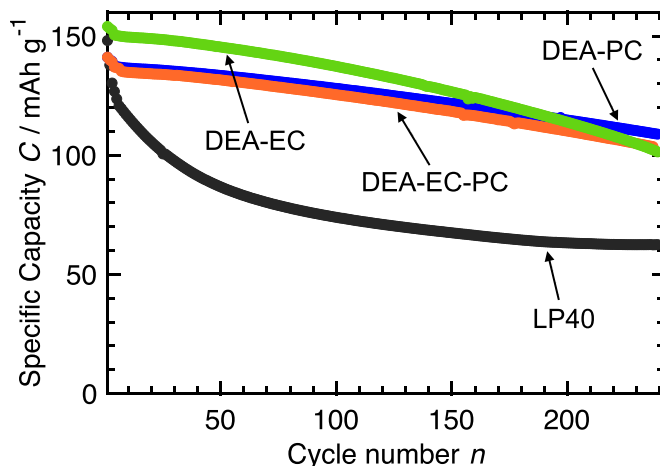


Figure 5. Specific discharge capacity of NCM/graphite cells containing 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt) and the benchmark electrolyte LP40 at $T_3 = 60$ °C. After formation, cells were cycled at C/2 under CCCV charging and CC discharging conditions. All LiBOB–DEA-based electrolytes show reduced capacity fade compared to LP40.

LiBOB–DEA–EC–PC cells exhibit similar behavior in terms of both capacity and degradation, with the LiBOB–DEA–EC–PC cell showing slightly higher capacity fade.

After 240 cycles, the remaining capacity amounts to approximately 79.8% for the LiBOB–DEA–PC cell, 75.6% for the LiBOB–DEA–EC–PC cell, and 68.2% for the LiBOB–DEA–EC cell, all referenced to the capacity after formation. In contrast, the LP40 cell retains only about 52.2% under the same conditions and already exhibits a significantly lower capacity at the beginning of cycling compared to the LiBOB–DEA-based cells. The pronounced degradation is likely related to the thermal instability of the conducting salt LiPF₆, whose decomposition is known to accelerate at elevated temperatures, leading to the formation of reactive species that promote parasitic side reactions and ongoing interfacial degradation. These results clearly demonstrate the significantly improved thermal stability of the LiBOB–DEA-based electrolyte systems under high-temperature operating conditions.

High temperature (70 °C).—In parallel to the measurements at 60 °C, additional cycling experiments were conducted at 70 °C to further assess electrolyte stability under more severe thermal conditions. The corresponding results are shown in Fig. 6. Figure 6a presents the specific discharge capacity over 200 cycles following formation at 25 °C. The LiBOB–DEA–EC and LP40 cells show the highest initial discharge capacities after formation, whereas the LiBOB–DEA–PC and LiBOB–DEA–EC–PC cells start at slightly lower capacity levels. Despite these differences in initial capacity, all LiBOB–DEA-based electrolytes exhibit improved capacity retention compared to LP40, highlighting their enhanced stability under elevated temperature conditions. Among the investigated formulations, the LiBOB–DEA–PC electrolyte shows the highest capacity retention, maintaining 68.1% of its capacity after 200 cycles (referenced to the capacity after formation). The LiBOB–DEA–EC–PC electrolyte retains 59.1% of its capacity, while the LiBOB–DEA–EC electrolyte exhibits the strongest capacity fading with a retention of 51.3% after 200 cycles. The trends observed for the LiBOB–DEA-based electrolytes are consistent with those at 60 °C. In particular, the beneficial effect of the PC-containing electrolyte formulation observed at 60 °C is maintained, with the LiBOB–DEA–PC electrolyte showing the highest capacity retention among the investigated systems. In contrast, the LP40 cell shows significantly more pronounced capacity fading, which is likely related to the limited thermal stability of

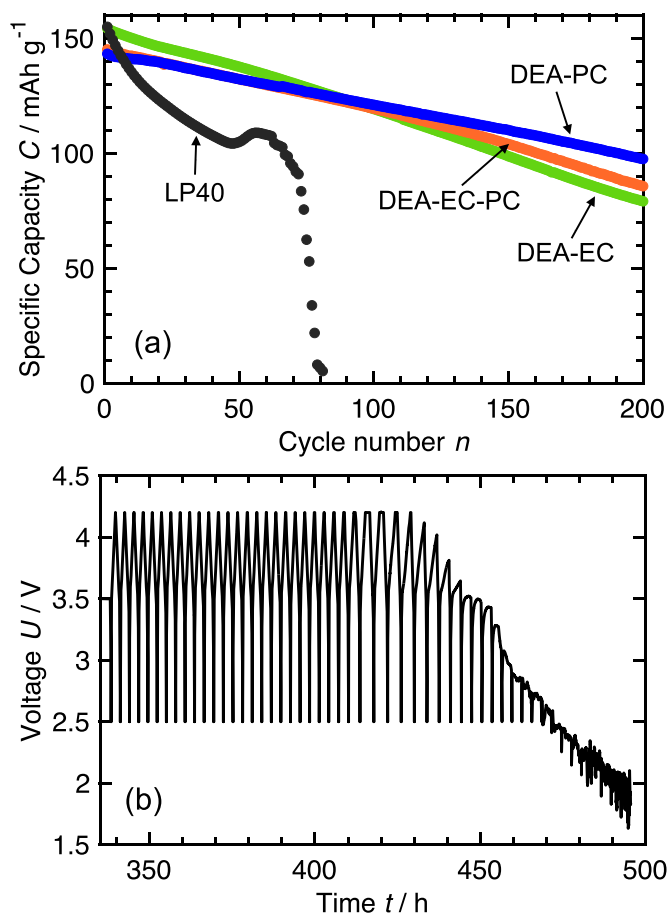


Figure 6. Cycling performance at $T_4 = 70\text{ }^{\circ}\text{C}$ following formation at $25\text{ }^{\circ}\text{C}$. (a) Specific discharge capacity of NCM/graphite cells containing 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt), and the benchmark electrolyte LP40. Cells were cycled at C/2 under CCCV charging and CC discharging conditions. The LiBOB-DEA-based electrolytes exhibit improved capacity retention compared to LP40. (b) Voltage profiles of the LP40 cell starting from cycle 45, showing deviations from regular behavior, including a prolonged CV phase, decreasing maximum voltage, and ultimately leading to cell failure at approximately cycle 80.

the LiPF₆-based electrolyte system. The overall behavior is similar to that observed at $60\text{ }^{\circ}\text{C}$, but even more pronounced. The capacity decreases rapidly during the initial cycles, followed by a temporary capacity increase starting around cycle 50, reaching a local maximum at cycle 56, before dropping sharply toward zero, ultimately leading to cell failure at approximately cycle 80.

Figure 6b shows the voltage profiles of the LP40 cell from cycle 45 onwards. While the initial cycles appear largely regular, deviations become noticeable from approximately cycle 70 (around 410 h) onwards, including a prolonged CV phase. The extended CV phase suggests increasing cell polarization and impedance, consistent with an earlier transition from the constant-current to the constant-voltage charging step and a prolonged constant-voltage period. In the subsequent cycles, the cell no longer reaches the upper cut-off voltage of 4.2 V. The maximum voltage gradually decreases, and the voltage profiles become increasingly irregular and noisy. This transition indicates that degradation has progressed beyond increased polarization alone and is likely associated with severe degradation of the electrode/electrolyte interfaces and accelerated electrolyte decomposition at elevated temperature, resulting in a loss of normal cell functionality. In the final stage, the voltage drops below the lower cut-off limit of 2.5 V, indicating severe cell degradation. This irregular evolution

of the voltage curves reflects the onset of pronounced degradation processes, ultimately leading to rapid cell failure.

Low temperature ($10\text{ }^{\circ}\text{C}$).—Figure 7 presents the cycling performance of the cells at $10\text{ }^{\circ}\text{C}$. Following the standard formation procedure, cycling was carried out at C/4 instead of C/2 in order to account for the reduced ionic conductivity and slower reaction kinetics at lower temperatures.

The initial cycling of the LiBOB-DEA-EC cell is characterized by a rapid, approximately exponential capacity loss, which stabilizes at around 120 mAh g^{-1} after roughly 100 cycles and then remains relatively constant up to cycle 250 (end of the measurement). In contrast, the capacity fade of the cells with the other electrolytes exhibits an almost linear decrease from the beginning. The LiBOB-DEA-EC-PC cell was also evaluated for 250 cycles and showed a similar capacity-fade trend to the LiBOB-DEA-PC cell, but at a consistently lower capacity. The LiBOB-DEA-PC cell and the reference LP40 cell behave similarly in terms of delivered capacity and degradation over a large portion of the 1000 cycles.

It should be noted that the measurement of the LiBOB-DEA-PC cell was temporarily paused at cycle 600 due to a failure and replacement of the data acquisition computer. This interruption is visible as a slight capacity jump at cycle 600. Overall, the LiBOB-DEA-PC cell starts at a slightly lower capacity but retains a higher capacity by the end of the measurement, resulting in reduced overall capacity loss compared to the LP40 cell. After 1000 cycles, the remaining capacity is 79.6% for the DEA-PC cell relative to its maximum capacity after formation, versus 72.3% for the LP40 cell relative to its capacity after formation.

Overall temperature-dependent cycling stability.—Across the investigated temperature range, a clear dependence of cycling stability on both temperature and electrolyte composition is observed. At low and ambient temperatures (10 and $25\text{ }^{\circ}\text{C}$), LiBOB-DEA-based electrolytes already exhibit improved capacity retention compared to the LP40 reference, despite slightly lower or comparable initial capacities. At $25\text{ }^{\circ}\text{C}$, the specific capacity curves of the LiBOB-DEA-EC and LP40 cells intersect at approximately cycle 210. Beyond this point, the LiBOB-DEA-EC cell maintains superior capacity, demonstrating a clear long-term stability benefit even under

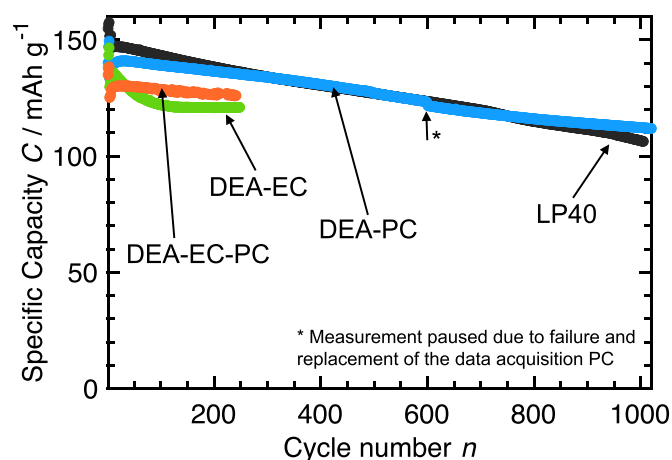


Figure 7. Specific discharge capacity of NCM/graphite cells containing 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt), 0.7 m LiBOB in DEA:EC:PC (60:20:20 wt) and the standard electrolyte LP40 at $T_5 = 10\text{ }^{\circ}\text{C}$. The initial three cycles were carried out at C/10, followed by three cycles at C/5 as part of the formation procedure. After formation, the cells were charged at C/4 under CCCV conditions and discharged at C/4 under CC conditions. The cell with LiBOB-DEA-PC electrolyte exhibits a slightly higher capacity retention compared to the cell with the LP40 electrolyte.

moderate operating conditions. This behavior may be related to the absence of LiPF_6 , which tends to form corrosive HF and starts to decompose at temperatures around 55°C ⁴⁶ or possibly even lower.⁴⁷ In comparison, LiBOB is known to exhibit higher thermal stability, with decomposition reported above 300°C ,⁴⁸ effectively limiting salt-driven degradation reactions within the investigated temperature range.

At 40 and 60°C , the differences in degradation behavior are significantly amplified. While LP40 shows accelerated capacity fading, particularly at higher temperatures, LiBOB–DEA-based electrolytes maintain markedly improved stability, with reduced capacity loss and more gradual degradation. Among the investigated systems, LiBOB–DEA–PC and LiBOB–DEA–EC–PC tend to exhibit the best long-term stability, whereas LiBOB–DEA–EC shows higher initial capacities but somewhat increased degradation at elevated temperatures.

At 70°C , the contrast between the electrolyte systems becomes most pronounced. The LP40 cell undergoes rapid degradation and early failure, while the LiBOB–DEA-based cells continue to operate with a comparatively stable, nearly linear capacity decay. Overall, these results demonstrate the superior thermal robustness of LiBOB–DEA-based electrolytes, particularly under demanding high-temperature conditions.

Differential scanning calorimetry.—The thermal behavior of the electrolyte formulations was investigated by DSC measurements, as shown in Fig. 8. The glass transition temperature (T_g) and liquidus temperature (T_{liq}) were determined from the inflection point of the baseline shift and the peak temperature of the corresponding endothermic transition, respectively.

The 0.7 m LiBOB in DEA:EC (60:40 wt) electrolyte exhibits a glass transition temperature of -93.9°C and a liquidus temperature of 11.2°C . In addition, the DSC thermogram of the DEA–EC-based electrolyte shows two distinct endothermic transitions, indicating the occurrence of multiple thermal events during heating. These transitions suggest the presence of multiple thermal events, which may be related to different phase transformations or melting processes within the electrolyte system. In comparison, the LiBOB in DEA:PC (60:40 wt) electrolyte shows a slightly lower glass transition temperature of -97.4°C and a significantly lower liquidus temperature of -33.7°C . The reduced T_{liq} of the DEA–PC-based electrolyte indicates improved low-temperature phase stability and a reduced tendency for crystallization compared to the DEA–EC formulation.

The relatively high liquidus temperature of the DEA–EC-based electrolyte may contribute to the reduced electrochemical performance observed at 10°C , where a pronounced capacity decay was observed during the initial cycling period. At this temperature, the electrolyte is close to its liquidus transition, which may indicate reduced low-temperature phase stability and limited ion mobility, potentially affecting lithium-ion transport and interfacial processes during cycling.

The reference electrolyte LP40 exhibits the lowest glass transition temperature of -110.4°C , suggesting the highest molecular mobility among the investigated electrolyte systems. The higher T_g values of the LiBOB-based electrolytes compared to LP40 suggest reduced molecular mobility, which is consistent with their lower ionic conductivity. However, LP40 shows a liquidus temperature of -0.6°C , which is lower than that of the DEA–EC-based electrolyte but higher than that of the DEA–PC-based electrolyte. The differences in thermal transitions can be attributed to the distinct solvent properties and interactions between lithium ions, anions, and solvent molecules.

Electrolyte conductivity.—Figure 9a presents the ionic conductivity of the LiBOB–DEA-based electrolytes as a function of temperature, benchmarked against the reference electrolyte LP40. Across the investigated temperature range from 5°C to 60°C , all electrolytes exhibit the expected monotonic increase in ionic conductivity with increasing temperature, reflecting enhanced ion mobility

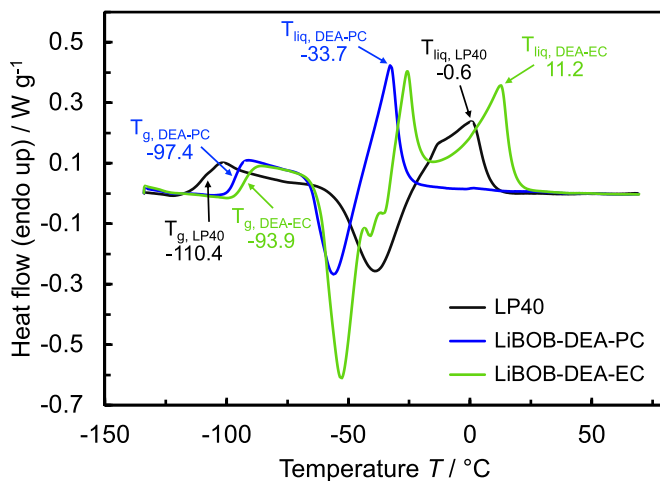


Figure 8. Differential scanning calorimetry (DSC) thermograms of the 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt) electrolytes, and the reference electrolyte LP40. The heat flow signal (endothermic up) is plotted as a function of temperature in the range from -135 to 70°C at a heating rate of $10^\circ\text{C min}^{-1}$. Measurements were performed using comparable sample masses (DEA–EC: 35.18 mg ; DEA–PC: 34.57 mg ; LP40: 36.7 mg).

and reduced viscosity at elevated temperatures. However, the absolute conductivity values of the LiBOB–DEA-based systems remain consistently lower than those of LP40 across the full temperature window.

At $T = 25^\circ\text{C}$, the ionic conductivity of both LiBOB–DEA-based electrolytes is 2.7 mS cm^{-1} , compared to 7.7 mS cm^{-1} for LP40, corresponding to a conductivity that is lower by a factor of 2.9. While the absolute difference decreases at lower temperatures, the relative deviation between the LiBOB–DEA-based electrolytes and LP40 increases from 2.3 at 60°C to 3.7 at 5°C .

Figure 9b shows the corresponding Arrhenius plots of the ionic conductivity for the LiBOB–DEA-based electrolytes and the reference electrolyte LP40. All electrolytes exhibit an approximately linear relationship over the investigated temperature range, indicating Arrhenius-type behavior. The apparent activation energies (E_a) were determined from the slopes of the linear fits according to the Arrhenius equation. The LiBOB–DEA–EC and LiBOB–DEA–PC electrolytes exhibit apparent activation energies of 20.6 and 19.7 kJ mol^{-1} , respectively, compared to 14.3 kJ mol^{-1} for LP40. The similar ionic conductivities and apparent activation energies of the LiBOB–DEA–EC and LiBOB–DEA–PC electrolytes suggest that differences in electrochemical performance between the two formulations cannot be explained by the ionic conductivity alone.

The higher activation energies of the LiBOB–DEA-based electrolytes indicate a larger energy barrier for ionic transport and a stronger temperature dependence of the ionic conductivity. This behavior is reflected in the conductivity data shown in Fig. 9a, where the LiBOB-based electrolytes exhibit ionic conductivities that are approximately two to three times lower than those of LP40. Although the electrolytes remain within the same order of magnitude, this reduction is expected to limit ion transport, particularly at low temperatures and elevated current densities. This represents a relevant limitation for high-power operation, where sufficient ionic transport is required to mitigate polarization losses. The consequences of the reduced ionic conductivity are reflected in the rate capability measurements discussed in a later section. The reduced conductivity and higher activation energies can be attributed to the higher viscosity of the DEA-based electrolytes as well as the lower degree of dissociation and reduced ionic mobility of LiBOB compared to LiPF_6 . Recent studies have demonstrated the feasibility of LiBOB as a stand-alone conducting salt in fluorine-free electrolytes.^{26,27} The present results

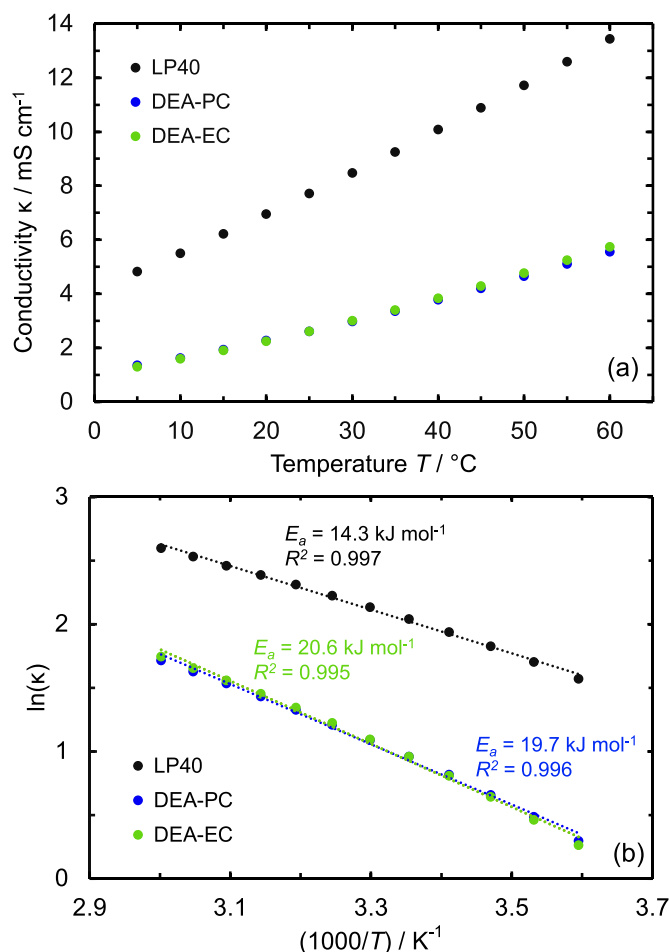


Figure 9. (a) Temperature-dependent ionic conductivity of 0.7 m LiBOB in DEA:EC (60:40 wt) and 0.7 m LiBOB in DEA:PC (60:40 wt) compared to the reference electrolyte LP40 over 5 – 60 °C. The DEA-based electrolytes exhibit ionic conductivities approximately 2–3 times lower than those of LP40 over the investigated temperature range. (b) Arrhenius plots of the ionic conductivity ($\ln(\kappa)$ versus $1000/T$) with linear fits used to determine the apparent activation energies. Data represent the mean of three independent measurements.

further show that, despite the lower ionic conductivity compared to conventional LiPF₆-based electrolytes, LiBOB–DEA-based electrolytes can provide excellent long-term cycling stability together with significantly improved thermal safety.

Voltage profiles at different temperatures.—Figure 10 presents the voltage profiles as a function of specific capacity for NCM/graphite cells employing (a) the LiBOB–DEA–EC electrolyte, (b) the LiBOB–DEA–PC electrolyte and (c) the reference electrolyte LP40, recorded at temperatures between 10 and 60 °C at a C/4 rate. For both LiBOB–DEA-based electrolytes, a clear temperature dependence of the accessible capacity is observed, with increasing temperature leading to higher extractable capacities. The most pronounced increase occurs between 10 and 20 °C, indicating a substantial reduction of kinetic limitations in this temperature range. In comparison to 20 °C, the accessible capacity at 10 °C is reduced by approximately 10%, which can be attributed to reduced ionic conductivity of the electrolyte and slower lithium-ion diffusion in the electrode materials, leading to increased polarization and limited capacity utilization. For the LiBOB–DEA–EC electrolyte, this performance limitation may also be related to its relatively high liquidus temperature ($T_{liq} = 11.2$ °C), as the operating temperature is close to this

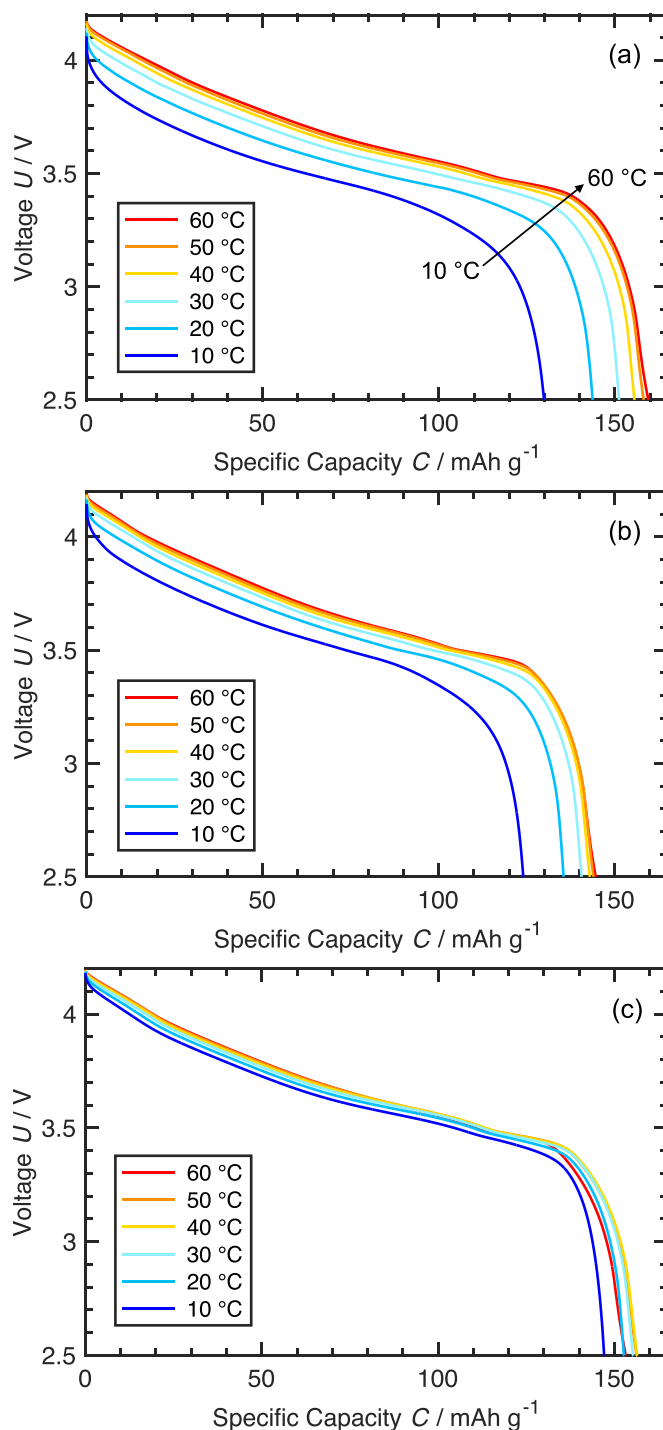


Figure 10. Voltage profiles as a function of specific capacity for NCM/graphite cells with (a) 0.7 m LiBOB in DEA:EC (60:40 wt), (b) 0.7 m LiBOB in DEA:PC (60:40 wt) and (c) the reference electrolyte LP40 at different temperatures, recorded at a C/4 rate.

transition, indicating less favorable low-temperature phase behavior. With further increasing temperature, the incremental capacity gains of the LiBOB–DEA-based electrolytes become progressively smaller, suggesting that the dominant transport and charge-transfer limitations are increasingly mitigated. At elevated temperatures, the accessible capacity exceeds that at 20 °C by approximately 10% at 50 and 60 °C. The voltage profiles at these temperatures nearly overlap, indicating that the capacity approaches a limiting value

under these conditions. This behavior suggests that kinetic limitations present at lower temperatures are largely alleviated at elevated temperatures, resulting in more efficient charge transfer and lithium-ion transport. The LiBOB–DEA–PC electrolyte exhibits consistently lower accessible capacities than the LiBOB–DEA–EC electrolyte over the investigated temperature range, consistent with its lower initial discharge capacity observed during long-term cycling.

In contrast, the LP40 electrolyte exhibits only minor changes in both the voltage profiles and accessible capacity over the investigated temperature range. The highest capacity is obtained at 40 and 50 °C, whereas a slight decrease is observed at 60 °C. This suggests that the beneficial effect of enhanced transport properties at elevated temperature is partly compensated by competing temperature-dependent processes, resulting in a slight reduction in accessible capacity at 60 °C. The comparatively weak temperature dependence of LP40 is consistent with its higher ionic conductivity and lower activation energy, resulting in less pronounced transport limitations over the investigated temperature range.

Rate capability.—The C-rate performance of an NCM/graphite cell employing the LiBOB–DEA–EC electrolyte was evaluated at 25 °C. Discharge profiles were recorded at C-rates of C/10, C/4, C/2, 1C, 1.5C, and 2C, while charging was consistently performed using a C/5 CCCV protocol to ensure that each discharge started from a well-defined and comparable state of charge. The corresponding voltage profiles as a function of specific capacity are shown in Fig. 11.

Up to a discharge rate of C/2, only a minor reduction in accessible capacity is observed, with about 98% of the C/10 capacity retained, indicating good rate capability in the low-to-moderate current regime. A more pronounced drop occurs at 1C, where only approximately 80% of the C/10 capacity is accessible, with further reductions at 1.5C and 2C. This behavior suggests the onset of significant kinetic limitations at higher current densities, likely caused by increased polarization and limited lithium-ion transport due to the relatively low ionic conductivity of the LiBOB–DEA–EC electrolyte. These results indicate that the electrolyte is well suited for low-to-moderate C-rate operation, whereas its application in high-power systems requiring sustained high current densities may be limited by increased polarization losses, which contribute to the pronounced reduction in accessible capacity at rates above 1C.

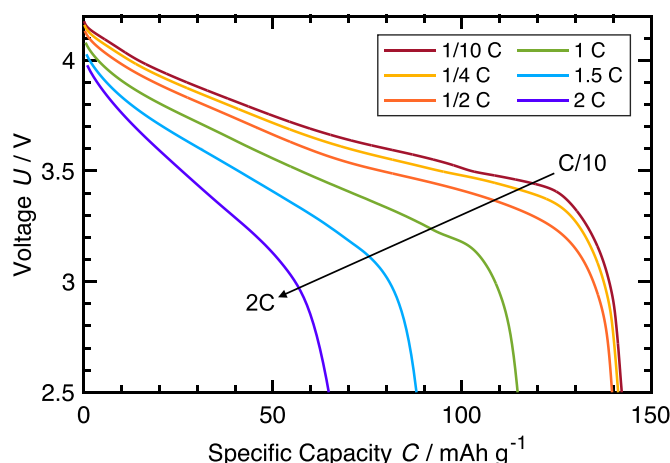


Figure 11. Voltage profiles vs. specific discharge capacity of an NCM/graphite cell with 0.7 m LiBOB in DEA:EC (60:40 wt) electrolyte at $T = 25$ °C, discharged at C/10, C/4, C/2, 1C, 1.5C and 2C. Up to C/2, capacity loss is minor ($\approx 98\%$ of C/10), while higher rates lead to more pronounced reductions (80% at 1C), reflecting the onset of kinetic limitations at elevated discharge rates.

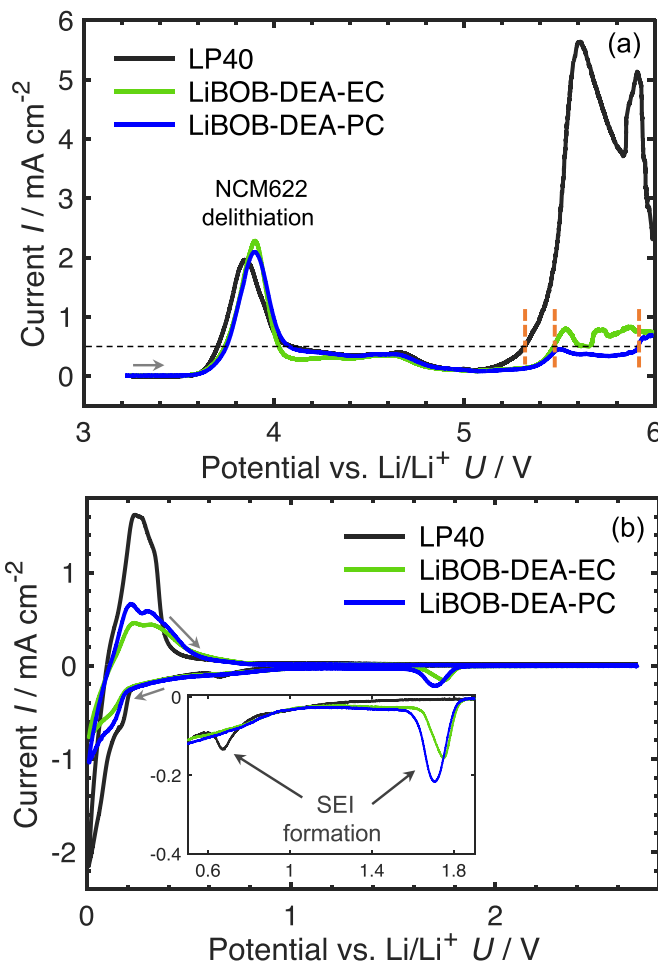


Figure 12. Electrochemical stability of 0.7 m LiBOB in DEA:EC (60:40 wt), 0.7 m LiBOB in DEA:PC (60:40 wt) and the reference electrolyte LP40, measured at a scan rate of 0.1 mV s^{-1} using lithium metal as the counter electrode and a lithium reference ring. (a) Oxidation stability determined with NCM622 as the working electrode by LSV. The apparent oxidative stability limits of the electrolytes, defined at a current density of 0.5 mA cm^{-2} , are indicated by dashed lines. (b) Reductive behavior determined with graphite as the working electrode during the first CV cycle.

Electrochemical stability.—The electrochemical stability of the DEA-based electrolytes was evaluated using linear sweep voltammetry (LSV) and cyclic voltammetry (CV) and compared with the reference electrolyte LP40. Lithium metal was used as the counter electrode and a lithium reference ring as the reference electrode. The measurements were performed in a three-electrode configuration, initiated at the open-circuit voltage (OCV), and conducted at a scan rate of 0.1 mV s^{-1} .

For oxidative stability, NCM622 was employed as the working electrode and the potential was swept anodically toward 6.0 V vs. Li/Li^+ (Fig. 12a). The anodic current response reflects both NCM622 delithiation and possible electrolyte oxidation. For all electrolytes, an increase in current associated with NCM622 delithiation is observed from approximately 3.6 V vs. Li/Li^+ . For the LiBOB–DEA-based electrolytes, this feature is slightly shifted toward higher potentials by approximately 50–80 mV compared to LP40. At higher potentials, the current response is increasingly affected by electrolyte oxidation and is therefore more relevant for assessing the oxidative stability of the electrolyte. As no universally defined current-density criterion exists for determining the oxidative stability limit, a threshold of 0.5 mA cm^{-2} was used based on previously reported criteria.⁴⁹ Based on this criterion, the apparent oxidative stability limits were

determined to be approximately 5.35 V for LP40 and 5.5 V for the LiBOB–DEA–EC electrolyte. The LiBOB–DEA–PC electrolyte also shows a slight increase in current at approximately 5.5 V; however, the current remains below 0.5 mA cm^{-2} and reaches this threshold only at approximately 5.9 V. Compared to LP40, both LiBOB–DEA-based electrolytes exhibit a delayed onset and less pronounced increase in anodic current at higher potentials. The earlier and more pronounced current increase observed for LP40 indicates a higher susceptibility to anodic electrolyte decomposition. These results suggest an improved apparent oxidative stability of the LiBOB–DEA-based electrolytes compared to LP40.

For reductive stability, graphite was used as the working electrode and a CV was recorded between the OCV and 0.01 V vs. Li/Li^+ (Fig. 12b shows the first cycle). The first cathodic scan provides information on the reduction processes occurring at the graphite/electrolyte interface and the associated formation of the solid electrolyte interphase (SEI). Distinct reduction features are observed for LP40 and the LiBOB–DEA-based electrolytes. The LiBOB–DEA-based electrolytes exhibit a pronounced reduction feature at approximately 1.8–1.6 V vs. Li/Li^+ , consistent with the reported reduction of LiBOB and the formation of a LiBOB-derived interphase on graphite.⁵⁰ In LP40, the corresponding reduction occurs at lower potentials of approximately 0.8–0.6 V vs. Li/Li^+ , consistent with the reduction of carbonate solvents and SEI formation in LiPF_6 -based electrolytes.⁵⁰ At potentials below approximately 0.25 V vs. Li/Li^+ , all electrolytes exhibit the characteristic current increase associated with graphite lithiation. During the reverse scan, the characteristic anodic current response corresponding to graphite delithiation is observed. Overall, these results provide complementary information on the reductive behavior of the electrolytes and the initial interfacial processes on graphite.

Flash point.—Under practical operating conditions, battery cell temperatures can readily exceed 50°C .⁵¹ Under such conditions, especially in the presence of mechanical damage or internal short circuits, the formation and ignition of flammable vapors may occur. Conventional carbonate-based electrolytes, such as LP40, exhibit relatively low flash points of approximately $T_{\text{FP}} \approx 37^\circ\text{C}$, which poses a significant safety risk. Therefore, enhancing the intrinsic fire safety of electrolyte formulations represents a key objective in this work.

In contrast to the aforementioned conventional commercial electrolytes, the DEA-based solvent systems investigated in this work exhibit significantly higher flash points. The solvent mixtures DEA:EC (60:40 wt) and DEA:PC (60:40 wt), both without lithium salt, show flash points of $T_{\text{FP,DEA:EC}} = 132 \pm 2^\circ\text{C}$ and $T_{\text{FP,DEA:PC}} = 125 \pm 2^\circ\text{C}$, respectively, as determined according to ISO 3679. These values correspond to increases of around 90 K compared to the flash point of LP40. Previous measurements performed in our group on comparable LiBOB-based electrolyte systems containing different solvent mixtures indicated that the addition of LiBOB had no significant influence on the measured flash point values. Therefore, the determined flash points of the DEA-based solvent mixtures provide a useful indication of the improved flammability characteristics of the corresponding LiBOB-based electrolyte formulations.

The markedly increased flash points of the DEA-based solvent systems highlight their favorable flammability characteristics and suggest an improved inherent safety potential compared to conventional carbonate-based electrolytes. This aspect is particularly relevant considering that lithium-ion cells typically operate at temperatures approaching an upper limit of around 60°C . Even at such elevated temperatures, both DEA-based systems remain well below their flash points, resulting in a significantly wider thermal safety margin compared to conventional carbonate-based electrolytes. Consequently, the use of DEA-based solvent systems may contribute to reducing the risk associated with electrolyte ignition under abusive conditions such as overheating, mechanical damage, or internal failure.

Thermal abuse test.—NCM/graphite coin cells were prepared with the new electrolyte, 0.7 m LiBOB in DEA:EC (60:40 wt). For comparison, reference cells were assembled using the standard electrolyte LP40 as well as 1 m LiPF_6 in EC:PC (50:50 wt), which does not contain volatile linear carbonates. After formation using the standard formation protocol applied for all measurements, all cells were charged to 100% state of charge.

Thermal stability was evaluated using heat–wait–seek (HWS) experiments in an accelerating rate calorimeter. During testing, the cell temperature was increased in 5°C steps, each followed by a 20 min (quasi-)adiabatic hold, allowing detection of self-heating that signals the onset of exothermic reactions.

The thermal response of NCM/graphite cells containing the different electrolytes is compared in Fig. 13. All cells exhibit pronounced exothermic activity around 175°C , consistent with the onset of cathode decomposition and associated reactions.^{52–54} While cathode decomposition represents a common high-temperature failure mechanism, variations in electrolyte composition can lead to differences in the onset temperature and the intensity of the exothermic events.⁵⁵

In contrast to the similar thermal behavior observed at elevated temperatures, clear differences between the electrolyte systems emerge at lower temperatures. Cells containing LiPF_6 -based electrolytes—both LP40 (Fig. 13a) and the EC:PC formulation without linear carbonates (Fig. 13b)—show additional exothermic reactions at approximately 110°C . This early self-heating, which occurs well below the temperature associated with cathode decomposition, is commonly attributed to the thermal breakdown of the solid electrolyte interphase (SEI) and is considered an important precursor to thermal runaway.^{53,55} Once these reactions are initiated, the temperature increase can proceed autonomously, representing a critical safety concern.

Unlike the LiPF_6 -based systems, cells containing the LiBOB–DEA-based electrolyte (Fig. 13c) do not exhibit comparable self-heating in this temperature range. No detectable self-heating is observed before the onset of the high-temperature exothermic reactions at approximately 175°C , representing a shift in the onset of detectable self-heating from approximately 110°C for the LiPF_6 -based electrolytes to approximately 175°C for the LiBOB–DEA-based system. This delayed onset of exothermic activity indicates improved thermal stability of the LiBOB–DEA electrolyte system compared to conventional LiPF_6 -based electrolytes.

Conclusions

In this work, electrolyte formulations based on DEA in combination with LiBOB were successfully developed and systematically evaluated in NCM/graphite lithium-ion cells with regard to their electrochemical performance, thermal stability, and safety characteristics. The primary objective of enhancing thermal robustness by avoiding linear carbonates and replacing LiPF_6 was achieved.

Optimization of salt concentration and solvent composition revealed that 0.7 m LiBOB provides a suitable balance between solubility and ionic conductivity. The incorporation of EC and PC as co-solvents significantly improves ionic conductivity, with only minor differences between the respective formulations. The additional reference electrolytes containing LiBOB in EC:DEC and LiPF_6 in DEA:EC further indicate that both the conducting salt and solvent system influence the resulting electrochemical performance and aging behavior.

Electrochemical testing demonstrated that LiBOB–DEA-based electrolytes exhibit slightly lower initial capacities at low and moderate temperatures compared to the benchmark electrolyte LP40, which can be attributed to increased formation losses and lower ionic conductivity. However, all LiBOB–DEA systems show markedly improved capacity retention during long-term cycling. This trend becomes increasingly pronounced with rising temperature.

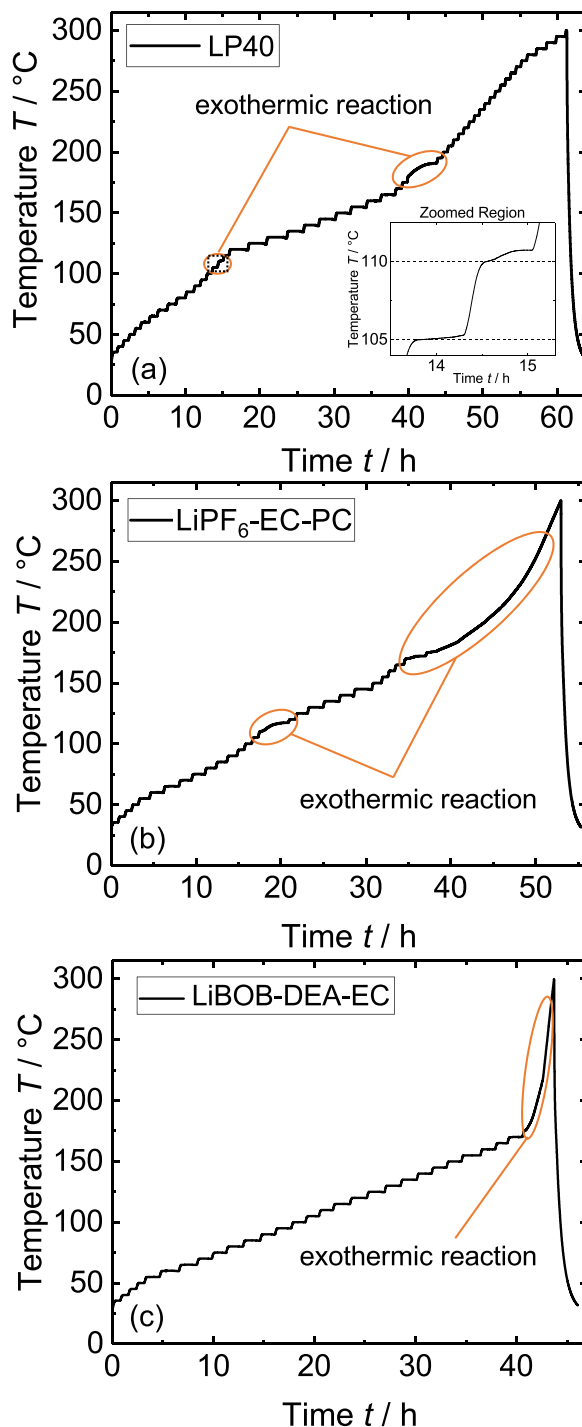


Figure 13. Thermal response of NCM/graphite cells with (a) LP40 (b) 1 m LiPF_6 in EC:PC (50:50 wt) and (c) 0.7 m LiBOB in DEA:EC (60:40 wt). All cells undergo exothermic reactions near 175 °C, whereas LiPF_6 -based electrolytes display additional self-heating at approximately 110 °C.

At 25 °C, the LiBOB–DEA–EC system surpasses LP40 in long-term performance beyond approximately 200 cycles and retains about 85.1% of its initial capacity after 965 cycles, compared to only 71.4% for LP40. At elevated temperatures (40–70 °C), the superiority of LiBOB–DEA-based systems becomes even more evident, with significantly reduced capacity fade and no premature cell failure observed within the investigated cycling periods. Among the studied solvent systems, the DEA:EC (60:40 wt) electrolyte provides favorable rate capability and high initial capacities, while the DEA:PC (60:40 wt) electrolyte exhibits slightly improved

long-term stability at elevated temperatures and more favorable low-temperature performance.

The electrochemical stability measurements further indicate favorable stability of the LiBOB–DEA-based electrolytes. Compared to LP40, both DEA-based electrolytes exhibit a delayed and less pronounced anodic current increase at high potentials, resulting in higher apparent oxidative stability limits. The reductive behavior on graphite shows distinct reduction features at higher potentials for the LiBOB–DEA-based electrolytes, consistent with LiBOB reduction and the formation of a LiBOB-derived interphase.

In addition to electrochemical performance, the developed electrolytes exhibit substantial safety advantages. The flash point of the DEA:EC (60:40 wt) solvent formulation is 132 °C, corresponding to an increase of approximately 95 K compared to LP40, significantly reducing flammability risks. Furthermore, accelerating rate calorimetry measurements reveal the absence of early exothermic reactions associated with SEI decomposition, which are observed in LiPF₆-based systems around 110 °C. This delayed onset of thermal reactions indicates improved thermal stability and safety characteristics.

Although the ionic conductivity of the LiBOB–DEA-based electrolytes is approximately a factor of 2–3 lower than that of LP40, it remains sufficient to enable stable cell operation. This reflects a trade-off between reduced conductivity and significantly enhanced thermal stability and safety of the system.

Overall, the results highlight the strong thermal robustness and improved safety of LiBOB–DEA-based electrolytes while maintaining competitive electrochemical performance compared to conventional LiPF₆-based systems. The combination of fluorine-free LiBOB with DEA-based mixed solvent systems thus represents a promising pathway toward safer and more thermally robust lithium-ion battery electrolytes.

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CRediT authorship contribution statement

Larissa Kiefer: Conceptualization, Methodology, Projekt administration, Investigation, Data curation, Formal analysis, Visualization, Writing—original draft. Yannick Lubik: Investigation, Formal analysis, Writing—review & editing. Philipp Finster: Methodology, Investigation, Data curation, Formal analysis, Writing—review & editing. Carlos Ziebert: Methodology, Resources, Writing—review & editing. Kai Peter Birke: Conceptualization, Funding acquisition, Resources, Supervision, Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

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