Understanding the Role of SEI Layer in Low-Temperature Performance of Lithium-Ion Batteries

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Cite This: https://doi.org/10.1021/acsami.1c23934 **Read Online** ACCESS III Metrics & More Article Recommendations s Supporting Information (Li*)₁(BN)₅ ABSTRACT: Low-temperature electrolytes (LTEs) have been C/20 BN/FEC BN/EC+FEC (mAh g⁻¹) considered as one of the most challenging aspects for the wide Unstable adoption of lithium-ion batteries (LIBs) since the SOA electrolytes C/10 SEI layer cannot sufficiently support the redox reactions at LT resulting in capacity (dramatic performance degradation. Although many attempts have been taken by employing various noncarbonate solvent electrolytes, there was a lack of fundamental understanding of the limiting Specific 05 Stable factors for low-temperature operations (e.g., -20 to -40 °C). In SEI layer this paper, the crucial role of the solid–electrolyte-interface (SEI) -40°C Temp.: in LIB performance at low temperature using a butyronitrile (BN)-(Li⁺)₁(EC)₁(BN)₄ 10 15 2 Cycle number 20 based electrolyte was demonstrated. These results suggested that

dictates the LT performance in terms of capacity and cycle life, presenting a useful guideline in designing new electrolytes to address the LT issue.

KEYWORDS: solid-electrolyte-interface, graphite electrodes, butyronitrile-based electrolytes, low-temperature performance, lithium-ion batteries

INTRODUCTION

Since their commercialization, lithium-ion batteries (LIBs) have transformed our society, providing unprecedented freedom of mobility.^{1,2} LIBs have been a key device not only in portable electronics such as smartphones, smartwatches, and laptops, but also in applications for environmentally harsh conditions such as drones, space exploration, and defense.³ While many aspects of LIB performance need to be improved, low-temperature capability is the most challenging one since the conventional electrolytes cannot operate properly at subzero temperatures due to sharp drops in capacity and rate capability.^{4,5}

an additive formed SEI with low resistance and low charge transfer

At low temperatures LIBs have intrinsically slow kinetics at the electrode/electrolyte interface, in the bulk electrolyte, and in the active electrode materials. Li⁺ has insufficient thermal energy for ion transfer at the interfaces or ion diffusion within the bulk electrolyte and active materials, and it cannot supply the current density normally required during charge and discharge processes at room temperature.^{6,7} The sluggish kinetics at every level causes high cell impedance and contributes to a large cell overpotential, resulting in lowered capacity and energy. In addition, during the charging process, the large overpotential at the graphite anode causes lithium plating, which not only impairs the cell performance but also exacerbates safety issues associated with a potential short-circuit.^{8,9} Furthermore, since there are many factors affecting the performance at low temperature such as the active materials, electrolytes, and electrode configurations, it is hard to pinpoint the actual limiting factor and find a solution to address the issue.

Conventional LIB electrolytes are based on a mixture of carbonate solvents dissolved with a lithium salt. The cyclic carbonate, ethylene carbonate (EC), is known to be an indispensable component due to its unique capability of forming a stable solid-electrolyte-interphase (SEI).^{10,11} This SEI passivates the graphite surface, preventing the continuous reaction of electrolyte components with lithiated graphite and enabling the reversible intercalation/deintercalation chemistry of LIBs. However, EC has a high melting point of 34 °C (solid state at room temperature); therefore, electrolytes with a high portion of EC, for example, >50 vol %, have adversely affected ionic conductivity at temperatures below -20 °C.¹² Tertiary^{13,14} and quaternary^{15,16} carbonate solvent systems with a low portion of EC have been proposed and studied for lowtemperature application.

Carbonate derivatives and noncarbonate solvents as well have been widely investigated to solve the sluggish ion transport in electrolyte bulk such as fluorinated carbonates,^{17,18} ethers,¹⁹

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Figure 1. Voltage profiles of (a) graphite/Li half-cells and (b) NMC622/Li half-cells with Gen 2 electrolyte at 25 °C and -20 °C, and (c) theoretical lithium-ion battery overpotential evolution with limiting factors of electrolyte ionic conductivity and interfacial resistance at low temperature.

nitriles,^{20–22} esters,^{23–27} or fluorinated esters.^{28,29} However, the improved LT performance has been exclusively attributed to the high conductivity of the electrolyte bulk, and there has been a lack of systematic study to pinpoint the limiting factors and electrolyte design principle for low-temperature applications.

In this report, a low-melting-point butyronitrile (BN)-based electrolyte with enhanced conductivity^{27–29} at low temperature has been systematically investigated. It reveals that instead of improved conductivity, the limiting factor for LT mainly lies in the graphite anode. Specifically, the SEI formation and its chemical composition are the dominating factors. Lithium nitride (Li₃N)-containing SEI formed via the reduction of butyronitrile solvent^{30–32} is beneficial in decreasing the interfacial impedance of the anode. Lithium fluoride (LiF), known as a stable component in SEI,^{33,34} acts as a resistor for ion conduction and can be minimized by controlling electrolyte formulations with nitrile solvent. This modified SEI layer enables the cells to operate at -40 °C, while conventional carbonate electrolyte could not operate at all. This study provides in-depth insights on designing principles for high-performance lithium-ion batteries for low-temperature applications.

RESULTS AND DISCUSSION

The graphite anode is more sensitive to LT performance than the LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) cathode, as evidenced by the much lower (7%) capacity of the graphite/Li half-cell at -20°C compared to 25 °C; in contrast, the NMC622/Li half-cell showed a smaller capacity decrease (64%), as shown in Figure 1a and Figure 1b. During the normal operation of a lithium-ion battery, electrode reaction kinetics is retarded by various factors, and among them, there are three main overpotentials: (1) activation overpotential (η_{act}) , (2) concentration overpotential (η_{conc}) , and (3) ohmic resistance. Since ohmic resistance is largely dominated by the ionic conductivity of the electrolyte and not the electrodes, we only considered the activation overpotential and concentration overpotential, which directly affect the kinetics of electrochemical reactions in lithium-ion battery systems. Figure 1c shows the evolution of theoretical overpotential with current density. Activation overpotential can be expressed by the classical Butler–Volmer equation³⁵

$$\eta_{\rm act} = -\frac{RT}{(1-\alpha)nF} \ln J_0 + \frac{RT}{(1-\alpha)nF} \ln J \tag{1}$$

where *R* is the ideal gas constant, α is the transfer coefficient, *n* is the number of electrons for the reaction, *F* is the Faraday constant, J_0 is the exchange current density, and *J* is the applied current density. The exchange current density (J_0) means the degree of reversibility of an electrode reaction; it has an inverse relation to the interfacial charge-transfer resistance. ($J_0 = \frac{RT}{nFR_{ct}}$, where R_{ct} is an interfacial charge-transfer resistance of an electrode.)

Concentration overpotential can be derived from the law of diffusion and is given by the following equation³⁶

$$\eta_{\rm conc} = \frac{RT}{nF} \ln \frac{J_{\rm lim} - J}{J_{\rm lim}}$$
(2)

where $J_{\rm lim}$ is a limiting current density when surface ion concentration goes to zero. The limiting current density $(J_{\rm lim})$ has a proportional relation to the diffusion coefficient. ($J_{\rm lim} = \frac{nFD_{\rm Li}+c_{\rm Li}+}{\delta}$, where $D_{\rm Li}$ is the diffusion coefficient, $c_{\rm Li}$ is the concentration of Li ion in an electrolyte, and δ is the distance



Figure 2. (a) Temperature dependence of ionic conductivity of Gen 2, 1 M LiPF₆ BN/FEC (75/25 v/v), and 1 M LiPF₆ BN/EC (75/25 v/v) + 5 wt % FEC electrolytes and (b) calculated activation energy (E_a) from plots in panel (a).

between electrodes.) The top plot in Figure 1c shows the evolution of these two overpotentials and their sum when J_0 is 2 mA cm⁻² and J_{lim} is 10 mA cm⁻² at room temperature. In this condition, the total overpotential stays low and slightly increases governed by the activation overpotential at a low-to-moderate current density, and as the current density goes to J_{lim} , the total overpotential sharply increases governed by the concentration overpotential. We assumed two different situations at low temperatures. One is when J_{lim} drops to 2 mA cm⁻². In this case, the total overpotential grows large even at low current density and the cell would not exhibit any capacity as the potential directly hits the cutoff voltage. The other is when J_0 drops to 2 \times 10^{-3} mA cm⁻². The total overpotential becomes high at very low current density and slightly increases until the current density goes to $J_{\rm lim}$. From these overpotential increase trends, we prioritized the electrolyte properties: (1) high ionic conductivity and (2) low interfacial resistance.

To validate the above theory, we selected a nitrile-based electrolyte due to their high ionic conductivities.^{20,21} Butyronitrile (BN)-containing electrolytes BN/FEC (1 M LiPF₆ in BN/ FEC (75/25 v/v) and BN/EC + FEC $(1 \text{ M LiPF}_6 \text{ in BN/EC})$ (75/25 v/v) + 5 wt % FEC) were studied and compared with the conventional electrolyte Gen 2, which is 1.2 M LiPF₆ in EC/ EMC (3/7 w/w). Figure 2a shows the ionic conductivities of these electrolytes at various temperatures. While Gen 2 had the lowest ionic conductivity of 7.5×10^{-3} S cm⁻¹ at 20 °C, BN/ FEC and BN/EC + FEC showed much higher ionic conductivities of 13×10^{-3} and 11.6×10^{-3} S cm⁻¹ at 20 °C, respectively, due to the high dielectric constant and the low viscosity of BN present in the electrolytes. In addition, the activation energy (E_a) was calculated from the Arrhenius plots and is shown in Figure 2b. Compared to a high activation energy of 6.3 kJ mol⁻¹ for Gen 2, BN/FEC and BN/EC + FEC electrolytes showed a lower activation energy of 4.5 kJ mol⁻¹, indicating that both could maintain high ionic conductivity at lower temperatures. The high ionic conductivity and low activation energy of BN-based electrolytes result in a low concentration overpotential at low temperatures. We also conducted the voltage holding test of NMC622/graphite cells with different electrolytes for electrochemical stability windows. Although BN/FEC and BN/EC + FEC showed a slightly higher leakage current than Gen 2, they have negligible leakage current values up to 4.8 V (Figure S1).

Since interfacial resistance is largely determined by the SEI, we then analyzed the formation of the SEI with various characterization methods in Figure 3. The reduction potential of Li⁺-BN, Li⁺-EC, and Li⁺-FEC was calculated to be 0.39, 0.58, and 0.80 V vs Li/Li⁺, respectively (Figure 3a). This trend in reduction potential is in good agreement with the reduction peak at 3.1, 3.0, and 2.65 V in the dQ/dV plots of NMC622/ graphite cells during the first charging cycle, as shown in Figure 3b. It is worth noting that the BN solvent by itself could not form a stable SEI layer, and a BN/EC (75/25 v/v) cosolvent electrolyte also showed a low initial Coulombic efficiency (CE) due to the close reduction potential of EC and BN (Figure S2). However, a robust SEI layer could be tuned by adding 5 wt % FEC as an additive to BN/EC. Though FEC has a higher reduction potential than that of EC, the SEI is predominantly formed by the reduction of the first Li⁺-coordinated solvation sheath, which, according to MD calculations, contains far more EC than FEC. Thus, the large contribution of EC to the SEI layer formation is explained by MD results, which show that the Li⁺ coordination number of EC (0.55) is much higher than that of FEC (0.03) in the BN/EC + FEC electrolyte system (Figure 3c). The coordination numbers of electrolyte components at various temperatures in the BN/FEC or BN/EC + FEC electrolyte system are summarized in Tables S1 and S2.

The effect of the electrolytes/additive on the SEI chemical composition was examined by X-ray photoelectron spectroscopy (XPS) after three formation cycles (Figure 3d). The peaks in C 1s spectra at 289.6, 288.4, 286.8, 285.8, and 284.8 eV are assigned to OCOO, O-C=O, C=O, C-O-C, and C-C, respectively, and are attributed to EC and FEC decomposition products. No significant difference was observed between Gen 2, BN/FEC, and BN/EC + FEC electrolytes, which share a high portion of carbonate-derived functional groups. In the case of F 1s and N 1s spectra, the F 1s peaks at 687.8, 684.7 eV and the N 1s peak at 399 eV are assigned to Li_xPO_yF_z, LiF, and Li₃N, respectively. Compared to Gen 2, the SEI layer formed by BN/ FEC and BN/EC + FEC electrolytes is composed of new species Li₃N, which is a known SEI component with high ionic conductivity.^{30,32} In addition, the BN/EC + FEC electrolyte cycled graphite anode showed a lower concentration of LiF in the SEI layer than that formed by the BN/FEC cosolvent electrolyte.

Figure 4 shows the electrochemical impedance spectroscopy (EIS) for NMC622/graphite measured at 50% state of charge

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Figure 3. (a) Reduction potentials of Li⁺-BN, Li⁺-EC, and Li⁺-FEC, (b) dQ/dV profiles of the first charging cycle with Gen 2, 1 M LiPF₆ BN/FEC (75/25 v/v), and 1 M LiPF₆ BN/EC (75/25 v/v) + 5 wt % FEC electrolytes, (c) DFT calculated coordination number of electrolytes at 25 °C, and (d) XPS spectra of C 1s, F 1s, and N 1s of cycled graphite anodes after three C/10 formation cycles with three electrolytes.

(SOC) after three formation cycles. It is evident that as temperature decreases, the total cell resistance increases due to the lower thermal energy available for the electrochemical reaction. To separate each resistance contribution to the performance, we deconvoluted the measured data with an equivalent circuit with constant phase elements, which are bulk electrolyte (R_{elect}), SEI layer (R_{SEI}), CEI layer (R_{CEI}), charge transfer at the anode ($R_{\text{ct-anode}}$), and charge transfer at the cathode ($R_{\text{ct-cathode}}$). We matched the frequencies of each resistance component by using anode and cathode symmetric cells (Figure S3). EIS data were well fitted with the equivalent circuit at -15 °C, verifying the fitting model (Figure S4), and the fitting results of parameters are provided in Tables S3 and S5.

BN/FEC and BN/EC + FEC electrolyte cells showed significantly smaller total resistance compared to Gen 2 at all testing temperatures (Figure 4a-4c), indicating their lower interfacial resistance and lower overpotential during operation. When it comes to each resistance contribution (Figure S4), BN/ EC + FEC had a much smaller $R_{ct-anode}$ than BN/FEC due to the modified SEI layer with a lower concentration of LiF. We further analyzed the temperature effect on each resistance component by the Arrhenius plots (Figure 4d–4f). The slope of $\log R vs$ 1000/T plot indicates the activation energy (E_a) for the reaction, meaning the temperature dependence of the reaction. A higher E_{a} leads to a slower reaction and greater resistance at low temperature. For the Gen 2 electrolyte cell, the activation energies of R_{SEL}, R_{CEL}, R_{ct-anode}, and R_{ct-cathode} are 0.8, 11.3, 24.4, and 25.3 kJ mol⁻¹, respectively, indicating that charge-transfer resistance becomes the main limiting factor at low temperatures. While BN/FEC has a similar R_{ct-anode} activation energy of 24.3 kJ mol^{-1} as Gen 2, BN/EC + FEC has a lower activation energy of 22.1 kJ mol⁻¹. Considering that the overpotential on graphite anode is a limiting factor at low temperature, the significantly lower R_{ct-anode} activation energy of BN/EC + FEC enables superior rate capabilities at low temperature, confirming the effectiveness of the modified SEI layer.

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Figure 4. Nyquist plots of NMC622/graphite cells with (a) Gen 2, (b) BN/FEC, and (c) BN/EC + FEC electrolytes at various temperatures. Arrhenius plots of R_{SEI} , R_{CEI} , $R_{ct-anode}$ and $R_{ct-cathode}$ for cells with (d) Gen 2, (e) BN/FEC, and (f) BN/EC + FEC electrolytes.



Figure 5. (a-c) C-rate capability for NMC622/graphite cells with different electrolytes and (d-f) overpotential evolution with C-rate at 25, -20, and -40 °C.

At room temperature, when various currents were applied from C/10 to C/3, C/2, 1C, and 2C, Gen 2 and BN/FEC and BN/EC + FEC cells showed similar performance. However, when the temperature decreased to -20 °C, with the same Crate, Gen 2 showed significantly lower capacity. In contrast, the BN/EC + FEC electrolyte cell showed the highest rate capability and delivered 129, 102, 89, 63, and 29 mAh g^{-1} at C/10 to C/3, C/2, 1C, and 2C. Interestingly, when temperature further decreased to -40 °C, even the C/5 current was applied, Gen 2 cell only showed an 8 mAh g^{-1} cell capacity, while the BN/EC +



Figure 6. NMC622/graphite cell performance at (a) 25 °C and (b) -40 °C with different electrolytes, (c) -40 °C cycling performance and Coulombic efficiency of Gen 2 electrolyte cell with Gen 2 and BN/EC + FEC preformed SEI, and (d) BN/EC + FEC electrolyte cell with Gen 2 and BN/EC + FEC preformed SEI.

FEC cell still retained a high capacity of 41 mAh g⁻¹ due to its lower interfacial resistance. To correlate the effect of a modified SEI layer with overpotential, we calculated the overpotential evolution's dependence on C-rate (Figure 5d–5f) at 50% of normalized capacity. While the electrolytes exhibited a similar overpotential increase at room temperature, BN/EC + FEC showed a lower overpotential increase at -20 and -40 °C (Figure S5), reconfirming its lower interfacial resistance during low-temperature operation.

Figure 6a summarizes the galvanostatic cycling results with C/ 3 at room temperature. While Gen 2 showed stable cyclability retaining 98% of its initial capacity after 100 cycles, BN/FEC and BN/EC + FEC exhibited a slight capacity fade and only retained 86% and 91% of their original capacity after 100 cycles (Figure S6) due to the continuous BN solvent reduction during cycling and low thermal stability, which is also observed at a high temperature of 40 °C (Figure S7). Lower CEs were also evident for both BN/FEC and BN/EC + FEC cells compared to that of Gen 2 (Figure S8). However, at -40 °C, BN/EC + FEC exhibited a remarkably high capacity retention of 97% after 100 cycles, compared to only 61% for Gen 2 (Figure 6a). Because a large overpotential at the anode causes Li plating and electrolyte decomposition, which lowers CEs and capacity retention, the low interfacial resistance of BN/EC + FEC causes it to outperform Gen 2 at low temperature. This was directly observed from the charged graphite electrodes after five cycles at -40 °C (Figure S9).

To elucidate the correlation of the SEI layer and lowtemperature performance, cycling test with a preformed SEI by either Gen 2 or BN/EC + FEC was performed. After three formation cycles at room temperature, the cells were reassembled with the new electrolyte and cycled at -40 °C. The Gen 2 electrolyte cell (Figure 6c) with an SEI layer formed by Gen 2 showed a slight degradation, maintaining 87% of initial capacity during 30 cycles, while the same electrolyte cell with SEI layer formed by BN/EC + FEC did not show capacity decay. Similarly, the BN/EC + FEC electrolyte cell (Figure 6d) with the SEI layer formed by Gen 2 and by BN/EC + FEC showed the same initial capacity of 66 mAh g^{-1} (which is much higher than 45 mAh g^{-1} for Gen 2 cell). At the end of 100 cycles, the cell with the SEI layer formed by Gen 2 exhibited a dramatic decay with only 77% of capacity retention even in 30 cycles, while the cell with SEI layer formed by BN/EC + FEC displayed a high capacity retention of 98%, with an average CE close to 100%, confirming the significant role of SEI in the cell performance at low temperature.

CONCLUSIONS

In summary, the effect of the SEI on the low-temperature performance of lithium-ion batteries has been systematically studied. The overpotential resulting from a resistive SEI and high charge-transfer resistance dictates the cell performance at low temperature. By formulating a 1.0 M nitrile-based electrolyte LiPF₆ in BN/EC + FEC, we demonstrate that the new SEI composed of Li₃N and LiF significantly lowers the

anode charge-transfer resistance with a low activation energy, resulting in superior rate capability and cyclability even at -40 °C. This investigation provides a deep insight into designing principles of new electrolytes to enable low-temperature Li-ion batteries.

EXPERIMENTAL SECTION

Materials. Butyronitrile (BN), ethylene carbonate (EC), and fluoroethylene carbonate (FEC) were purchased from Sigma-Aldrich. All solvents used in this study were purified by vacuum distillation and then dried by 4 Å molecular sieves before use. Gen 2 electrolyte is 1.2 M LiPF₆ in EC/EMC (3/7 w/w ratio). All electrodes were provided by Argonne's Cell Analysis, Modeling and Prototyping (CAMP) facility. The cathode (NMC622) was composed of 90 wt % Li- $(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$, 5 wt % poly(vinylidene fluoride) binder (PVdF, Solvay), and 5 wt % C45 conductive carbon casted on an aluminum foil with a mass loading of 9.78 mg/cm². The graphite anode was composed of 91.83 wt % superior graphite (SLC1520P), 6 wt % PVdF binder (Kureha, 9300), 0.17 wt % oxalic acid additive, and 2 wt % C45 conductive carbon casted on a copper foil with a mass loading of 6.38 mg/cm². All electrodes were dried at 110 °C under vacuum overnight. Celgard 2500 was used as the separator. The diameters of the cathode, anode, and separator were 14, 15, and 16 mm, respectively.

Electrochemical Measurements. The electrochemical performance was evaluated by 2032 coin cells. The full cells were composed of NMC622 cathode and graphite anode with different electrolytes. The cell assembly was conducted in an argon-filled glovebox. All of the galvanostatic cycling was performed at 2.7–4.2 V following three initial C/10 formation cycles using a Neware battery tester. The electrochemical impedance spectroscopy (EIS) was obtained and fitted using a Solartron analyzer operated between 0.01 Hz and 1 MHz with an amplitude of 10 mV.

Characterization. The cycled cells were disassembled in an argonfilled glovebox. The graphite electrodes were obtained after three formation cycles with Gen 2, BN/FEC, or BN/EC + FEC electrolytes. The electrodes were rinsed with dry dimethyl carbonate for Gen 2 cycled electrodes or dry BN for BN/FEC and BN/EC + FEC cycled electrodes and characterized after vacuum-dried. X-ray photoelectron spectroscopy (XPS) was conducted in the fixed analyzer transmission mode using an Al K α radiation (h ν = 1486.6 eV, 100 μ m beam, 25 W) with Ar⁺ and electron beam sample neutralization. XPS spectra were calibrated to the C–C bond at 284.7 eV.

DFT Calculation. DFT calculation: structure optimizations of LiEC, LiFEC, and LiBN were performed with the ω B97X-d functional and def2-TZVPPD basis set in the QChem software package.³⁷ DFT calculations were performed with the SMD implicit solvent model parameterized to BN. Structures for LiEC and LiFEC were taken from the LIBE data set.³⁸ For BN, the bare solvent was first optimized at -1 charge before Li was inserted.

MD Simulation. We acquired OPLS force field parameters for BN from LigParGen³⁹ and calculated partial charges with a restrained electrostatic potential (RESP) fit using Antechamber.40 The RESP calculation used a geometry-optimized structure calculated with Gaussian 16 at the B3LYP/aug-cc-pvdz level of theory. BN partial charges were scaled to 80% of their initial value so that the simulated density of BN matched the experimental density. OPLS force field parameters for EC, FEC, and LiPF6 were taken from Hou et al.⁴¹ We performed molecular dynamics calculations with the large-scale atomic/molecular massively parallel simulator (LAMMPS) package.⁴² A random initial configuration of the molecular system was generated with PACKMOL⁴³ followed by an energy minimization with conjugate gradient descent. Each simulation began with a 1 ns pressure equilibration in the NPT ensemble at 1 atm, 298 K. The system was then annealed by increasing the temperature to 400 K, holding at 400 K, and then returning 298 K, each for 1 ns. After this equilibration, the production part of the simulation ran for 5 ns. All solvation structure geometries and statistics were taken from the production run.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c23934.

Voltage holding test, voltage profiles, coordination numbers, Bode plots, Nyquist plots, EIS fitting results, normalized voltage profiles, cycling performance at a high temperature, Coulombic efficiency, and photographs of cycled electrodes (PDF)

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Notes

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