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To overcome the energy limitations of conventional Li-ion batteries (LIB), renewed attention has been given to Li-metal anodes, which provide the highest capacity and lowest anode potential. To realize Li-metal batteries (LMBs), it is crucial to stabilize unwanted side reactions on the surface and to inhibit problematic dendrite growth, which causes short-circuit issues. Herein, diverse pyrrolidone-based molecular dipole additives controlled by different functional groups are introduced as trifunctional surface stabilizers. It is discovered that the Li–Li symmetric cell improves proportionally with the molar volume and corresponding polarizability values of the molecular dipoles. The highly polarizable pyrrolidone-based molecular dipoles offer exceptional benefits, including surface flattening of the Li metal anode, controlling the growth direction of crystalline Li, and forming durable solid electrolyte interface (SEI) components. The study is based on polarizability-controlled molecular dipoles, and offers an effective approach for designing advanced surface stabilizers to develop of highperformance LMBs.

1. Introduction

As the theoretical energy density in commercial Li-ion batteries (LIBs) approaches its limitations, development of next-generation batteries with exceptional energy capability is crucial.^[1] Exploring alternatives to the conventional graphite anode (372 mAh g⁻¹), Li metal emerged as a promising choice for realizing Li-metal

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tages: 1) an extremely high theoretical specific capacity (3860 mAh g^{-1}), 2) low density (0.59 g cm⁻³), and 3) the lowest electrochemical redox potential (-3.04 V vs. the)standard hydrogen electrode (SHE)).^[2] However, the surface instability issues of Li metal anodes pose challenges for their commercialization, despite their energy potential. For example, the uncontrolled growth of Li dendrites on the Li metal anode can lead to safety problems and shortcircuits. Moreover, the formation of "Dead Li", when these dendrites detach decreases the coulombic efficiency of the cell.^[3] Additionally, Li exhibits high reactivity, resulting in unwanted side reactions in most commercially available electrolytes.^[4] The solid electrolyte interface (SEI) layer formed on the Li metal is usually weak and incapable of withstanding structural and

morphological changes during continuous Li deposition and stripping processes.^[5] The unstable SEI layer cannot resist large volume changes and cracks, and the Li metal surface exposed to the cracked and damaged SEI layer repeatedly forms a new SEI layer and continuously depletes the electrolyte, resulting in low coulombic efficiency and a vicious cycle.^[5b]

Several strategies have been employed to address these barriers, including the introduction of 3D current collector hosts for Li metal,^[6] formation of artificial protective layers,^[7] modification of separators,^[8] and utilization of surface-stabilizing electrolyte additives.^[9] Among these approaches, incorporating functional electrolyte additives as a facile and effective method for enhancing the durability of SEI layers. This is because the additive with a further reducible lowest unoccupied molecular orbital (LUMO) level is preferentially decomposed prior to the reduction of the electrolyte components, such as salt and solvent, thereby offering a stronger SEI layer component.^[9] In addition to controlling the compositional inheritance of the SEI layer, it is important to develop additive alternatives that prevent random growth and formation of Li dendrites, which can cause a short-circuit. Our recent research successfully validated the effectiveness of pyrrolidone-based molecular dipole additives for Li-metal anode leveling, which are used to flatten the deposition layer in conventional electroplating techniques.^[10] We also found that molecular dipole additives strengthen the SEI layer by preferentially incorporating durable carbonate and fluoride species instead of weak oxide species. Nevertheless, further exploration



of optimized pyrrolidone-based additives and elucidating the property-determining factors of molecular dipole additives are necessary.

Herein, we report the importance of the polarizability factor of pyrrolidone-based molecular dipole additives controlled by different functional groups to achieve longer cycles and higherefficiency LMBs. The value of polarizability, indicative of the propensity of molecules to induce electric dipole moments under the influence of an external electric field, is modulated by a multitude of factors. These include the dimensions of the electron cloud, the electron configuration, the aggregate number of electrons, and the geometric configuration of the molecule. Enhanced polarizability is associated with electron clouds that are larger and more diffuse, elevated electron density, an increased count of electrons, the existence of bonds capable of polarization, and an expanded molecular surface area. Of these determinants, the molecular volume emerges as the preeminent factor, with polarizability being directly proportional thereto. Varying the polarizability of the molecular dipole additives could affect their surface adsorption behavior of molecular dipole additive and, consequently, the Li deposition/ stripping behavior of the Li-metal electrode for electrochemical reactions. Therefore, we deliberately regulated diverse functional groups (-H and -CH₃, -C₂H₅, -C₆H₅) on the pyrrolidone-based molecule, corresponding to the molecular volume and polarizability, respectively, in proportional to the induced electric dipole moment. We investigated the basic molecular properties and physical functions of diverse molecular dipoles with different functional groups using various calculation approaches. Li-Li symmetric cell tests were conducted to compare the electrochemical performances of the diverse molecular dipole additives. Various surface morphology observations validated the surface flattening effects achieved by employing the polarizability-controlled molecular dipole additives, which were consistent with the predicted calculations. We also confirmed the preservation of the planar Li surface by controlling the growth direction of the crystalline Li. The lower energy level of pyrrolidone-based molecules below the LUMO energy of tetraethylene glycol dimethyl ether (TEGDME) is associated with their predecomposition prior to general electrolyte decomposition and consequent modification of the SEI layer components containing durable carbonate and fluoride-rich components. We finally confirmed stabilization effects of the pyrrolidone-based molecular dipoles in Li-O2 full cell. This study investigates the trifunctional advantage of highly polarizable molecular dipole additives for surface flattening, controllable growth direction of crystalline Li, and formation of durable SEI components for the realization of highenergy LMB systems. Our approach further highlights the dominant effect of polarizability divergence on the performance enhancement, offering a potential key strategy for developing advanced electrolyte additives that promote stable and long-cycle performance in LMBs.

2. Results and Discussion

2.1. Pyrrolidone-Based Electrolyte Additives for Electrochemical Performance Enhancement

Dipole moment and polarizability calculations for various pyrrolidone-based additives were performed to understand the behavior of the additive molecules in the electrolyte. To validate the polarizability effects of the molecular dipole additives, we introduced four types of pyrrolidone-based molecular dipoles with different functional groups (-H, $-CH_3$, $-C_2H_5$, and $-C_6H_5$) into the LMB system as electrolyte additives and studied their positive effect on the stabilization of the metal anode surface. The prescreening calculations of the electrostatic potential maps, dipole moments, and polarizabilities for various pyrrolidone-based molecules were performed using Gaussian 16 to understand the molecular properties of different functional groups of the additives (**Figure 1a**, S1a–c, and Table S1, Supporting Information). The electron distribution in the molecules was confirmed using an electrostatic potential map (Figure 1a). Despite the different

molecular properties of different functional groups of the additives (Figure 1a, S1a-c, and Table S1, Supporting Information). The electron distribution in the molecules was confirmed using an electrostatic potential map (Figure 1a). Despite the different functional groups on the pyrrolidone-based molecules, similar dipole moments were observed ranging from 3.97D to 4.43D (Figure 1a and S1a, Supporting Information). However, all the additive molecules have different molecular volumes ranging from 69.7 to 140.5 cm³ due to different sizes of side groups (-H, -CH₃, -C₂H₅, and -C₆H₅) (Figure S1b, Supporting Information). Consequently, the difference in functional groups leads to proportional polarizability values ranging from 55.216 to 126.221 a.u. (8.9 to 18.5 Å) associated with the degree in molecular orbital distortion by applied electric field (Figure 1a and S1c,d, Supporting Information). The asymmetric polarizabilities of dipolar molecules are affected by the strong adsorption properties of Li electrodes with electrochemical potentials for both cathodic and anodic reactions. Based on this, we hypothesized that the molecules with a relatively higher proportion of positive regions would be more effective in covering the negative side of the dendrites grown on the surface of a Li-metal anode. In addition, negative regions can adhere to the excessively positive side of the Li-metal for reverse Li dissolution to prevent non-uniform Li stripping and digging. The unique adsorption properties of polarizable molecular dipole additives can stabilize the Li-metal anode surface and maintain flattened surface morphologies for repeated Li deposition and stripping reactions.

To examine the effects of polarizability on the electrochemical performance of the Li metal anodes, various electrochemical tests using Li-Li symmetric cells were conducted using a pyrrolidonebased molecular dipole with different functional groups (Figure 1b-i). The degradation mechanism of Li-Li symmetric cells can be due to excessive electrolyte consumption during cycling, the formation of an unstable SEI layer on the anode surface, dead Li formation, and short circuits originating from problematic dendrite growth.^[3] As the cycling progresses, these factors combine to cause voltage polarization. Figure 1b,c show the results of a Li-Li symmetric cell test conducted at a low current density of $1 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ and a high current density of 5 mA cm^{-2} . We terminated the cycling tests when the overpotential generated by cell degradation reached 1 V. At a current density of 1 mA cm⁻², the Li–Li symmetric cell without electrolyte additives maintained its performance for 146 h. Compared with the pristine cell, the Li-Li symmetric cells employing different pyrrolidone-based molecular dipoles showed an improved cycle life proportional to the polarizability value of the different molecular dipoles (133 h for pyrrolidone (p), 166 h for methyl pyrrolidone (mp), 178 h for vinyl pyrrolidone (vp), and 358 h for phenyl pyrrolidone (PP)). The Li-Li symmetric cell without electrolyte additives exhibited a short lifetime of 43 h at a high current density of 5 mA cm^{-2} . Conversely, consistent improvements with

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Figure 1. a) Electrostatic potential map, dipole moment, and polarizability of pyrrolidone-based electrolyte additive with various functional groups. Electrochemical test results using Li–Li symmetric cells with and without pyrrolidone-based additives. b) Cycling performance of the Li–Li symmetric cell with and without pyrrolidone-based additives. b) Cycling performance of the Li–Li symmetric cell with and without pyrrolidone-based additives. b) Cycling performance of the Li–Li symmetric cell with and without pyrrolidone-based additives. c) Proportional tendency between polarizability of pyrrolidone-based electrolyte additives. e) Proportional tendency between polarizability of pyrrolidone-based electrolyte additives and cycling performance of the Li–Li symmetric cell at both low and high current density conditions. f) Charge transfer resistance from Nyquist plot of cells using the pristine electrolyte and electrolyte with pyrrolidone-based additive at different cycle number and EIS spectra obtained for the Li–Li symmetric cells prepared with and without pyrrolidone-based additives g) after 1 cycle, and h) after 50 cycles. i) Electrochemical performance test of Li–O₂ full cell with different pyrrolidone additive containing electrolytes and Fe catalyst loaded N-doped carbon nanotube (Fe-NCNT) electrode.

stable cycle performances at a current density of 5 mA cm⁻² were observed for cells with different molecular dipoles (61, 97, 143, and 181 h for P, MP, VP, and PP, respectively). The observation

that the effect of the electrolyte additive is more pronounced at a higher current density of 5 mA cm^{-2} is very meaningful, especially because dendrite formation on Li metal surfaces is known

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to be more vulnerable under fast charge and discharge conditions.^[11] The proportional relationship between the molecular volume and polarizability of the pyrrolidone-based additives is plotted in Figure 1d. Based on the results shown in Figure 1b–d, as the polarizability of the additive increases, the cycling characteristics of the Li–Li symmetric cell also improve under both low and high current density conditions (Figure 1e), indicating that the polarizability values as a function of molecular volume can be intimately correlated with the degree of the stabilizing effect on the L-metal anode.

To measure the charge transfer resistance and interfacial resistance between the Li-metal anode and the electrolyte, electrochemical impedance spectroscopy (EIS) tests were performed with a Li-Li symmetric cell without additives and with different pyrrolidone-based molecular dipole additives (Figure 1f-h). The equivalent circuit used in the Li-Li symmetric cell tests is shown in Figure S2d, Supporting Information. The solution resistance (R_{sol}) and charge- transfer resistance (R_{ct}) values obtained from the EIS tests are summarized in Table S2 and S3, Supporting Information. R_{sol} is related to the resistance due to the movement of Li ions across the interface between the electrolyte, separator, and Li-metal electrode.^[12] R_{ct} is the resistance observed in the high-frequency region and is related to the diffusion of Li ions between the electrolyte/SEI layer and the SEI layer/Li metal electrode.^[12,13] A slight increase in the cell resistance for the cell with additives was observed before cycling, because of the absorption of the molecular dipoles onto the surface of the Li-metal anode (Figure S2a, Supporting Information). As the cycle progresses, electrolyte decomposition and other side reactions occur, which impede the movement of Li ions across the interface and reduce the Li ion conductivity. As a result, R_{sol} increased as charging and discharging progressed. The R_{ct} corresponding to the diameter of the semicircle, is the interfacial resistance between the electrode and electrolyte for the electrochemical reaction (Figure 1g,h and S2b,c, Supporting Information). When an unstable electrochemical interface is formed, the R_{ct} value is increased. For the pristine cell, the overall resistance value increased rapidly as the cycle progressed because of the problematic side reactions on the Li surface.^[14] A sudden increase in R_{ct} values was measured after the 1st (87.317 Ω), 20th (188.08 Ω), and 50th (380.42 Ω) cycles for the Li-Li symmetric cell without additives. However, the interface resistance values of the cells with all molecular dipole additives were stably maintained even after long cycles, regardless of the additive type. Figure S2c, Supporting Information, show the R_{ct} values obtained at different cycle numbers. All Li–Li symmetric cells showed a substantial decrease in the R_{ct} after one cycle. While the pristine cell showed a reverse increase in the R_{ct} after 50th cycle, the R_{ct} values of the Li–Li symmetric cells with pyrrolidone additives were successfully maintained without a sharp increase in resistance after the 50th cycles, verifying the advantages of pyrrolidone-based molecular dipole additives. The R_{ct} of PP exhibited the highest polarizability among the additives, however it was the lowest as compared to those of the other pyrrolidone additives, implying that the higher polarizability associated with a larger molecular volume can further improve the electrochemical performance of LMBs. Lastly, for the evaluation in a full cell, tests on Li-O2 cells were conducted using pristine electrolytes, those with P, and those with PP. After 10 cycles, the results confirmed the low overpotential effects attributable to the molecular dipole additive, as illustrated in Figure 1i.

2.2. Morphological Surface Flattening Effect of Pyrrolidone-Based Electrolyte Additives

The improved electrochemical stability is directly related to the surface flattening and dendrite inhibition effects of the different molecular dipole additives. To confirm the morphological changes in the Li-metal anode with and without additives, ex situ scanning electron microscopy (SEM) characterization was performed after 100 cycles at a high current density of 5 mA cm^{-2} (Figure 2). Figure 2a shows the bumpy surface of the cycled Li metal anode without additives. The uneven surface morphology was caused by a combination of needle-like and mossy dendrites, and the formation of dead Li and accumulation of side reaction products result in formation of a thick layer on the surface.^[15] Conversely, when pyrrolidone-based molecular dipole additives (P, MP, VP, and PP) were introduced, flat and smooth surfaces were observed without dendritic features or side products (Figure 2b-e). For the P additive with the smallest molar volume and lowest polarizability, the degree of unevenness was much more stable with the presence of the additive compared to that without the additive. However, slightly uneven surface was still observed (Figure 2b). In the case of Li-metal anodes with molecular dipole additives having relatively high polarizability (larger molar volume), such as MP, VP, and PP, smoother morphologies were observed (Figure 2c-e). Exsitu atomic force microscopy (AFM) analysis was performed to further identify the surface roughness and cross-sectional height of the Li metal anodes cycled for 100 cycles with and without different additives. Consistent with the SEM results, a bumpy and rough surface resulting from non-uniform Li deposition was observed for the Li-metal anode cycled without a molecular dipole additive (Figure 2f). In contrast, uniform and smooth surface characteristics were observed for all the Li electrodes cycled with pyrrolidone additives, resulting from homogeneous Li deposition and stripping by introducing molecular dipole additives (Figure 2g-j). A quantitative comparison of the vertical cross-sectional heights of the different Li metal anodes obtained after cycling is shown in Figure 2k. The Li anode cycled without additives showed deviations and fluctuations in the cross-sectional height. In contrast, the Li anodes with pyrrolidone additives exhibited a stable height geometry without significant surface curvature. While the surface roughness of the cycled Li electrode without additives was 147.606 nm, the surface roughness of the cycled Li electrodes with pyrrolidone-based molecular dipole additives was 4-5 times lower and ranged between 25.386 and 34.571 nm (Figure 2l). Among the different additives, PP molecules with the largest polarizability showed an excellent ability to retain their original Li features even after cycling.

2.3. Crystallinity Growth Rearrangement Effect of Molecular Dipole Additives

Ex situ X-ray diffraction (XRD) analysis was performed to check for possible structural changes in the crystalline Li-metal anode during Li deposition and stripping assisted by the molecular www.advancedsciencenews.com

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Figure 2. Ex situ surface analysis of Li–Li symmetric cells that form differently depending on electrolyte additives. SEM images of the Li-metal after 100 cycles at a current density of 5 mA cm⁻² in the electrolyte: a) without additive, b) with pyrrolidone, c) with methyl pyrrolidone, d) with vinyl pyrrolidone, and e) with phenyl pyrrolidone. AFM images of the li-metal morphology in the electrolyte: f) without additive, g) with pyrrolidone, h) with methyl pyrrolidone, i) with vinyl pyrrolidone, and j) with phenyl pyrrolidone. k) cross-sectional height and l) surface roughness values from the AFM analysis.

dipole additives (Figure 3a-c). For pristine Li metal, the typical peaks of Li metal corresponding to the high intensity of the (110) peak and low intensity of the (200) peak were observed (Figure 3a). After the 10th and 100th cycles, the crystalline structure of the Li-metal surface changed. After the 10th plating without the pyrrolidone additive, the peak intensities of the Li-metal anode significantly decreased and its crystallinity completely collapsed (Figure 3b,c). The pure Li part in the Li electrode unexpectedly transformed to thick side products (i.e., dead Li, SEI layer) on the surface, thereby losing the crystalline features of the Li metal. For the pyrrolidone additives, a crystalline rearrangement from the (110) plane to the (200) plane was observed. The XRD peak corresponding to the (200) plane remains even after 100 cycles. Although the crystallinity of the (110) plane of the pristine Li metal was aligned to the (200) plane after plating, it can be interpreted as a meaningful result that the pure Li peak was maintained and induced to a single plane by the electrolyte additive, even under rapid charge-discharge conditions.^[10a] Similar results are observed after longer cycling times (Figure 3c). When checking the crystallinity of the Li-metal anode surface after 100th cycles, we found that crystallinity was not confirmed for pure Li without additives or with P. However, in the remaining three additive conditions, where the polarizability of the electrolyte additive was relatively large, crystallinity was still

formed by pure Li even after 100th plating. These results show that the electrolyte side reaction and degradation behavior are controlled by the pyrrolidone-based electrolyte additive, which affects the surface crystallinity.

2.4. DFT Calculations of the Li-Metal Surface Reaction with Pyrrolidone-Based Additive Molecules

The binding energies of the Li adatom and electrolyte additives on the Li-metal anode were calculated considering the defectbinding sites and coverage. We assumed that the binding energy calculations could shed light on how different electrolyte additives drive the leveling of the Li anode surface. As discussed in the computational details section, BCC Li metal should have the (110) surface as the most stable owing to its high atomic density; however, the Li anode surface is expected to have defects because Li atoms are repeatedly reduced and oxidized during the charging and discharging cycles. Under these circumstances, we modeled the Li (110) surface in steps. The convex and concave sites originating from the step may indicate the effect of the defect, and the terrace site may be the binding site representing a general (110) surface. The atomic crystal structure of the Li-slab model is shown in Figure 3d. Here, the convex site refers to where the step is made or the topmost layer with the lowest





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Figure 3. Ex situ X-ray diffraction (XRD) peaks of the Li-metal electrode obtained, a) before cycling, b) after 10th plating, and c) after 100th plating with and without pyrrolidone-based additives. d) Illustration of Li (110) slab model with step. e) Molecular structure of pyrrolidone, methyl pyrrolidone, vinyl pyrrolidone, and phenyl pyrrolidone (from left to right). f) Binding energy of Li or each additive on the different binding sites: terrace, concave, and convex sites. g) Additive binding energy differences as coverage increases.

coordination number; the concave site is also the topmost layer because it touches the vacuum, but it shows a higher coordination number than the terrace atom because of the near-convex atom. Indeed, there were three binding sites in the topmost layer, but with different coordination numbers: pyrrolidone (P), methyl pyrrolidone (MP), vinyl pyrrolidone (VP), and phenyl pyrrolidone (PP), as illustrated in Figure 3e.

First, we calculated the binding energy of a single adsorbate at different binding sites shown in Figure 3f. According to the binding energy calculation equation used in this study, a negative sign indicates a favorable or natural process, and a high absolute value indicates strong binding. The binding energy of the Li adatom in our study was positive; however, it was still kinetically possible. As shown in the binding energy graph, all the additives show a stronger binding energy than the Li adatom, and all the additives prefer to stay at either the concave or convex defect sites, which implies that if proper amounts of the additive are present in the electrolyte, it can selectively cover the defect sites rather than the terrace sites before the Li cation approaches the anode surface. Subsequently, the Li cations gradually bond to the perfect Li anode surface without forming a bumpy structure. We also wanted to understand the differences in different kinds of additives in terms of binding energy, but there was no clear trend because the binding energy is strongly correlated with which atom is directly in contact with the metal atom rather than the shape or length of the carbon chain in other parts.

In the previous discussions, we stated that the additive selectively covered the defect sites and opened the terrace sites for the Li cations. Thus, we consider the coverage effect to confirm our assumption. Each additive was bonded to its strongest binding site based on coverage. The binding energy shown in Figure 3g is the average binding energy of the additive, which gradually decreases owing to the hindrance effect. The hindrance effect of the P additive was smaller than that of the other additives because of its small size. As assumed, there was no problem in covering the entire defect site with additives. Therefore, we can claim that any additive can be helpful for the cyclability of LMB at the point of binding energy calculation.

2.5. Modifying Chemical Components of the SEI Layer with Pyrrolidone-Based Molecular Dipoles

A pyrrolidone-based molecular dipole can form a stable SEI layer via pre-decomposition before solvent decomposition. To investigate the decomposition characteristics of the molecular dipole additives with different functional groups, we calculated the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their orbital energy gaps (**Figure 4**a). The LUMO energy levels of all the pyrrolidone-based molecules are lower than those of tetraethylene glycol dimethyl ether (TEGDME), implying that the reduction of the molecules preferentially occurs prior to the decomposition of the TEGDME solvent. These results demonstrate that pyrrolidone-based molecules can become the dominant interlayer components on the Li electrode surface and ADVANCED SCIENCE NEWS _____ www.advancedsciencenews.com

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Figure 4. a) The HOMO and LUMO energy levels of electrolyte solvent and pyrrolidone-based electrolyte additives. XPS spectra of the Li-metal anode after 10 cycles at current density of 1 mA cm⁻². b) C 1s, c) Li 1s, d) O 1s, and e) F 1s spectra of the Li-metal anode cycled in the electrolyte with and without pyrrolidone-based additives.

prevent unnecessary electrolyte consumption during cell operation.

The low LUMO energies of the pyrrolidone-based molecular dipoles can modify the chemical composition of the SEI layers on the Li metal surface. To further elucidate the interface structure of the SEI layer on the Li-metal anodes cycled with molecular dipole additives, ex situ X-ray photoelectron spectroscopy (XPS) measurements of the Li-metal anodes collected after 10 cycles were performed (Figure 4b-e). The XPS signals for C 1s, Li 1s, O 1s, and F 1s show notable changes in the chemical composition of the SEI layer due to the presence of the additive. In the C 1s XPS spectrum, significant C-H and C-O peaks were observed, corresponding to the decomposition reaction products of the TEGDME electrolyte composed mainly of C, O, and H, respectively (Figure 4b). In the case of the cycled Li metal without additives, an additional Li-C peak (282.4 eV) was strongly formed as a result of typical electrolyte decomposition.^[16] Previous studies have shown that flexible and stable SEI components are formed from a combination of carbonate and fluoride components.^[17] While the Li metal electrode cycled without additives showed a CF₂ peak, the Li metals cycled with pyrrolidone-based electrolyte additives showed the further dominant formation of a CF₃ peak. Referring to the reactivity of -CF groups ($-CF > -CF_2 > -CF_3$), it can be said that the -CF3 component formed by pyrrolidonebased additives improves the structural durability of the SEI layer.^[18] In the Li 1s spectrum, the Li₂O (53.5 eV) peak is strongly shown when no additive was added (Figure 4c). In contrast, for the Li electrodes cycled with additives, peaks related to Li₂CO₃ (55 eV) and LiF (56 eV) were observed. In the O 1s spectrum, consistent with the results for Li 1s, we found that for electrodes without additives, oxide-based SEI layer components such as Li₂O and Li₂O₂ were dominantly formed (Figure 4d). Carbonate-type Li₂CO₃ and O-C peaks were prominent for the Li anodes cycled with pyrrolidone-based additives. In the F 1s spectrum, the LiF peak was weak for the cycled Li electrode without additives (Figure 4e). In contrast, an SEI layer containing large amounts of LiF and C-F components can be fabricated by employing pyrrolidone-based molecular dipoles. It is known that



oxide-rich SEI layers are weak, whereas carbonate- or fluoriderich SEI layers are strong and durable against unwanted side reactions and mechanical stresses during repeated Li deposition and stripping.^[10] Our results suggest that in the absence of pyrrolidone-based additives, an oxide-rich SEI layer was formed, whereas in the presence of pyrrolidone additives in the electrolyte, carbonate- and fluoride-rich SEI layers were formed. From the XPS results, the structural enhancement of the SEI layer with durable carbonate- and fluoride-rich phases instead of a weak oxide phase can be successfully achieved by introducing a pyrrolidone-based electrolyte additive. The formation of a carbonate- and fluoride-dominant SEI layer is accelerated by adsorbing molecular dipole additives on the Li metal surface and subsequently reducing them prior to electrolyte decomposition. Therefore, a modified passivation layer with better chemical stability and structural durability can 1) prevent continuous side reactions with the electrolyte during cycling, 2) reinforce huge volume changes of Li for charge and discharge, 3) afford strong mechanical properties, and 4) facilitate Li diffusion kinetics owing to the low Li diffusion barrier of LiF.^[10a,19] Interestingly. the type of pyrrolidone molecules with regard to the molecular volume and relevant polarizability did not notably affect the composition and amount of carbonate and fluoride species in the SEI layers. The difference in electrochemical performance among the diverse pyrrolidone-based molecular dipoles with different polarizability values shown in Figure 1 closely depends on the surfaceflattening ability associated with the polarizability difference

among the molecular dipoles rather than the composition of the SEI layer. From the EIS results, the reduced R_{ct} value can be correlated with the interface composition of the modified

SEI layer formed by the pyrrolidone-based molecular dipoles. Digital images of the cycled Li metal anode used for SEM and AFM analysis are shown in Figure S3, Supporting Information, to directly show the surface stabilizing effect of pyrrolidonebased molecular dipoles. The cycled Li anode without the molecular dipole additive was mostly covered with dark and black side products (Figure S3a, Supporting Information). In the case of the samples with electrolyte additives, a relatively high portion of shiny and silver-colored Li metal remained, confirming the interface-stabilizing effects of the pyrrolidone-based molecular dipole additives (Figure S3b–e, Supporting Information).

Highly polarizable molecular dipole additives provide multifunctional stabilizing effects on the reacting surfaces of Li metal electrodes. **Figure 5** illustrates the three functions of highly polarizable molecular dipole additives: 1) flattening the surface morphology of the Li electrode, 2) controlling the growth direction of the crystalline Li structure, and 3) strengthening the chemical components of the SEI layer. Pyrrolidone-based additives with different types of functional groups exhibit different molecular polarizabilities depending on the molecular volume, which determines the degree of the surface-stabilizing effect of the Li metal anode. We found that the pyrrolidone-based additive with lower polarizability, associated with a smaller molecular volume, insufficiently covered the Li surface, resulting in a relatively non-uniform



Figure 5. A schematic illustration of the multifunctional effects of highly polarizable molecular dipole additives on the surface of a Li-metal electrode. Images showing the effects of I) surface flattening, II) crystal growth control, and III) the chemical composition of the SEI layer formed on the surface of the Li-metal anode.



Li deposition. In contrast, highly polarizable pyrrolidone-based molecules with larger molecular volumes are sufficiently adsorbed on problematic and unstable reaction sites, enabling uniform Li deposition/stripping and flat surfaces for repeated cell operation. Molecular dipole additives also play a role in controlling the growth direction of crystalline Li metal. Generally, Li species are adsorbed on unstable defect sites and nodular Li deposition occurs. By adsorbing molecular dipoles onto the defect sites, the Li growth direction is changed, and lateral growth can preferentially occur. Finally, the presence of highly polarizable molecular dipole additives also influenced the chemical components of the SEI layer formed on the Li metal anode surface. Unlike oxide-rich SEI layers formed on Li surfaces without additives, pyrrolidone-based additives can form carbonateand fluoride-rich SEI layers by the electrochemical reduction of pyrrolidone molecules prior to electrolyte decomposition, offering a more durable and stable environment.^[20] Inducing the formation of a SEI layer with strong components is possible owing to the presence of molecular dipole additives.

To investigate the impact of pyrrolidone-based molecular dipoles included as electrolyte additives on the cathode in a full cell configuration, full cell tests in Li-O2 battery system were conducted. Li-O₂ cells are representative next generation battery systems utilizing Li metal anode.^[21] The Li-O₂ batteries offer exceptional energy densities (>3500 Wh kg⁻¹ and >6900 Wh L⁻¹) by employing infinite and lightweight oxygen cathode. Two types of molecular dipoles, one with relatively poor stabilization performance denoted as P and another with excellent stabilization performance denoted as PP, were evaluated in Li-O2 cell. To access the advantages of the molecular dipole additives, charge-discharge cycle tests were performed at a current density of 100 mA g_{carbon} in a 1 M LiTFSI + TEGDME electrolyte. Figure S4a, Supporting Information, shows the charge-discharge profiles after 10 cycles for each electrolyte condition, including pristine, with P, and with PP. The cell containing the molecular dipoles exhibited lower charge voltage profiles, indicating that the introduction of molecular dipoles promotes the decomposition of discharge products. However, Figure S4b-d, Supporting Information, reveal that cells operated without the molecular dipoles exhibited a sharp decrease in capacity after 20 cycles. In contrast, cells containing P and PP showed stable cycle performance with no capacity decrease up to 40 cycles. This demonstrates the applicability of these molecular dipoles for diverse Li metal battery systems including Li–O₂ battery.

3. Conclusion

In summary, we report the effects of the polarizability of pyrrolidone-based molecular dipole electrolyte additives with different functional groups on the stabilization function of Li metal anodes. The molecular volume was controlled by altering the diverse functional groups on the molecules, thereby adjusting their polarizability values. We demonstrated that the lifetime characteristics of LMBs are proportional to the polarizability of the molecular dipole additives. Highly polarizable molecular dipoles can be easily adsorbed on Li metal electrodes with an applied potential and subsequently inhibit the growth of Li dendrites, indicating a surface-flattening effect. We found that the pyrrolidone-based additives helped maintain the crystallinity of pure Li and the preferred orientation to a single plane, even after long cycles. The pyrrolidone-based molecular dipoles not only inhibited the reductive degradation of the TEGDME electrolyte solvent but also facilitated the dominant formation of durable carbonate and fluoride-rich SEI layers, which enhanced the surface stability of the Li metal electrode against side reactions. Furthermore, we confirmed the stabilization effects of pyrrolidone-based molecular dipole additives on Li–O₂ full cells. This study provides an efficient guideline for the development of functional electrolyte additives for safe and long-cycle Li metal batteries.

4. Experimental Section

Materials and Chemicals: 2-Pyrrolidone (P, 99%), 1-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%), 1-Vinyl-2-pyrrolidone (VP, 99%), 1-Phenyl-2-Pyrrolidione (PP, 99%), tetraethylene glycol dimethyl ether (TEGDME, 99%), and bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, 99.95%) was purchased from Sigma–Aldrich (Korea). Tetraethylene glycol dimethyl ether (TEGDME, 99%) was used as the electrolyte after dipping in freshly activated 4 Å molecular sieves for two weeks. Bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, 99.95%) was added to TEGDME.

Preparation of Li–Li Symmetric Cells: A 12-mm diameter Li metal foil was used for both the electrodes, and Celgard 2500 polypropylene was used as the separator. Li–Li symmetric cells were assembled using R2032 coin-type cells (Wellcos Corp.) in an argon-purged glovebox. 1 M LiTFSI in TEGDME with and without a 200 ppm pyrrolidone-based additive was stirred for 24 h at room temperature and used as the electrolyte.

Preparation of *Li*–O₂ *Cells*: The oxygen electrode was fabricated using Fe metal based atomic catalyst loaded nitrogen-doped multiwalled carbon nanotubes (Fe-NCNT; 90 wt%) and PVdF (10 wt%) dissolved in NMP. The slurry was pasted onto a 12-mm diameter gas diffusion layer (GDL) current collector and was dried for 4 h at 40 °C in a vacuum. The average slurry mass loading was 0.4 mg per Ø12 mm GDL. A 12-mm diameter Li-metal foil was used as the anode, and glass fiber (Whatman GF/A microfiber filter paper) was used as the separator. The prepared oxygen electrode was assembled with 130 µL of prepared electrolyte in sequence in an HS air-type cell (HS flat cell combine with Swagelok type, EK cell, Wellcos Corp.) in an Ar-filled glove box. All the cells were assembled into R2032 coin-type cells with several holes (Wellcos Corp.).

Electrochemical Measurements: All electrochemical analyses were performed at room temperature. A charge/discharge test using Li–Li symmetric cells was conducted using a battery cycler (WBCS3000S battery test system, WonATech). Li–O₂ cells were tested at a current density of 100 mA g⁻¹ in the voltage ranges of 2.3–4.5 V vs Li/Li⁺. Electrochemical impedance spectroscopy (EIS) measurements were performed from 1 MHz to 0.01 Hz with an amplitude of 5 mV.

Ex situ Characterization: The morphologies and surfaces of the samples were verified using field-emission scanning electron microscopy (FE-SEM, JSM-7600F, JEOL) operated at an accelerating voltage of 5 keV. The surface roughness was investigated using AFM (NX-10, Park Systems, Korea) in an argon-filled glove box. The surface characteristics of the Li metal electrodes after cycling were investigated using X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo UK). The crystal structure of the Li metal electrode was characterized using XRD (D8 Advance, Bruker) using Cu-K α ($\lambda = 1.54$ Å). After charging and discharging, the cells were disassembled in an Ar-filled glovebox.

Computational Details: Generalized gradient approximation-based (GGA) based density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP) was performed in this work. The electron exchange correlation was predicted using the revised Perdew–Burke–Ernzerhof (RPBE) functional^[22] known to be suitable for chemical reaction studies. To consider the solvation effect on the adsorption energy and structure changes of adsorbate, we employed the

implicit solvation method with VASPsol.^[23] The cutoff energy was set to 400 eV to properly describe the electronic structure. The Brillouin zone was sampled at $2 \times 2 \times 1$ based on the Monkhorst–Pack scheme. The conver-

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and 10^{-2} eV Å⁻¹, respectively. In this study, we used a Li (110) slab in the same step as in our previous study.^[10a] In principle, the (110) surface was the most stable owing to its highest coordination number when the bulk metal was Li (BCC metal). However, the actual surface of a Li anode can have many defects, such as vacancies, steps, edges, kinks, and grain boundaries, on a large scale. In our case, we had to simplify the system without losing generality because computational resources and time are limited. Thus, we used the most stable Li (110) surface with a step to compare the binding energy changes at different binding sites: non-defective and defective sites. Our slab model is centered in the 20 Å vacuum gap along the z-axis. The two bottom layers on the top were relaxed during geometry optimization. To calculate the binding energy of Li or the additives, the following equation was used:

gence criteria for the electronic and geometric optimizations were 10⁻⁵ eV

$$\Delta E_{\text{bind.}} = (\Delta E_{\text{Li slab} + \text{adsorbate}} - \Delta E_{\text{Li slab}} - n\Delta E_{\text{adsorbate}})/n \tag{1}$$

where, $\Delta E_{\text{bind.}}$ where is the binding energy of the adsorbate (Li or additives), $\Delta E_{\text{Lislab}+\text{adsorbate}}$ is the total energy of the system after the binding of the adsorbate, ΔE_{Lislab} is the total energy of the Li slab, $\Delta E_{\text{adsorbate}}$ is the cohesive energy of Li or gas phase energy of the additives, and *n* is the number of adsorbates.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrolyte additive, functional group, Li-metal batteries, polarizability, pyrrolidone-based molecules

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a) B. Dunn, H. Kamath, J.-M. Tarascon, *Science* 2011, 334, 928; b)
 M. Arbabzadeh, J. X. Johnson, G. A. Keoleian, P. G. Rasmussen,
 L. T. Thompson, *Environ. Sci. Technol.* 2016, 50, 1046; c) D. Choi,

- [2] a) L. Chen, Y. Su, J. Zhang, H. Zhang, B. Fan, G. Shao, M. Zhong, C.-A. Wang, ACS Appl. Mater. Interfaces 2021, 13, 37082; b) X. Lin, J. Yu, M. B. Effat, G. Zhou, M. J. Robson, S. C. Kwok, H. Li, S. Zhan, Y. Shang, F. Ciucci, Adv. Funct. Mater. 2021, 31, 2010261; c) F. Duffner, N. Kronemeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, Nat. Energy 2021, 6, 123.
- [3] a) Y. Liu, Q. Liu, L. Xin, Y. Liu, F. Yang, E. A. Stach, J. Xie, Nat. Energy 2017, 2, 17083; b) F. Wu, Y.-X. Yuan, X.-B. Cheng, Y. Bai, Y. Li, C. Wu, Q. Zhang, Energy Storage Mater. 2018, 15, 148; c) L. Ma, J. Cui, S. Yao, X. Liu, Y. Luo, X. Shen, J.-K. Kim, Energy Storage Mater. 2020, 27, 522; d) J. Xiao, Q. Li, Y. Bi, M. Cai, B. Dunn, T. Glossmann, J. Liu, T. Osaka, R. Sugiura, B. Wu, Nat. Energy 2020, 5, 561; e) B. D. Adams, J. Zheng, X. Ren, W. Xu, J. G. Zhang, Adv. Energy Mater. 2018, 8, 1702097.
- [4] a) N. W. Li, Y. Shi, Y. X. Yin, X. X. Zeng, J. Y. Li, C. J. Li, L. J. Wan, R. Wen, Y. G. Guo, Angew. Chem. 2018, 130, 1521; b) X. Q. Zhang, X. B. Cheng, Q. Zhang, Adv. Mater. Interfaces 2018, 5, 1701097.
- [5] a) F. Liu, R. Xu, Y. Wu, D. T. Boyle, A. Yang, J. Xu, Y. Zhu, Y. Ye, Z. Yu,
 Z. Zhang, *Nature* **2021**, 600, 659; b) N. W. Li, Y. X. Yin, C. P. Yang,
 Y. G. Guo, *Adv. Mater.* **2016**, 28, 1853.
- [6] a) Q. Li, S. Zhu, Y. Lu, Adv. Funct. Mater. 2017, 27, 1606422; b)
 C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li, Y.-G. Guo, Nat. Commun. 2015, 6, 8058; c)
 Y. Fan, J. Liao, D. Luo, Y. Huang, F. Sun, J. Nan, Chem. Eng. J. 2023, 453, 139903.
- [7] a) R. Xu, X.-B. Cheng, C. Yan, X.-Q. Zhang, Y. Xiao, C.-Z. Zhao, J.-Q. Huang, Q. Zhang, *Matter* 2019, *1*, 317; b) S. Li, J. Huang, Y. Cui, S. Liu, Z. Chen, W. Huang, C. Li, R. Liu, R. Fu, D. Wu, *Nat. Nanotechnol.* 2022, *17*, 613; c) A.-L. Chen, N. Shang, Y. Ouyang, L. Mo, C. Zhou, W. W. Tjiu, F. Lai, Y.-E. Miao, T. Liu, *EScience* 2022, *2*, 192.
- [8] a) R. Pan, X. Xu, R. Sun, Z. Wang, J. Lindh, K. Edström, M. Strømme, L. Nyholm, *Small* **2018**, *14*, 1704371; b) S. Yao, Y. Yang, Z. Liang, J. Chen, J. Ding, F. Li, J. Liu, L. Xi, M. Zhu, J. Liu, *Adv. Funct. Mater.* **2023**, *33*, 2212466.
- [9] a) H. Zhang, G. G. Eshetu, X. Judez, C. Li, L. M. Rodriguez-Martínez, M. Armand, Angew. Chem., Int. Ed. 2018, 57, 15002; b) L. Li, H. Dai, C. Wang, Nano Select 2021, 2, 16; c) G. Wang, X. Xiong, D. Xie, X. Fu, X. Ma, Y. Li, Y. Liu, Z. Lin, C. Yang, M. Liu, Energy Storage Mater. 2019, 23, 701; d) D. Wang, H. Liu, M. Li, D. Xia, J. Holoubek, Z. Deng, M. Yu, J. Tian, Z. Shan, S. P. Ong, Nano Energy 2020, 75, 104889.
- [10] a) J.-S. Lee, K. Shin, S.-Y. Jun, S. Kim, W.-H. Ryu, *Chem. Eng. J.* 2023, 458, 141383; b) S. Y. Jun, K. Shin, J. S. Lee, S. Kim, J. Chun, W. H. Ryu, *Adv. Sci.* 2023, 10, 2301426.
- [11] Y. Lu, C. Z. Zhao, H. Yuan, X. B. Cheng, J. Q. Huang, Q. Zhang, Adv. Funct. Mater. 2021, 31, 2009925.
- [12] a) J.-J. Woo, V. A. Maroni, G. Liu, J. T. Vaughey, D. J. Gosztola,
 K. Amine, Z. Zhang, J. Electrochem. Soc. 2014, 161, A827; b)
 W. Choi, H.-C. Shin, J. M. Kim, J.-Y. Choi, W.-S. Yoon, J. Electrochem. Sci. Technol. 2020, 11, 1.
- [13] a) W. Waag, S. Käbitz, D. U. Sauer, *Appl. Energy* 2013, 102, 885; b)
 H. Dai, K. Xi, X. Liu, C. Lai, S. Zhang, J. Am. Chem. Soc. 2018, 140, 17515.
- [14] E. Peled, S. Menkin, J. Electrochem. Soc. 2017, 164, A1703.
- [15] a) M. Sadd, S. Xiong, J. R. Bowen, F. Marone, A. Matic, *Nat. Commun.* 2023, 14, 854; b) W. Li, H. Yao, K. Yan, G. Zheng, Z. Liang, Y.-M. Chiang, Y. Cui, *Nat. Commun.* 2015, *6*, 7436.
- [16] a) J. Zheng, P. Yan, D. Mei, M. H. Engelhard, S. S. Cartmell,
 B. J. Polzin, C. Wang, J. G. Zhang, W. Xu, Adv. Energy Mater.

2016, 6, 1502151; b) D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, Electrochim. Acta 2002, 47, 1423.

[17] M. Ma, H. Cai, C. Xu, R. Huang, S. Wang, H. Pan, Y. S. Hu, Adv. Funct. Mater. 2021, 31, 2100278.

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ENCE NEWS www.advancedsciencenews.com

S

- [18] A. Nova, R. Mas-Balleste, A. Lledos, Organometallics 2012, 31, 1245.
- [19] a) M. He, R. Guo, G. M. Hobold, H. Gao, B. M. Gallant, Proc. Natl. Acad. Sci. 2020, 117, 73; b) X. Q. Zhang, X. B. Cheng, X. Chen, C. Yan, Q. Zhang, Adv. Funct. Mater. 2017, 27, 1605989; c) J. D. McBrayer, C. A. Apblett, K. L. Harrison, K. R. Fenton, S. D. Minteer, Nanotechnology 2021, 32, 502005.
- [20] Z. Xue, D. He, X. Xie, J. Mater. Chem. A 2015, 3, 19218.
- [21] a) S. Kim, H. S. Kim, B. Kim, Y. J. Kim, J. W. Jung, W. H. Ryu, Adv. Energy Mater. 2023, 13, 2301983; b) H. S. Kim, B. Kim, H. Park, J. Kim, W. H. Ryu, Adv. Energy Mater. 2022, 12, 2103527; c) F. Peng, Y. Lim, B. Kim, H.-S. Kim, Z. Li, Z. Zhou, J. Li, W.-H. Ryu, Sustainable Mater. Technol. 2023, 35, e00531.
- [22] a) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865; b) Y. Zhang, W. Yang, Phys. Rev. Lett. 1998, 80, 890; c) B. Hammer, L. B. Hansen, J. K. Nørskov, Phys. Rev. B 1999, 59, 7413.
- [23] a) K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T. Arias, R. G. Hennig, J. Chem. Phys. 2014, 140, 084106; b) K. Mathew, V. Kolluru, S. Mula, S. N. Steinmann, R. G. Hennig, J. Chem. Phys. **2019**, *151*, 234101.