Opportunities and Limitations of Ionic Liquid- and Organic Carbonate Solvent-Based Electrolytes for Mg-Ion-Based Dual-Ion Batteries

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Supporting Information

Opportunities and Limitations of Ionic-Liquid- and Organic Carbonate Solvent-Based Electrolytes for Mg-Ion-Based Dual-Ion Batteries

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Table S1. List of abbreviations.

| Abbreviation | Description |
|--------------|-------------|
| AC           | Activated carbon |
| AGG          | Aggregate |
| cc-          | cis-cis conformer of |
| CE           | Counter electrode |
| C-eff        | Coulombic efficiency |
| CEI          | Cathode electrolyte interphase |
| CIP          | Contact ion pair |
| CMC          | Sodium carboxymethylcellulose |
| ct-          | cis-trans conformer of |
| DEC          | Diethyl carbonate |
| DIB          | Dual-ion battery |
| DMC          | Dimethyl carbonate |
| EG           | Expanded graphite |
| ES           | Ethylene sulfide |
| Fc           | Ferrocene |
| I            | Areal intensity |
| Li           | Lithium |
| LIB          | Lithium ion battery |
| M            | Mol per liter solvent |
| Mg           | Magnesium |
| OCP          | Open-circuit potential |
| Pt           | Platinum |
| PTFE         | Polytetrafluoroethylene |
| Pyr\textsuperscript{TFSI or Pyr (in electrolyte abbreviations)} | 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyle)imide |
| QRE          | Quasi-reference electrode |
| RE           | Reference electrode |
| RMB          | Rechargeable magnesium battery |
| SDC          | Specific discharge capacity |
| SEI          | Solid electrolyte interphase |
| SHE          | Standard hydrogen electrode |
| Si           | Silicon |
| SSIP         | Solvent separated ion pair |
| TFSI\textsuperscript{-} | Bis(trifluoromethanesulfonyle)imide anion |
| WE           | Working electrode |
| XRD          | X-ray diffraction |
Table S2a. Description of different cycling procedures used within this work. Before the first step, an open circuit potential (OCP) step of 10 h was applied for every cycling procedure. The electrolytes used in cells cycled with this procedure are indicated in brackets. The device used for all cells with this procedure is enclosed in square brackets.

### Procedure 1:
Constant current cycling (Mg-Pyr, Li-Pyr, Mg-Pyr+ES, Mg-DMC, Mg-DEC) [MACCOR]

| Step | Specific current / mA g⁻¹ | Cut-off potential vs. Li|Li⁺ / V | Repetition |
|------|--------------------------|------------------------|----------|
| 1    | Charge 10                | 5.0 (Mg-ion-based)     | 1        |
|      |                          | 4.9 (Li-ion-based)     |          |
|      | Discharge 10             | 3.4                    |          |
| 2    | Charge 100               | 5.0 (Mg-ion-based)     | 300      |
|      |                          | 4.9 (Li-ion-based)     |          |
|      | Discharge 100            | 3.4                    |          |

### Procedure 2:
Constant current cycling at high cut-offs (Mg-Pyr) [VMP3]

| Step | Specific current / mA g⁻¹ | Cut-off potential vs. Li|Li⁺ / V | Repetition |
|------|--------------------------|------------------------|----------|
| 1    | Charge 10                | 5.0                    | 1        |
|      | Discharge 10             | 3.4                    |          |
| 2    | Charge 100               | 5.3                    | 300      |
|      | Discharge 100            | 3.4                    |          |

### Procedure 3:
Constant current cycling at high cut-offs and currents (Mg-Pyr+ES) [VMP3]

| Step | Specific current / mA g⁻¹ | Cut-off potential vs. Li|Li⁺ / V | Repetition |
|------|--------------------------|------------------------|----------|
| 1    | Charge 10                | 5.0                    | 1        |
|      | Discharge 10             | 3.4                    |          |
| 2    | Charge 300               | 5.3                    | 400      |
|      | Discharge 300            | 3.4                    |          |
Table S2b. Description of different cycling procedures used within this work. Before the first step, an OCP step of 10 h was applied for every cycling procedure. The electrolytes used in cells cycled with this procedure are indicated in brackets. The device used for all cells with this procedure is enclosed in square brackets.

Procedure 4:
Constant current cycling at varying cut-offs potentials
(Mg-Pyr, Li-Pyr, Mg-Pyr+ES, Mg-DMC, Mg-DEC) [VMP3]

For an easier comparison of the cell performance depending on the cut-off potential, the SDCs and C<sub>eff</sub> of the 10<sup>th</sup> cycle of step 2-12 are shown in Figure 4a, 7a and 10b, and Table S6.

| Step | Specific current / mA g<sup>-1</sup> | Cut-off potential vs. Li|Li<sup>+</sup>| V | Repetition |
|------|----------------------------------|-------------------------|-------------------------|-------|
| 1    | Charge 10                        | 5.0 V (Mg-ion-based)    | 4.9 V (Li-ion-based)    | 1     |
|      | Discharge 10                     | 4.9                     | 3.4                     |       |
| 2    | Charge 100                       | 4.5                     |                          | 10    |
|      | Discharge 100                    | 4.6                     |                          |       |
| 3    | Charge 100                       | 4.6                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 4    | Charge 100                       | 4.7                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 5    | Charge 100                       | 4.8                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 6    | Charge 100                       | 4.9                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 7    | Charge 100                       | 5.0                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 8    | Charge 100                       | 5.1                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 9    | Charge 100                       | 5.2                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 10   | Charge 100                       | 5.3                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 11   | Charge 100                       | 5.4                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
| 12   | Charge 100                       | 5.5                     |                          | 10    |
|      | Discharge 100                    | 3.4                     |                          |       |
Table S2c. Description of different cycling procedures used within this work. Before the first step, an OCP step of 10 h was applied for every cycling procedure. The electrolytes used in cells cycled with this procedure are indicated in brackets. The device used for all cells with this procedure is enclosed in square brackets.

**Procedure 5:**
Constant current cycling with varying specific currents (Mg-Pyr, Li-Pyr, Mg-Pyr+ES, Mg-DMC, Mg-DEC) [MACCOR]

For an easier comparison of the cell performance depending on the specific current, the SDCs and Ceff of the 5th cycle of step 3-11 are shown in Figure 4b, 7b and 10c, and Table S7.

| Step | Specific current / mA g⁻¹ | Cut-off potential vs. Li/Li⁺ / V | Repetition |
|------|---------------------------|----------------------------------|------------|
| 1    | Charge 10                 | 4.9/5.0 (Li⁺/Mg-ion-based)       | 1          |
|      | Discharge 10              | 3.4                              |            |
| 2    | Charge 100                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 30         |
|      | Discharge 100             | 3.4                              |            |
| 3    | Charge 10                 | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 10              | 3.4                              |            |
| 4    | Charge 20                 | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 20              | 3.4                              |            |
| 5    | Charge 50                 | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 50              | 3.4                              |            |
| 6    | Charge 100                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 100             | 3.4                              |            |
| 7    | Charge 200                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 200             | 3.4                              |            |
| 8    | Charge 300                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 300             | 3.4                              |            |
| 9    | Charge 500                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 500             | 3.4                              |            |
| 10   | Charge 1000               | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 1000            | 3.4                              |            |
| 11   | Charge 2500               | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 2500            | 3.4                              |            |
| 12   | Charge 5000               | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 5000            | 3.4                              |            |
| 13   | Charge 10000              | 4.9/5.0 (Li⁺/Mg-ion-based)       | 5          |
|      | Discharge 10000           | 3.4                              |            |
| 14   | Charge 100                | 4.9/5.0 (Li⁺/Mg-ion-based)       | 80         |
|      | Discharge 100             | 3.4                              |            |
Table S2d. Description of different cycling procedures used within this work. Before the first step, an OCP step of 10 h was applied for every cycling procedure. The electrolytes used in cells cycled with this procedure are indicated in brackets. The device used for all cells with this procedure is enclosed in square brackets.

**Procedure 6:**
Constant current cycling prior to XRD measurements
(Mg-Pyr, Li-Pyr, Mg-Pyr+ES, Mg-DMC, Mg-DEC) [MACCOR]

| Step | Specific current / mA g⁻¹ | Cut-off potential vs. Li|Li⁺ / V | Repetition |
|------|---------------------------|------------------------|----------|-----------|
| 1 Charge | 10 | 4.9/5.0 (Li-/Mg-ion-based) | 3 |
| Discharge | 10 | 3.4 | |
| 2 Charge | 10 | 4.9/5.0 (Li-/Mg-ion-based) | 1 |
Table S3. Specific discharge capacities (SDC) and Coulombic efficiencies (CEff) of selected cycles of graphite \textregistered AC cells with selected electrolytes at 100 mA g\(^{-1}\) (1\textsuperscript{st} cycle: 10 mA g\(^{-1}\)) with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li\textbar Li\(^+\).

| Li-Pyr | Mg-Pyr (20 °C) | Mg-Pyr (upper cut-off potential: 5.3 V vs. Li\textbar Li\(^+\)) | Mg-Pyr (60 °C)* |
|--------|----------------|-------------------------------------------------|-----------------|
|        | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % |
| 1\textsuperscript{st} cycle | 32 ± 1 | 64 ± 2 | 29 ± 1 | 74 ± 1 | 32 ± 2 | 64 ± 2 | 29 ± 1 | 74 ± 1 |
| 50\textsuperscript{th} cycle | 37 ± 4 | 99.1 ± 0.3 | 34 ± 4 | 99.5 ± 0.1 | 37 ± 4 | 99.1 ± 0.3 | 34 ± 4 | 99.5 ± 0.1 |
| 300\textsuperscript{th} cycle | 34 ± 3 | 99.5 ± 0.2 | 35 ± 3 | 99.8 ± 0.1 | 34 ± 3 | 99.5 ± 0.2 | 35 ± 3 | 99.8 ± 0.1 |

| Mg-Pyr (upper cut-off potential: 5.3 V vs. Li\textbar Li\(^+\)) | Mg-Pyr (60 °C)* |
|-------------------------------------------------|-----------------|
|        | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % |
| 1\textsuperscript{st} cycle | 33 ± 2 | 72.9 ± 0.7 | 52 ± 1 | - | 33 ± 2 | 72.9 ± 0.7 | 52 ± 1 | - |
| 50\textsuperscript{th} cycle | 86 ± 5 | 97.2 ± 0.9 | 56 ± 2 | 95.0 ± 0.9 | 86 ± 5 | 97.2 ± 0.9 | 56 ± 2 | 95.0 ± 0.9 |
| 300\textsuperscript{th} cycle | 55 ± 11 | 97.7 ± 0.5 | 47 ± 2 | 95.8 ± 0.5 | 55 ± 11 | 97.7 ± 0.5 | 47 ± 2 | 95.8 ± 0.5 |

| Mg-Pyr+ES | Mg-Pyr+ES, (at 300 mAh g\(^{-1}\), upper cut-off potential: 5.3 V vs. Li\textbar Li\(^+\)) |
|-------------------------------------------------|-------------------------------------------------|
|        | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % |
| 1\textsuperscript{st} cycle | 45 ± 2 | 73 ± 2 | 40.9 ± 0.7 | 79.2 ± 0.8 | 45 ± 2 | 73 ± 2 | 40.9 ± 0.7 | 79.2 ± 0.8 |
| 50\textsuperscript{th} cycle | 53 ± 4 | 99.1 ± 0.3 | 93 ± 2 | 99.1 ± 0.2 | 53 ± 4 | 99.1 ± 0.3 | 93 ± 2 | 99.1 ± 0.2 |
| 300\textsuperscript{th} cycle | 50 ± 3 | 99.4 ± 0.2 | 84 ± 5 | 98.9 ± 0.2 | 50 ± 3 | 99.4 ± 0.2 | 84 ± 5 | 98.9 ± 0.2 |
| 400\textsuperscript{th} cycle | 50 ± 4 | 99.3 ± 0.2 | 82 ± 4 | 98.8 ± 0.2 | 50 ± 4 | 99.3 ± 0.2 | 82 ± 4 | 98.8 ± 0.2 |

| Mg-DMC | Mg-DEC |
|--------|--------|
|        | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % | SDC / mAh g\(^{-1}\) | CEff / % |
| 1\textsuperscript{st} cycle | 46 ± 3 | 73.1 ± 0.7 | 45.9 ± 0.9 | 76 ± 2 | 46 ± 3 | 73.1 ± 0.7 | 45.9 ± 0.9 | 76 ± 2 |
| 50\textsuperscript{th} cycle | 39 ± 3 | 99.5 ± 0.2 | 39 ± 5 | 99.57 ± 0.01 | 39 ± 3 | 99.5 ± 0.2 | 39 ± 5 | 99.57 ± 0.01 |
| 300\textsuperscript{th} cycle | 41 ± 4 | 99.3 ± 0.7 | 41 ± 5 | 99.75 ± 0.02 | 41 ± 4 | 99.3 ± 0.7 | 41 ± 5 | 99.75 ± 0.02 |

*At 60 °C, strong parasitic side reactions could be observed at 10 mA g\(^{-1}\) in the first cycle below 5.0 V vs. Li\textbar Li\(^+\), why the cut-off potential of 5.0 V vs. Li\textbar Li\(^+\) was not reached, before the time determination (10 hours, 100 mAh g\(^{-1}\)) was reached.
Table S4. TFSI⁻ intercalation onset potentials (threshold: 10 mAh g⁻¹ V⁻¹) in V vs. Li|Li⁺ of selected cycles of graphite ‖ AC cells with selected electrolytes at 100 mA g⁻¹ (1st cycle: 10 mA g⁻¹) with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li|Li⁺.

|         | Li-Pyr   | Mg-Pyr (20 °C) | Mg-Pyr (60 °C) |
|---------|----------|----------------|----------------|
| 1st cycle | 4.61 ± 0.01 | 4.82 ± 0.01   | 4.54 ± 0.02    |
| 50th cycle | 4.39 ± 0.01 | 4.48 ± 0.01   | 4.43 ± 0.03    |
| 100th cycle | 4.38 ± 0.02 | 4.47 ± 0.02   | 4.40 ± 0.04    |
| 300th cycle | 4.38 ± 0.02 | 4.45 ± 0.02   | 4.17 ± 0.10*    |

|         | Mg-Pyr+ES | Mg-DMC | Mg-DEC |
|---------|-----------|--------|--------|
| 1st cycle | 4.64 ± 0.02 | 4.61 ± 0.01 | 4.64 ± 0.01 |
| 50th cycle | 4.44 ± 0.03 | 4.53 ± 0.01 | 4.53 ± 0.02 |
| 100th cycle | 4.44 ± 0.03 | 4.52 ± 0.02 | 4.52 ± 0.02 |
| 300th cycle | 4.45 ± 0.03 | 4.51 ± 0.01 | 4.50 ± 0.02 |

* The lower onset potential is based on low capacities at low potentials. The main intercalation (threshold of 20 mAh g⁻¹) starts at 4.47 ± 0.03 V vs. Li|Li⁺ (at 20 °C: 4.45 ± 0.02 V vs. Li|Li⁺).
Table S5. $d_{(00n+2)} / d_{(00n+1)}$ ratio, dominant stage and specific charge and discharge capacities at selected potentials of graphite electrodes after three full cycles between 5.0 respectively 4.9 V vs. Li|Li$^+$ for Li-Pyr and 3.4 V vs. Li|Li$^+$ at 10 mA g$^{-1}$ cycled in graphite II AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with Mg-Pyr and Li-Pyr electrolytes.

| Mg-Pyr | Charge | Discharge |
|--------|--------|-----------|
| Cut-off potential / V vs. Li|Li$^+$ | 4.5 | 4.6 | 4.8 | 5 | 4.5 | 4.4 | 4.2 | 3.4 |
| $d_{(00n+2)} / d_{(00n+1)}$ | - | 1.16 | 1.24 | 1.29 | 1.21 | 1.13 | - | - |
| Dominant stage ($n$) | - | 5 | 3 | 2 | 3 | 4 | 6 | - | - |
| Specific charge capacity / mAh g$^{-1}$ | 5 | 13 | 29 | 42 | 14 | 26 | 36 | 36 |
| Specific discharge capacity / mAh g$^{-1}$ | | | | | | | | |

| Li-Pyr | Charge | Discharge |
|--------|--------|-----------|
| Cut-off potential / V vs. Li|Li$^+$ | 4.4 | 4.5 | 4.7 | 4.9 | 4.4 | 4.3 | 4.1 | 3.4 |
| $d_{(00n+2)} / d_{(00n+1)}$ | - | 1.19 | 1.26 | 1.29 | 1.24 | 1.17 | 1.14 | - |
| Dominant stage ($n$) | - | 5 | 3 | 2 | 3 | 3 | 5 | 6 | - |
| Specific charge capacity / mAh g$^{-1}$ | 1 | 14 | 31 | 44 | 13 | 20 | 23 | 39 |
| Specific discharge capacity / mAh g$^{-1}$ | | | | | | | | |

| Mg-Pyr+ES | Charge | Discharge |
|-----------|--------|-----------|
| Cut-off potential / V vs. Li|Li$^+$ | 4.5 | 4.6 | 4.8 | 5 | 4.5 | 4.4 | 4.2 | 3.4 |
| $d_{(00n+2)} / d_{(00n+1)}$ | - | 1.12 | 1.25 | 1.33 | 1.14 | - | - |
| Dominant stage ($n$) | - | 6 | 3 | 2 | 6 | - | - |
| Specific charge capacity / mAh g$^{-1}$ | 4 | 16 | 44 | 55 | 22 | 45 | 49 |
Table S6. Specific discharge capacities (SDC) and Coulombic efficiencies (C\textsubscript{Eff}) of TFSI\textsuperscript{−} intercalation into graphite of graphite I AC cells (three-electrode configuration; RE/QRE: Li metal) with selected electrolytes at different upper cut-off potentials at 100 mA g\textsuperscript{−1} (pre-cycle cycle: 10 mA g\textsuperscript{−1} with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li|Li⁺).

| Potential / V vs. Li|Li⁺ | Li-Pyr SDC / mAh g\textsuperscript{−1} | Li-Pyr C\textsubscript{Eff} / % | Mg-Pyr SDC / mAh g\textsuperscript{−1} | Mg-Pyr C\textsubscript{Eff} / % |
|---------------------|-----------------|------------------|-----------------|-----------------|-----------------|
| 4.5                 | 1.6 ± 0.2       | 101.4 ± 0.3      | 0.5 ± 0.1       | 100.6 ± 0.2     |
| 4.6                 | 12.3 ± 0.7      | 99.4 ± 0.2       | 2 ± 2           | 100.0 ± 0.2     |
| 4.7                 | 18.0 ± 0.4      | 99.2 ± 0.2       | 10 ± 3          | 99.6 ± 0.1      |
| 4.8                 | 21.7 ± 0.6      | 99.0 ± 0.3       | 14 ± 4          | 99.49 ± 0.08    |
| 4.9                 | 25.5 ± 0.8      | 98.3 ± 0.5       | 21 ± 5          | 99.2 ± 0.1      |
| 5.0                 | 30 ± 1          | 96.9 ± 0.9       | 30 ± 6          | 98.8 ± 0.1      |
| 5.1                 | 36 ± 3          | 95 ± 2           | 42 ± 6          | 98.37 ± 0.05    |
| 5.2                 | 44 ± 5          | 93 ± 2           | 55 ± 8          | 98.13 ± 0.09    |
| 5.3                 | 56 ± 10         | 92 ± 2           | 78 ± 15         | 97.6 ± 0.5      |
| 5.4                 | 66 ± 12         | 89 ± 6           | 100 ± 12        | 92 ± 9          |
| 5.5                 | 65 ± 15         | 83 ± 9           | 104 ± 9         | 73 ± 11         |

| Potential / V vs. Li|Li⁺ | Mg-Pyr+ES SDC / mAh g\textsuperscript{−1} | Mg-Pyr+ES C\textsubscript{Eff} / % |
|---------------------|-----------------|-----------------|
| 4.5                 | 1 ± 1           | 100.16 ± 0.04   |
| 4.6                 | 8 ± 4           | 99.83 ± 0.03    |
| 4.7                 | 23 ± 4          | 99.69 ± 0.02    |
| 4.8                 | 37 ± 3          | 99.56 ± 0.04    |
| 4.9                 | 42 ± 2          | 99.47 ± 0.05    |
| 5.0                 | 54 ± 3          | 98.9 ± 0.1      |
| 5.1                 | 76 ± 8          | 97.9 ± 0.5      |
| 5.2                 | 97 ± 7          | 97 ± 2          |
| 5.3                 | 105 ± 8         | 96 ± 2          |
| 5.4                 | 107 ± 11        | 82 ± 12         |
| 5.5                 | 96 ± 9          | 55 ± 10         |

| Potential / V vs. Li|Li⁺ | Mg-DMC SDC / mAh g\textsuperscript{−1} | Mg-DMC C\textsubscript{Eff} / % | Mg-DEC SDC / mAh g\textsuperscript{−1} | Mg-DEC C\textsubscript{Eff} / % |
|---------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 4.5                 | 1.1 ± 0.3       | 100.41 ± 0.05   | 1.0 ± 0.2       | 100.14 ± 0.01   |
| 4.6                 | 2 ± 2           | 100.2 ± 0.2     | 1.4 ± 0.4       | 99.97 ± 0.01    |
| 4.7                 | 6 ± 5           | 99.9 ± 0.2      | 9 ± 4           | 99.85 ± 0.04    |
| 4.8                 | 14 ± 8          | 99.74 ± 0.09    | 20 ± 5          | 99.70 ± 0.03    |
| 4.9                 | 22 ± 10         | 99.6 ± 0.2      | 31 ± 5          | 99.56 ± 0.04    |
| 5.0                 | 30 ± 10         | 99.5 ± 0.3      | 40 ± 5          | 99.3 ± 0.1      |
| 5.1                 | 43 ± 21         | 99 ± 1          | 55 ± 8          | 98.4 ± 0.5      |
| 5.2                 | 61 ± 22         | 98 ± 2          | 76 ± 10         | 96.7 ± 0.8      |
| 5.3                 | 75 ± 16         | 97 ± 2          | 92 ± 11         | 94 ± 2          |
| 5.4                 | 84 ± 12         | 96 ± 3          | 90 ± 13         | 91 ± 3          |
| 5.5                 | 85 ± 5          | 94 ± 4          | Decomposition   |
Table S7. Specific discharge capacity (SDC) and the corresponding Coulombic efficiencies (CEff) of TFSI\textsuperscript{−} intercalation of graphite || AC cells (three-electrode configuration; RE/QRE: Li metal) at different specific currents with selected electrolytes (pre-cycle at cycle: 10 mA g\textsuperscript{−1}) with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li|Li\textsuperscript{+}.

| Specific current / (mA g\textsuperscript{−1}) | Li-Pyr | Mg-Pyr |
|---------------------------------------------|--------|--------|
| SDC / (mAh g\textsuperscript{−1}) | SDC / (mAh g\textsuperscript{−1}) | CEff / % | SDC / (mAh g\textsuperscript{−1}) | CEff / % |
| 10  | 40 ± 6 | 89 ± 5 | 46 ± 3 | 94 ± 2 |
| 20  | 38 ± 6 | 94 ± 3 | 44 ± 3 | 97 ± 1 |
| 50  | 36 ± 6 | 97 ± 1 | 41 ± 3 | 98.5 ± 0.7 |
| 100 | 34 ± 6 | 98 ± 1 | 39 ± 3 | 99.2 ± 0.4 |
| 200 | 33 ± 6 | 99.1 ± 0.6 | 36 ± 3 | 99.6 ± 0.2 |
| 300 | 31 ± 5 | 99.4 ± 0.4 | 34 ± 3 | 99.8 ± 0.2 |
| 500 | 30 ± 5 | 99.7 ± 0.3 | 31 ± 3 | 99.93 ± 0.07 |
| 1000| 25 ± 4 | 99.9 ± 0.2 | 25 ± 4 | 100.07 ± 0.05 |
| 2500| 6 ± 3 | 100 ± 1 | 9 ± 6 | 100.7 ± 0.7 |

| Specific current / (mA g\textsuperscript{−1}) | Mg-Pyr+ES | CEff / % |
|-----------------------------------------------|-----------|---------|
| SDC / mAh g\textsuperscript{−1}                |            |         |
| 10  | 58.8 ± 0.4 | 94 ± 1  |
| 20  | 58.6 ± 0.2 | 96 ± 1  |
| 50  | 58 ± 1    | 98 ± 1  |
| 100 | 56 ± 2    | 98.9 ± 0.9 |
| 200 | 54 ± 2    | 99.4 ± 0.6 |
| 300 | 51 ± 2    | 99.6 ± 0.5 |
| 500 | 48 ± 4    | 99.8 ± 0.3 |
| 1000| 42 ± 6    | 99.9 ± 0.2 |
| 2500| 20 ± 15   | 99.9 ± 0.1 |

| Specific current / (mA g\textsuperscript{−1}) | Mg-DMC | Mg-DEC |
|-----------------------------------------------|--------|--------|
| SDC / mAh g\textsuperscript{−1} | SDC / mAh g\textsuperscript{−1} | CEff / % | CEff / % |
| 10  | 51 ± 9 | 51 ± 9 | 95 ± 3 | 58 ± 8 | 92 ± 3 |
| 20  | 51 ± 10 | 51 ± 10 | 97 ± 1 | 58 ± 9 | 96 ± 2 |
| 50  | 43 ± 4 | 43 ± 4 | 99.3 ± 0.2 | 54 ± 9 | 98.3 ± 0.8 |
| 100 | 38 ± 4 | 38 ± 4 | 99.8 ± 0.2 | 48 ± 8 | 99.4 ± 0.4 |
| 200 | 30 ± 5 | 30 ± 5 | 100.0 ± 0.1 | 42 ± 8 | 99.8 ± 0.2 |
| 300 | 22 ± 5 | 22 ± 5 | 100.1 ± 0.2 | 36 ± 10 | 99.9 ± 0.1 |
| 500 | 11 ± 3 | 11 ± 3 | 100.8 ± 0.7 | 24 ± 10 | 100.0 ± 0.1 |
| 1000| 1.0 ± 0.6 | 1.0 ± 0.6 | 103.7 ± 0.3 | 5 ± 4 | 100.8 ± 0.6 |
Table S8. Calculated ratios of the area of the bands of ‘free’ TFSI\(^-\) (743 ± 1 cm\(^{-1}\)) \(A_{\text{uncoord}}\), the coordinated TFSI\(^-\) at 746 ± 1 cm\(^{-1}\) \(A_{\text{coord1}}\) and at 752 ± 1 cm\(^{-1}\) \(A_{\text{coord2}}\) of the total obtained area calculated using a pseudo Voigt function.

|                | \(A_{\text{uncoord}} / A_{\text{total}}\) | \(A_{\text{coord1}} / A_{\text{total}}\) | \(A_{\text{coord2}} / A_{\text{total}}\) |
|----------------|------------------------------------------|------------------------------------------|------------------------------------------|
| Mg-Pyr         | 69 ± 1                                   | 8 ± 1                                    | 24 ± 1                                   |
| Mg-Pyr+ES      | 71 ± 1                                   | 10 ± 1                                   | 19 ± 1                                   |
| Mg-Pyr+10ES    | 69 ± 6                                   | 17 ± 5                                   | 15 ± 1                                   |
| Mg-Pyr+EC      | 69 ± 1                                   | 13 ± 1                                   | 18 ± 1                                   |

Table S9. Specific discharge capacities (SDC) and Coulombic efficiencies (C\(\text{Eff}\)) of selected cycles of graphite \(\parallel\) AC cells (three-electrode configuration; QRE: Li metal) with Mg-Pyr at 100 mA g\(^{-1}\) using pre-cycled graphite and pristine or pre-cycled AC (three pre-cycles in graphite \(\parallel\) AC cells with Mg-Pyr+ES at 10 mA g\(^{-1}\)) with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li\(^+\). The first cycle corresponds to the first cycle after pre-cycling.

|                | Pristine AC | Pre-cycled AC |
|----------------|-------------|---------------|
|                | SDC / mAh g\(^{-1}\) | C\(\text{Eff}\) / % | SDC / mAh g\(^{-1}\) | C\(\text{Eff}\) / % |
| 1\text{st} cycle | 42.0 ± 0.2  | 96.07 ± 0.02 | 46 ± 3 | 97 ± 2 |
| 50\text{th} cycle | 40 ± 3     | 99.3 ± 0.2  | 52 ± 4 | 99.3 ± 0.3 |
| 300\text{th} cycle | 38 ± 3     | 99.7 ± 0.1  | 49 ± 3 | 99.6 ± 0.3 |

Table S10. \(d_{\text{00n}+2}/d_{\text{00n}+1}\) ratio and dominant stage of graphite electrodes after three full cycles between 5.0 V and 3.4 V vs. Li|Li\(^+\) at 10 mA g\(^{-1}\) cycled in graphite \(\parallel\) AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with Mg-Pyr and Mg-Pyr+ES and one charging step to 5.0 V vs. Li|Li\(^+\) at 10 mA g\(^{-1}\), respectively 5.3 V vs. Li|Li\(^+\) at 100 mA g\(^{-1}\).* 

|                | Mg-Pyr     | Mg-Pyr+ES  |
|----------------|------------|------------|
|                | 5.0 V vs. Li|Li\(^+\) | 5.3 V vs. Li|Li\(^+\) | 5.0 V vs. Li|Li\(^+\) | 5.3 V vs. Li|Li\(^+\) |
| \(d_{\text{00n}+2}/d_{\text{00n}+1}\) | 1.29       | 1.50       | 1.33       | 1.51       |
| Dominant stage (\(n\)) | 2, 3       | 1          | 2          | 1          |

*Graphite \(\parallel\) AC cells cycled with 10 mA g\(^{-1}\) did not reach the cut-off potential of 5.3 V vs Li|Li\(^+\) within 10 h, similar to the cells cycled at 60 °C, likely resulting from side reactions, why a current of 100 mA g\(^{-1}\) was used for high cut-off potentials.

Table S11. TFSI\(^-\) intercalation onset potentials in V vs. Li|Li\(^+\) of graphite \(\parallel\) AC cells (three-electrode configuration; QRE: Li metal) with selected electrolytes at selected specific currents with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li\(^+\).

| Specific current / mA g\(^{-1}\) | Mg-Pyr     | Mg-Pyr+ES  |
|----------------------------------|------------|------------|
| 100                              | 4.46 ± 0.02| 4.45 ± 0.01|
| 1000                             | 4.61 ± 0.02| 4.60 ± 0.04|
| 2500                             | 4.83 ± 0.07| 4.79 ± 0.07|
Table S12. Calculated ratios of the area of the bands of ‘free’ TFSI\(^-\) (743 ± 1 cm\(^{-1}\)) \(A_{\text{uncoord}}\), the coordinated TFSI\(^-\) at 746 ± 1 cm\(^{-1}\) \(A_{\text{coord1}}\) and at 752 ± 1 cm\(^{-1}\) \(A_{\text{coord2}}\) of the total obtained area calculated using a pseudo Voigt function.

|          | \(\frac{A_{\text{uncoord}}}{A_{\text{total}}} / \%\) | \(\frac{A_{\text{coord1}}}{A_{\text{total}}} / \%\) | \(\frac{A_{\text{coord2}}}{A_{\text{total}}} / \%\) |
|----------|-----------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|
| Mg-DMC   | 32 ± 2                                               | 36 ± 2                                               | 32 ± 1                                               |
| Mg-DEC   | 39 ± 10                                              | 24 ± 9                                               | 37 ± 2                                               |

Table S13. Raman bands of selected electrodes and references between 830 and 960 cm\(^{-1}\), associated with the C-O stretching mode of carbonates.

|          | DMC                    | Mg-DMC                   | Association               |
|----------|------------------------|--------------------------|---------------------------|
|          | 861 cm\(^{-1}\) (w)    | 862 cm\(^{-1}\) (w)      | Free DMC (ct)             |
|          | 882 cm\(^{-1}\)        | 917 cm\(^{-1}\)          | Coordinated DMC (ct)      |
|          | 917 cm\(^{-1}\)        | Free DMC (cc)            |                           |
|          | 945 cm\(^{-1}\)        | Coordinated DMC (cc)     |                           |

|          | DEC                    | Mg-DEC                   | Association               |
|----------|------------------------|--------------------------|---------------------------|
|          | 854 cm\(^{-1}\) (w)    |                          | Free DEC (ct)             |
|          | 857 cm\(^{-1}\)        | 903 cm\(^{-1}\)          | Coordinated DEC (ct)      |
|          | 913 cm\(^{-1}\)        | 903 cm\(^{-1}\)          | Free DEC (cc)             |
|          | 913 cm\(^{-1}\)        | Coordinated DEC (cc)     |                           |

Table S14. \(\frac{d_{(00n+2)}}{d_{(00n+1)}}\) ratio and dominant stage of graphite electrodes after three cycles between 5.0 V and 3.4 V vs. Li|Li\(^+\) at 10 mA g\(^{-1}\) cycled in graphite II AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with Mg-DMC and Mg-DEC and one charging step to 5.0 V vs. Li|Li\(^+\) at 10 mA g\(^{-1}\).

|          | Mg-DMC | Mg-DEC |
|----------|--------|--------|
| \(\frac{d_{(00n+2)}}{d_{(00n+1)}}\) | 1.35   | 1.33   |
| Dominant stage \((n)\) | 2      | 2      |
Figure S1. a) Coulombic efficiency and specific discharge capacity of graphite || AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ (red) and 1 M LiTFSI (black) in Pyr$_{14}$TFSI at 100 mA g$^{-1}$ with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$. The corresponding differential capacity vs. potential plots of b) the 1$^{\text{st}}$ and 50$^{\text{th}}$ cycle.

Figure S2. Cyclic voltammograms of Pt || AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with 0.05 M Fc in 0.5 M Mg(TFSI)$_2$ (red) and a) 1 M LiTFSI (black), respectively b) 0.5 M Mg(TFSI)$_2$ + 2 wt.% ES in Pyr$_{14}$TFSI at 5 mV s$^{-1}$ with cut-off potentials of 2.8 and 4.0 V, respectively 2.5 and 4.5 V (Mg-Pyr+ES) vs. Li|Li$^+$. 
Figure S3. a) Coulombic efficiency and specific discharge capacity of graphite || AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with 0.5 M Mg(TFSI)₂ in Pyr14TFSI at 100 mA g⁻¹ with cut-off potential of 3.4 V and 5.0 V vs. Li|Li⁺ with 1 pre-cycle at 10 mA g⁻¹ (red) or 100 mA g⁻¹ (blue). b) The corresponding differential capacity vs. potential plots of the 1st cycle.
Figure S4. Ex situ XRD patterns of graphite composite electrodes at selected potentials (vs. Li[Li⁺]) in graphite ‖ AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with a) 0.5 M Mg(TFSI)$_2$ and b) 1 M LiTFSI in Pyr$_{14}$TFSI after three cycles at 10 mA g$^{-1}$ with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li[Li⁺]. c) The corresponding typical differential capacity vs. potential plots (4th cycle at 10 mA g$^{-1}$). For an easier comparison, the potential of the Mg-ion-based cell (red, upper x-axis) is shifted 0.1 V compared to the Li-ion-based cell (black, lower x-axis), according to variations in the potential of the Li metal QRE. The first XRD pattern (3.4 V, bottom) was recorded after the three pre-cycles.
Figure S5. Normalized ex situ Raman spectra of a pristine graphite composite electrode (90% graphite) using a laser intensity of 1% (acquisition time: 5 x 30 s, red) and 10% (acquisition time: 60 x 5 s, black).

Figure S6. Cyclic voltammograms of the 1st and 2nd cycle of modified graphite || AC pouch-type cells (three-electrode configuration; RE/QRE: Li metal, scan speed: 0.5 mV s⁻¹, cut-off potentials of 3.4 to 4.9 V (Li-ion-based), respectively 5.0 V vs. Li|Li⁺ (Mg-ion-based)) of in situ Raman measurements (Figure 3) with a) Li-Pyr and b) Mg-Pyr.
Figure S7. SEM images at a magnification of 25k of a pristine graphite electrode as well as washed electrodes after 100 cycles at 100 mA g⁻¹ (1 pre-cycle: at 10 mA g⁻¹) with cut-off potentials of 3.4 V and 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based) vs. Li|Li⁺ in graphite ll AC Swagelok-type cells (three-electrode configuration; RE/QRE: Li metal) with different electrolytes in the discharged (final potential of 3.4 V vs. Li|Li⁺) and charged (an additional charging step to 4.9 V (Li-ion-based) respectively 5.0 V (Mg-ion-based)) state, and the corresponding ex situ Raman spectra between 1200 and 1700 cm⁻¹ at a laser intensity of 10% (acquisition time: 60 x 5 s) of the non-washed electrodes (discharged: solid line; charged: dashed line).
Figure S8. a) Differential capacity vs. potential plots of graphite || AC Swagelok-type cell (three-electrode configuration; QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI at 100 mA g$^{-1}$ with various upper cut-off potentials (1 pre-cycle: 10 mA g$^{-1}$; 3.4 to 5.0 V vs. Li|Li$^+$). b) The differential capacity vs. potential plots of the 50th and 300th cycle and c) Coulombic efficiency and specific discharge capacity of graphite || AC Swagelok-type cell with 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI at 100 mA g$^{-1}$ with cut-off potential of 3.4 V and 5.0 V (red) respectively 5.3 V (brown) vs. Li|Li$^+$ (1 precycle: 10 mA g$^{-1}$; 3.4 to 5.0 V vs. Li|Li$^+$).
Figure S9. a) Coulombic efficiency and specific discharge capacity of graphite || AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ in Pyr$_14$TFSI at 20 °C (red) and 60 °C (pink) at 100 mA g$^{-1}$ (1st cycle: 10 mA g$^{-1}$) with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$. b) The corresponding differential capacity vs. potential plots of the 1st and 50th cycles. The Coulombic efficiency of the first cycle (Mg-Pyr: 74 ± 1%) is not shown.

At 60 °C, strong parasitic side reactions could be observed at 10 mA g$^{-1}$ in the first cycle below 5.0 V vs. Li|Li$^+$, why the cut-off potential of 5.0 V vs. Li|Li$^+$ was not reached, before the time determination (10 hours, 100 mAh g$^{-1}$) was reached.
**Figure S10.** Raman spectra of 0.5 M Mg(TFSI)$_2$ (red) and 0.5 M Mg(TFSI)$_2$ + 2 wt.% ES (blue) between 720 and 780 cm$^{-1}$ respectively 800 cm$^{-1}$ a) including the fitted (pseudo Voigt) spectra and with b) pure ES (brown), 0.5 M Mg(TFSI)$_2$ in ES (pink), Pyr$_{14}$TFSI (grey) and 0.5 M Mg(TFSI)$_2$ + approximately 10 wt.% ES (bright blue) as references. The fitted spectra were normalized according to the maximal intensity of the band at $\approx 742$ cm$^{-1}$ of the experimental spectra.

**Figure S11.** Raman spectra of 0.5 M Mg(TFSI)$_2$ (red) and 0.5 M Mg(TFSI)$_2$ + 2 wt.% ES (blue) and 0.5 M Mg(TFSI)$_2$ + 2 wt.% EC (grey) between 720 and 800 cm$^{-1}$. 
Figure S12. Cyclic voltammograms of the 1st and 2nd cycle of modified graphite \( \parallel \) AC pouch-type cells (three-electrode configuration; RE/QRE: Li metal, scan speed: 0.5 mV s\(^{-1}\), cut-off potentials of 3.4 to 5.0 V vs. Li|Li\(^+\)) of in situ Raman measurements (Figure 6) with Mg-Pyr+ES.
Figure S13. a) and b) Coulombic efficiency and specific discharge capacity (including a magnification of the first 20 cycles) of graphite || AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ in Pyr14TFSI (red), 0.5 M Mg(TFSI)$_2$ in Pyr14TFSI + 2 wt.% ES (blue) at 100 mA g$^{-1}$ (1 pre-cycle at 10 mA g$^{-1}$) and 0.5 M Mg(TFSI)$_2$ in Pyr14TFSI with pre-cycled graphite and a) pristine AC (grey) or b) pre-cycled AC (black) at 100 mA g$^{-1}$ (3 pre-cycles with Mg-Pyr+ES at 10 mA g$^{-1}$) with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$. c) The corresponding differential capacity vs. potential plots of the 50th cycle (Mg-Pyr and Mg-Pyr+ES) and the 3rd pre-cycle with Mg-Pyr+ES (cyan) and first and 50th subsequent cycle with Mg-Pyr using pristine AC (grey) and precycled AC (black).
Figure S14. a) Differential capacity vs. potential plots of graphite || AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI (red) and 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI + 2 wt.% ES (blue) at 100 mA g$^{-1}$ with cut-off potentials of 3.4 V and 5.3 V vs. Li|Li$^+$. b) XRD patterns of graphite electrodes charged in 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI (red) and 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI + 2 wt.% ES (blue) at 100 mA g$^{-1}$ to 5.3 V vs. Li|Li$^+$ (upper part) and 10 mA g$^{-1}$ to 5.0 V vs. Li|Li$^+$ (lower part).

Figure S15. Differential capacity vs. potential plots of graphite || AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI (upper part) and 0.5 M Mg(TFSI)$_2$ in Pyr$_{14}$TFSI + 2 wt.% ES (lower part) at 10 mA g$^{-1}$ (grey) 100 mA g$^{-1}$ (red), 1000 mA g$^{-1}$ (blue), and 2500 mA g$^{-1}$ (black) with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$. 
**Figure S16.** Potential vs. specific capacity of the first cycle of graphite // AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with Mg(TFSI)$_2$ in a) DMC and b) DEC with various concentrations at 10 mA g$^{-1}$ with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$.  

**Figure S17.** Raman spectra of 2.5 M Mg(TFSI)$_2$ in DMC (purple) and 2 M Mg(TFSI)$_2$ in DEC (cyan) between 720 and 780 cm$^{-1}$ including the fitted (pseudo Voigt) spectra. The fitted spectra were normalized according to the maximal intensity of the band at ~743 cm$^{-1}$ of the experimental spectra.
Figure S18. Cyclic voltammogram of the 1st and 2nd cycle of modified graphite II AC pouch-type cells (three-electrode configuration; RE/QRE: Li metal scan speed: 0.5 mV s$^{-1}$, cut-off potentials of 3.4 to 5.0 V vs. Li|Li$^+$) of in situ Raman measurements (Figure 11) with Mg-DEC.

Figure S19. Differential capacity vs. potential plots of graphite II AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 2.5 M Mg(TFSI)$_2$ in DMC (purple) and 2 M Mg(TFSI)$_2$ in DEC (cyan) at 100 mA g$^{-1}$ with cut-off potentials of 3.4 V and 5.3 V vs. Li|Li$^+$. 
Figure S20. Differential capacity vs. potential plots of graphite‖AC Swagelok-type cells (three-electrode configuration; QRE: Li metal) with 2.5 M Mg(TFSI)$_2$ in DMC (upper part) and 2 M Mg(TFSI)$_2$ in DEC (lower part) at 10 mA g$^{-1}$ (red) 100 mA g$^{-1}$ (blue) and 500 mA g$^{-1}$ (black) with cut-off potentials of 3.4 V and 5.0 V vs. Li|Li$^+$.

Figure S21. Schematic illustration of the in situ pouch cell design. A: Graphite composite electrode with an Al mesh current collector casted on a glass window. B: GF/A separator soaked with electrolyte. C: Li metal reference electrode on carbon-coated copper mesh. D: AC reference electrode with an Al mesh current collector.