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### Electrochemistry

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# **Two-Plateau Li-Se Chemistry for High Volumetric Capacity Se Cathodes**

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Abstract: For Li-Se batteries, ether- and carbonate-based electrolytes are commonly used. However, because of the "shuttle effect" of the highly dissoluble long-chain lithium polyselenides (LPSes,  $Li_2Se_m$ ,  $4 \le n \le 8$ ) in the ether electrolytes and the sluggish one-step solid-solid conversion between Se and Li<sub>2</sub>Se in the carbonate electrolytes, a large amount of porous carbon (>40 wt % in the electrode) is always needed for the Se cathodes, which seriously counteracts the advantage of Se electrodes in terms of volumetric capacity. Herein an acetonitrile-based electrolyte is introduced for the Li-Se system, and a two-plateau conversion mechanism is proposed. This new Li-Se chemistry not only avoids the shuttle effect but also facilitates the conversion between Se and Li<sub>2</sub>Se, enabling an efficient Se cathode with high Se utilization (97%) and enhanced Coulombic efficiency. Moreover, with such a designed electrolyte, a highly compact Se electrode (2.35  $g_{Se} cm^{-3}$ ) with a record-breaking Se content (80 wt%) and high Se loading  $(8 \text{ mg cm}^{-2})$  is demonstrated to have a superhigh volumetric energy density of up to 2502 Wh  $L^{-1}$ , surpassing that of  $LiCoO_2$ .

#### Introduction

As a congener of sulfur (S), selenium (Se) is chemically and electrochemically analogous to S. When used in rechargeable lithium batteries, Se can be electrochemically lithiated/ delithiated reversibly. Based on the conversion reaction between Li and Se ( $2Li + Se \leftrightarrow Li_2Se$ ), the theoretical gravimetric capacity of Se is 675 mAh g<sup>-1</sup>, lower than that of S (1672 mAh g<sup>-1</sup>). While considering its high density, Se could deliver a comparable volumetric capacity (3253 mAh cm<sup>-3</sup>) to

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that of S (3467 mAhcm<sup>-3</sup>).<sup>[1]</sup> Additionally, Se has a higher electrical conductivity and better compatibility than S with commercial carbonate electrolytes.<sup>[2]</sup> All these features make Li-Se batteries attractive for energy-storage applications requiring both high power and high volumetric energy densities.

As the "blood" of the batteries, electrolytes directly affect their reaction pathways and electrochemical behaviors. For Li-Se batteries, ether- and carbonate-based electrolytes are most investigated. In ether electrolytes, Se undergoes a similar lithiation/delithiation process to that of S, exhibiting a solidliquid-solid conversion mechanism, during which Se is first reduced to dissoluble long-chain lithium polyselenides (LPSes), and finally to Li<sub>2</sub>Se.<sup>[3]</sup> Because of the high solubility of the LPSe intermediates in ether, Li-Se batteries face a similar "shuttle" problem to that of Li-S batteries, which leads to the continuous corrosion of the Li anode and irreversible loss of the active materials. While in carbonate electrolytes, Se is reduced into Li<sub>2</sub>Se directly without the formation of LPSes.<sup>[2b,4]</sup> Although such a single-step solidsolid reaction could avoid the shuttling of the long-chain LPSes, low utilization of active materials and poor rates are always observed for Se cathodes because of the high reaction barrier of the one-step solid reaction.<sup>[5]</sup>

In light of the successful strategies for high-performance S cathodes, many researchers tried to encapsulate nanosized Se into porous conductive matrices to either suppress the shuttle of LPSes in ether electrolytes or facilitate the conversion between Se and Li<sub>2</sub>Se in carbonate electrolytes.<sup>[1,6]</sup> Following this direction, various Se cathodes based on Se-impregnated porous carbon have been developed, and excellent electrochemical performance has been achieved by many groups.<sup>[7]</sup> However, the electrochemical behaviors of such Se@C compositions greatly depend on the properties (such as specific surface area, pore size, etc.) of the carbon hosts, and the reported high Se utilization and/or long cycle lives were obtained for the electrodes with low Se content (< 60 wt %) and/or low Se loading ( $< 2.0 \text{ mg cm}^{-2}$ ). The excessive use of the inactive carbon greatly counteracts the advantage of Se electrodes in volumetric capacity and makes Li-Se batteries noncompetitive. In contrast, cathodes with high Se loading, as fabricated by Dutta et al. with 5 to  $10 \text{ mg}_{\text{Se}} \text{ cm}^{-2}$ , experience a fast capacity decay in the initial 10 cycles.<sup>[8]</sup>

Different from the strategies encapsulating Se into porous carbon with higher specific area, higher pore volume, or better chemisorption capability for LPSes, we report a new solution to increase the Se content of Se electrodes by redirecting the conversion pathway between Se and  $Li_2Se$  with an acetonitrile (AN) based electrolyte. Dilute AN solution has poor reductive stability against graphite (or Li metal). As pioneered by Yamada et al., the increase in salt concentration could enhance the reductive stability of an AN solution and enable faster reaction kinetics than the commercial carbonate electrolytes for the lithium intercalation (into graphite) reaction.<sup>[9]</sup> The group of Nazar investigated the nonsolvating and sparingly solvating AN electrolytes for the Li-S system, and demonstrated a high sulfur utilization.<sup>[10]</sup> The use of AN-based electrolytes in Li-S batteries is still not popular, possibly because of the unsatisfactory conversion kinetics at room temperature.

Herein, we found Li-Se batteries display different electrochemical behaviors in AN-based electrolytes compared to those in either ether or carbonate electrolytes. During the discharge (charge) process, LPSes are formed without dissolving into the electrolyte, which not only eliminates the shuttle of LPSes in ether electrolytes but also demonstrates better conversion kinetics than that in carbonate electrolytes. Benefiting from this new conversion mechanism, the Se utilization, Coulombic efficiency, and cycling stability of Se cathodes are significantly improved compared to those in either ether or carbonate electrolytes. A highly reversible capacity of 545.2 mAhg<sup>-1</sup>, corresponding to a Se unitization of 80.8% was demonstrated by a highly compact Se electrode with a record-breaking Se content (80 wt%) and a high Se loading (8.0 mg cm<sup>-2</sup>), leading to a highly efficient Se cathode with volumetric energy density (2502 Wh L<sup>-1</sup>) surpassing that of LiCoO<sub>2</sub> ( $\approx 2100 \text{ Wh L}^{-1}$ ).

#### **Results and Discussion**

With high oxidative stability and high ionic conductivity, AN-based electrolytes have been widely used in electrochemical devices.<sup>[9,10b,11]</sup> Here, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) was chosen as the salt because of its high solubility in AN. In an  $(AN)_x$ -LiTFSI mixture, the salt concentration greatly affects the Li salt–solvent coordination.<sup>[12]</sup> When the molar ratio of AN to LiTFSI decreases to 2, all the free AN molecules are fully eliminated in the solution (see Figure S1 in the Supporting Information), leading to the significantly improved reductive stability against Li metal (see Figure S2).

The reduction of free AN molecules in solution significantly eliminates the solubility of the long-chain LPSes. Saturated Li<sub>2</sub>Se<sub>6</sub>/AN and Li<sub>2</sub>Se<sub>6</sub>/(AN)<sub>x</sub>-LiTFSI (x = 10, 5, 3, and 2) solutions were prepared to evaluate the solubility. In the inset of Figure 1, the saturated Li<sub>2</sub>Se<sub>6</sub>/AN solution shows a dark brown color, demonstrating the high solubility of Li<sub>2</sub>Se<sub>6</sub> in AN. Upon adding LiTFSI, the color of the solution turns to light brown and finally to colorless, implying the absence of soluble Li<sub>2</sub>Se<sub>6</sub> in the salt-concentrated solutions (x = 3 and 2). The solubility of Li<sub>2</sub>Se<sub>6</sub> in the solutions with different AN-to-LiTFSI ratios was quantified by an ultraviolet (UV) spectrophotometer based on the UV absorption intensity at 420 nm (see Figures S3 and S4; see the experimental section for details). It confirms that the solubility of Li<sub>2</sub>Se<sub>6</sub> is significantly reduced from 47.2 mgmL<sup>-1</sup> in the AN



**Figure 1.** The visual discrimination of the  $Li_2Se_6$ -saturated  $(AN)_x$ -LiTFSI solutions and the variation of the solubility of  $Li_2Se_6$  versus 1/x. Here, x refers to the molar ratio of AN to LiTFSI.

solvent to less than  $2 \ \mu g m L^{-1}$  in  $(AN)_2$ -LiTFSI (Figure 1), which is in agreement with the simulation results based on the density-functional theory calculation (see Figure S5). In addition, the salt-concentration strategy improves the oxidative stability of AN solutions (see Figure S6).

Similar to Li-S batteries, the dissolution of the long-chain LPSes in the electrolyte is the origin of the shuttle, which leads to the continual loss of the active materials during cycling. In this context, besides the requests for conventional electrolytes for Li metal batteries, an ideal electrolyte for Li-Se batteries should also avoid the dissolution of LPSes. Based on the results of the reductive stability and solubility, the (AN)<sub>2</sub>-LiTFSI solution with high reductive stability and a negligible LPSes solubility was selected for Li-Se batteries. The highly concentrated (AN)<sub>2</sub>-LiTFSI solution was further diluted with 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (HFE) to reduce the viscosity and facilitate the reaction kinetics.<sup>[13]</sup> Because of the elimination of the free AN and nonflammable nature of the highly fluorinated HFE,<sup>[14]</sup> the as-designed (AN)<sub>2</sub>-LiTFSI-HFE electrolyte (denoted as the AN electrolyte) displays higher flammability resistance and is safer than the commercial carbonate and ether electrolytes (see Videos S1–S6 and Figure S7).

The AN electrolyte was tested in CR2025 coin cells with a Li anode and a Se cathode separated by a Celgard-2000 separator. To reveal the superiority of the AN electrolyte, we chose commercial Ketjenblack (KB) instead of the specially designed porous carbon used in most Li-Se batteries as the conductive matrix for Se (see the experimental section for the details of the cathode preparations). The use of such low-cost and commercially available carbon guarantees the practical validity of Li-Se batteries. The Se content in the Se@KB composites were determined by thermogravimetric analysis (see Figure S8).

The Li-Se cells with Se@KB cathodes were first discharged/charged at C/5 in AN, ether, and carbonate electrolytes. Figure S9a depicts the typical discharge-charge profile for the Li-Se cells with the ether electrolyte. Two distinct discharge plateaus at 2.13 and 2.04 V correspond to the reduction of Se to long-chain LPSes and then to  $Li_2Se.^{[3]}$ 





*Figure 2.* a) The typical discharge-charge profile of Li-Se cells with the AN electrolyte at C/5 ( $1 C = 675 \text{ mAg}^{-1}$ ), with enlarged discharge profile in the range of 1.94 to 2.06 V. b) The CV curve of Li-Se cells with the AN electrolyte at a scan rate of 0.1 mVs<sup>-1</sup>, with enlarged reduction peaks in the range of 1.8 to 2.0 V. c,d) The ex situ colorimetric experiments for the Se cathodes at different lithiated/delithiated extents discharged/charged in the AN electrolyte (d). e) The in situ XRD characterization (2 $\theta$ : 20–35°) of the Se cathode in the AN electrolyte.

However, the cell with the carbonate electrolyte shows only one discharge plateau related to the direct reduction of Se into Li<sub>2</sub>Se with a high initial irreversible capacity loss of about  $300 \text{ mAh g}^{-1}$  (see Figure S10a), which might be caused by the irreversible reaction between the porous carbon or LPSes and the electrolyte.<sup>[1,7a,15]</sup> In sharp contrast, the discharge-charge profile for the Li-Se cell with the AN electrolyte displays two closely adjacent discharge plateaus at around 2.01 and 1.98 V (Figure 2a), which are apparently different from those obtained in either the conventional ether or carbonate electrolytes. The reversible capacity of the cell using the AN electrolyte is  $655 \text{ mAh g}^{-1}$ , corresponding to a high Se utilization of 97%, which is higher than most, if not all, of the reported values obtained in ether or carbonate electrolytes. The cell with the AN electrolyte exhibits a low polarization with a voltage gap of 0.22 V, lower than that of carbonate electrolyte (0.32 V), implying facile kinetics of Li-Se batteries in the AN electrolyte. Here, it should be mentioned that Li-S batteries show a much higher polarization (0.69 V) than Li-Se batteries in the AN electrolyte when being tested under a same conditions (see Figure S11). In addition, the cell with the AN electrolyte demonstrates an initial high Coulombic efficiency (defined as  $Q_{delithiation}$ /  $Q_{\text{lithiation}}$ ) without obvious LPSe shuttling or irreversible capacity loss. All the above features make the as-proposed AN electrolyte an ideal candidate for the applications in Li-Se batteries.

The electrochemical kinetic process of Li-Se batteries was further studied with cyclic voltammetry (CV) at a scanning speed of  $0.1 \text{ mV s}^{-1}$ . The CV profile for Li-Se batteries with the AN electrolyte (Figure 2b) shows two sharp reduction peaks located at 1.95 and 1.90 V in the cathodic scan, which is consistent with the galvanostatic discharge-charge profiles. Based on the discharge-charge and CV results, it is clear that the AN electrolyte has redirected the Li-Se reaction pathway, leading to a new two-step conversion between Se and Li<sub>2</sub>Se.

To understand the new conversion mechanism of Se cathodes in the AN electrolyte, ex situ colorimetric experiments and in situ XRD characterization were performed. For the ex situ colorimetric experiments, we firstly discharged/ charged the Se cathodes to different extents in the AN electrolyte, and soaked the lithiated/delithiated cathodes in dimethoxyethane (DME) and the AN electrolyte. As shown in Figure 2 c, for the cathode-soaked DME solutions, the color turned to dark brown for the Se cathode with a discharge capacity of 100 mAhg<sup>-1</sup> because of the formation of long-chain LPSes, which were identified by ex situ UV absorption (see Figure S12) and Raman spectra (see Figure S13). With the discharge process continuing, the color of the solutions faded gradually, which could be explained by as-formed long-

chain LPSes undergoing further reduction to DME-insoluble products. At the end of the discharging, the color of the cathode-soaked DME solution was almost colorless, implying full reduction of the soluble LPSes. In the charging process, the light brown color of the cathode-soaked DME solutions did not change too much until being charged to  $400 \text{ mAh g}^{-1}$ , corresponding to the beginning of the formation of long-chain LPSes. The color of the DME solution turned colorless at the end of the charging, demonstrating the superb reversibility of the Li-Se chemistry in the AN electrolyte. In contrast, as shown in Figure 2d, the cathode-soaked AN electrolyte remained colorless during the entire discharge-charge process, confirming the absence of the dissolved LPSes in the AN-electrolyte-based Li-Se batteries. The absence of the dissolved LPSes in the AN electrolyte was also confirmed by the energy dispersive X-ray analysis (EDX) characterization on the surface of cycled Li anodes. As the EDX results show in Figure S14, no signal belonging to Se was detected on the cycled Li anode with the AN electrolyte (see Figure S14c), indicating shuttle-free Li-Se chemistry in the AN electrolyte. Based on the results of the ex situ colorimetric experiments, we can confirm the formation of undissolved long-chain LPSes during the discharge-charge process for the Li-Se cells with the AN electrolyte, which is a hybrid process of what occurs in the ether and carbonate electrolytes.

The in situ XRD characterization was further performed to investigate the phase-conversion process of the Se cathode in the AN electrolyte. As shown in Figure 2e, at the beginning of the discharge process, only diffraction peaks belonging to Se were detected, and might result from the fact that the discharge products in this range are mainly amorphous longchain LPSes. And then a new diffraction signal for  $Li_2Se$  (2 $\theta$  = 26°) formed at the end of the first discharge plateau and grew stronger with the discharge process, indicating the gradual conversion from the solid long-chain LPSes into Li<sub>2</sub>Se. In the charging process, the diffraction patterns present a reverse process with the Li<sub>2</sub>Se peak gradually weakening to a negligible intensity at the fully charged state. Combining the results of the electrochemical tests (Figure 2a and b), ex situ colorimetric experiments (Figure 2c and d), in situ XRD characterization (Figure 2e), ex situ UV absorption (see Figure S12), and ex situ Raman spectra (see Figure S13), the electrochemical conversion between Se and Li2Se could be described as a two-step solid reaction. In step I (corresponding to the first discharge plateau), the possible reaction is given as

Se (solid) + Li 
$$\rightarrow$$
 Li<sub>2</sub>Se<sub>n</sub> (solid, 2  $\leq$  n  $\leq$  8) (1)

In the following step II (corresponding to the second discharge plateau), the reaction is assigned to the following reaction

$$Li_2Se_n (solid) + Li \rightarrow Li_2Se (solid)$$
 (2)

As discussed above, the electrolytes directly affect the reaction pathways for the Li-Se chemistry. In ether electrolytes, Se is reduced first to dissolved long-chain LPSes and then gradually to Li<sub>2</sub>Se. Such a solid-liquid-solid conversion

mechanism leads to the shuttle problem and thus continuous corrosion of Li anode and irreversible loss of active materials. Whereas in carbonate electrolytes, Se is reduced to Li<sub>2</sub>Se directly without the formation of intermediates by a one-step solid reaction. Herein, the new two-step solid-solid reaction pathway observed in the AN electrolyte has the following advantages: 1) the formation of LPSe intermediates leads to a lower Li-Se reaction barrier than that of the one-step solid reaction in carbonate electrolyte, facilitating the conversion between Se and Li<sub>2</sub>Se; 2) the absence of the dissolved LPSes completely eliminates the shuttle effect generally observed in the ether electrolyte, and thus guarantees the long-term cycling stability. A similar two-step solid-solid conversion mechanism has not been reported previously for the Li-Se system. This new reaction pathway may revolutionize Li-Se chemistry and enable Li-Se batteries with superior electrochemical performances.

The superiority of the AN electrolyte in Li-Se batteries was investigated by electrochemical impedance spectroscopy (EIS) over a frequency range from 100 kHz to 10 mHz. Figure 3a shows the Nyquist plots of the as-assembled Li-Se cells with different electrolytes. All the spectra display an intercept at high frequency, a semicircle at medium frequency, and a straight line in the low-frequency region. Benefiting from the high dielectric constant of AN, the cell with the AN electrolyte shows the smallest semicircle, suggesting that the cell with the AN electrolyte possesses the lowest charge transfer resistance compared to those for the ether and carbonate electrolytes. The low resistance ensures the high utilization of Se during the electrochemical process. Figure 3 b shows the galvanostatic discharge/charge behaviors of the Li-Se cell with the Se cathode containing a Se content of 64 wt % (80 wt % Se in Se@KB) and a Se loading of  $2.0 \text{ mg cm}^{-2}$ measured at different C rates. With the AN electrolyte, the cell presents long and flat plateaus in a voltage range from 3.5 to 1.0 V vs. Li<sup>+</sup>/Li, and the reversible capacities are 620, 631, 598, 565, and 532 mAh  $g^{-1}$ , respectively, at 0.1, 0.2, 0.3, 0.5, and 1 C. Even at a high rate of 2 C, a high discharge capacity of  $476 \text{ mAhg}^{-1}$  is still obtained, corresponding to 70.5% of the theoretical value. In contrast, the cell with the carbonate electrolyte delivers much lower capacities (Figure 3c) though the same Se cathode is used. The outstanding rate performance of the cells with the AN electrolyte could be attributed to the better electrochemical environment for the Li-Se redox in the as-proposed AN electrolyte.

The electrochemical process and kinetics of the Li-Se cells were further evaluated by CV tests at scan rates from 0.05 to  $0.5 \text{ mV s}^{-1}$ . For the Li-Se cells with the AN and carbonate electrolytes, all the CV curves show well-defined reduction/oxidation peaks at all scan rates (Figures 3d and e). Compared with the cell of carbonate electrolyte, the cell of the AN electrolyte displays sharper peaks with higher peak intensities, indicative of better conversion kinetics of the Li-Se chemistry. Furthermore, the AN electrolyte achieves much lower overpotentials than the carbonate electrolyte at all scan rates (Figure 3 f), showing the superior reversibility of the electrochemical process.

Figure 3 g compares the long-term cycling performance at C/5 among the cells with the ether, carbonate, and AN

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*Figure 3.* Electrochemical performance of the Li-Se cells: a) Nyquist plots of as-assembled Li-Se cells in the ether, carbonate, and AN electrolytes at open-circuit potential. b) Discharge/charge profiles at different C rates (0.1, 0.2, 0.3, 0.5, 1, and 2 C) in the AN electrolyte. c) Rate performance of the Li-Se cells in the carbonate and AN electrolytes. CV curves of the Li-Se cells in the AN (d) and carbonate (e) electrolytes at different scan rates (0.05, 0.1, 0.2, 0.3, and 0.5 mVs<sup>-1</sup>) and the corresponding overpotential comparison (f). g) Cycling performance of the Li-Se cells in the ether, carbonate, and AN electrolytes at C/5. Here, the voltage range for the electrochemical tests is 3.5 to 1.0 V vs. Li<sup>+</sup>/Li for the carbonate and AN electrolyte.

electrolytes. For the cell with the AN electrolyte, the discharge capacity is 646 mAh  $g^{-1}$  for the first cycle and then increases to  $655 \text{ mAh g}^{-1}$  for the fifth cycle, corresponding to a superhigh Se utilization of 97%. After 200 cycles, the discharge capacity is 554 mAhg<sup>-1</sup>, 86% of the initial value. In the carbonate electrolyte, the utilization of Se is only 66% and the capacity retention after 200 cycles is 47% compared to the stabilized capacity. In the ether electrolyte, although the Se utilization is as high as 94%, the capacity soon fades to less than 200 mAh  $g^{-1}$  after 20 cycles, which is ascribed to the severe shuttle effect of LPSes. It is also noticed that the Li-Se cell in the AN electrolyte demonstrates the highest reversibility with Coulombic efficiency of about 100%. For the ether electrolyte, the delithiation capacities are always higher than the lithiation ones, implying the continuous loss of the active materials during cycling. Moreover, the Li-Se cells also display stable discharge/charge curves with high reversible capacities and low polarizations under lean AN electrolyte conditions (see Figure S15).

The most attractive feature of Li-Se batteries is their high theoretical volumetric energy density. Disappointingly, most of the reported Li-Se batteries are based on Se@porous carbon-based cathodes with low areal Se loadings (usually  $< 2 \text{ mg cm}^{-2}$ ) and/or low Se content (usually < 60 wt %). With

such porous cathodes, it is impossible to realize a competitive volumetric energy density. Se has a much higher electrical conductivity ( $\approx 10^{-5} \,\mathrm{S \, cm^{-1}}$ ) than that of S ( $\approx 10^{-30} \,\mathrm{S \, cm^{-1}}$ ), but it faces similar challenges of high content and/or high loading. To understand the above predicament, we recalled the reaction mechanisms of Li-Se chemistry in conventional ether and carbonate electrolytes. In ether electrolytes, Se undergoes a solid-liquid-solid conversion with the formation of dissolved LPSes as intermediates, to avoid the loss of the LPSes resulting from the serious shuttle effect, high-content porous carbon is always needed for the Se cathodes, similar to S cathodes. While in carbonate electrolytes, where Se is reduced to Li<sub>2</sub>Se directly by a one-step solid conversion, the absence of the reaction intermediates leads to a high reaction barrier for the conversion between Se and Li<sub>2</sub>Se, and thus high-content conductive additives (e.g., carbons) are always added to the Se cathodes to promote the sluggish one-step solid reaction.

With the as-proposed AN electrolyte, since Se can be reduced to  $\text{Li}_2\text{Se}$  by a low-barrier two-step reaction without the shuttle effect, the utilization of high-density Se cathodes with low carbon content becomes possible. To verify this, we fabricated a high-mass-loading Se cathode (8.0 mg cm<sup>-2</sup>) with a record-breaking Se content of 80 wt% (89 wt% Se in

Se@KB) and a low carbon content of 15 wt %. The crosssection SEM image of the as-prepared Se cathode in Figure 4a clearly shows a porous structure. After being pressed under a pressure of 20 MPa, the thickness of the electrode was reduced from 82 to 34 µm (Figure 4b), and correspondingly, the density of Se in the cathodes increased from 0.98  $g_{Se}$  cm<sup>-3</sup> to 2.35  $g_{Se}$  cm<sup>-3</sup>. The electrochemical performance was evaluated by galvanostatic discharge/charge tests in the AN and carbonate electrolytes between 3.5 to 1.0 V, and in the ether electrolyte between 2.8 to 1.8 V. The highly pressed Se cathode demonstrates a high Se utilization of 79.7%  $(538.3 \text{ mAh g}^{-1})$  at the initial cycle in AN electrolyte. In the following cycles, the discharge capacity gradually increases from 433.6 to  $545.2 \text{ mAh g}^{-1}$  after 30 cycles (Figure 4c), corresponding to a volumetric energy density of 2502  $WhL^{-1}$ , higher than that of LiCoO<sub>2</sub> cathode ( $\approx 2100 \text{ Wh L}^{-1}$ ).<sup>[16]</sup> The increase in capacity over cycling could be attributed to the slow electrolyte infiltration in the dense electrode. A similar activation phenomenon was also observed in microporous electrodes.<sup>[17]</sup> Besides, the dense Se electrode also demonstrates high Coulombic efficiency of about 100% in the AN electrolyte during cycling, verifying the high reversibility of the Li-Se chemistry. In sharp contrast, although the dense Se electrode in carbonate electrolyte delivers a reasonable discharge capacity of  $419 \text{ mAh g}^{-1}$  at the initial cycle, the capacity fades quickly to 42 mAhg<sup>-1</sup> after only 15 cycles, accompanied by low Coulombic efficiency (80% to 95%). Whereas in the ether electrolyte, the cell delivers discharge capacities lower than  $60 \text{ mAh g}^{-1}$ . The outstanding electro-



**Figure 4.** Cross-section SEM images of the a) pristine and b) pressed Se cathodes with a high Se content (80 wt%) and a high Se loading (8.0 mg cm<sup>-2</sup>). c) The cycling performance of the pressed Se cathodes at 0.05 C in AN and carbonate electrolytes between 3.5 to 1.0 V and ether electrolyte between 2.8 to 1.8 V vs. Li<sup>+</sup>/Li. Here, the volumetric energy density refers to the volumetric energy density of pressed Se cathode calculated based on an average discharge voltage of 1.95 V and an average thickness of 34  $\mu$ m as determined by a micrometer screw gauge. The electrolyte to Se (E/Se) ratio used for the test is 5  $\mu$ L mg<sup>-1</sup>.

chemical performance of the dense cathodes with high loading and high Se content in the AN electrolyte can be ascribed to the shuttle-free and low-barrier reaction pathway facilitated by the AN electrolyte.

#### Conclusion

In summary, introducing the AN electrolyte into Li-Se batteries not only opens up a new low-barrier two-step solid reaction pathway for Li-Se chemistry, but also provides a new solution to achieving high energy density without specially designed Se electrodes. We believe that the as-proposed strategy may boost the development of the competitive Li-Se batteries for practical applications.

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#### Conflict of interest

The authors declare no conflict of interest.

**Stichwörter:** batteries · electrochemistry · lithium · reaction mechanisms · selenium

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