ithium-ion batteries are experiencing a huge surge in demand for electric vehicle and grid storage applications. To reduce the cost of batteries in these technologies there is a con tinual push to improve the energy density of the cells. Replacing the conventional graphite anode with lithium metal is one of the most popular approaches, as this can increase the cell energy den sity by 40–50% (refs?). However, this substantial increase in cell energy is achieved only if the excess thickness of the lithium anode is limited^{1,3}. Unfortunately, lithium-metal cells reported in the lit erature often use extremely thick anodes containing over 10 times the amount of lithium actually being cycled. This huge excess could never be used in a practical cell and makes interpretation of results more difficult, as cycling stability becomes artificially enhanced. As a result, researchers have called for limiting the lithium excess to less than 50m (ref. ⁴).

Limiting lithium excess is a challenge, as lithium metal is prone to form dendrites with high surface area, which reduce cycling effi ciency by increasing the reactivity of the anode with the electrolyte and forming isolated metallic lithium. The low cycling stability of lithium metal is especially apparent in the anode-free or zero-excess configuration, where cells are built with a bare copper anode and the lithium is plated directly from the cathode on the first charge cycle⁻¹². Since there is no excess lithium built into the cell, volume is minimized (Fig. 1a) and energy density is maximizebut per formance may be very poor since there is no reservoir of fresh lith ium to replenish the cell during cycling. For example, Cu//NMC111

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low uniaxial pressure ($\sim KPa$) applied to the cell stack (the method figure 1c shows the cycling performance of the ML Single-salt to apply pressure is shown in Supplementary Fig. 1). It should all DFOB electrolyte charged to 4.2, 4.3 or V4. Surprisingly, the be noted that these cells are operating under a very lean electapacity retention of single-salt LiDFOB cells improves with increas lyte condition of approximately Ah^1 . Capacity retention data areing upper cut-off voltage. Previous studies of LiDFOB electrolytes in summarized in Fig. 10 the 1M LiPF₆ and 1M LiBF₄ single-salt con lithium-metal cells cycled below 4/3 (refs.^{15,28,3}), so this high-volt trol cells clearly demonstrate the challenge of anode-free cycling enhancement has not been reported before. The problem with as they fall below 80% retention in fewer than 15 cycles. Cycling performance improvement is that the poor oxidative stability of stability was dramatically improved with the M1LiDFOB single- LiDFOB causes it to produce a lot of gas when cycled abd/ve 4.3 salt electrolyte, which reaches 60 cycles before falling below 80% performance Fig. 2) It is also impractical to require a cell to be capacity. Improved lithium-metal cycling with LiDFOB has been consistently cycled to the top of charge to maintain good perfor mance. Although the capacity retention for the dual-salt LiDFOB/

More interesting still is what happens when an additional saltLijsE₄ blend is similar to that for 1M2 LiDFOB when cycled to added to this LiDFOB electrolyte. The light-blue triangles in Fig. 415V, the dual-salt LiDFOB/LiB₄Fblend has the added benefit that show the capacity retention of a M16single-salt LiDFOB electro it maintains good cycling stability across varying upper cut-off volt lyte, which falls below 80% capacity just before 50 cycles. Wage (Fig. 1d). The dual-salt blend also produces less gas, especially 0.6 M LiPF₆ is added to this electrolyte there is little to no effect ownen charged only to 4V3(Supplementary Fig. 2). Since gassing is the number of cycles to 80% retention, but the onset of 'rolloverduced for the LiDFOB/LiB₄Fblend, cells with M LiDFOB and or complete cell failure is extended, since rollover is caused by0022eM LiBF₄ were able to undergo 100 charge–discharge cycles. This consumption of LiDFOB during cycling. With the addition of 10.6 was difficult for higher-concentration cells with only LiDFOB due LiBF₄, however (dark-blue circles), there is a substantial jump-in into the large amount of gas produced. Cells were almost ruptured tial capacity retention, with the cell making it to 80 cycles with 802% d could not remain in the test fixture. capacity, a considerable achievement for an anode-free configuraThe superior performance of the LiDFOB/LiBFhixture is tion under low applied pressure with limited excess electrolyte. Cells demonstrated in the cycling behaviour of Cu half-cells with a more optimized dual-salt blend of 11 in 200 M (200 M (20

with a more optimized dual-salt blend of M1LiDFOB and 0.24 (Supplementary Fig. 3). For the pure M1.2 iDFOB half-cell, the LiBF₄ made it to 90 cycles before dropping below 80% capacity. lithium plating/stripping Coulombic efficiency becomes unstable The unique properties of this LiDFOB/LiBFelend are further after only 15–20 cycles, while the M0.6 iDFOB 0.6 M LiBF₄ highlighted through a comparison of the single- and dual-sathows not only higher Coulombic efficiency but also much more electrolytes charged to varying upper cut-off voltage (Fig. 1c stable operation. Additionally, the half-cell voltage response



(Supplementary Fig. 3) shows that, while the pure and mixelightly improves capacity retention for the dual-salt LiDFOB/LiBF LiDFOB are initially very similar, after repeated cycling the puedectrolyte; cells at 50 cycles with this electrolyte show about 95% LiDFOB electrolyte demonstrates much larger polarization durapacity retention when cycled at kt/Fa and about 97% capacity ing lithium stripping. The maximum potential of these half-cells isstention when cycled at about 1,20% (Fig. 2a, blue circles). With limited to 1.0/, so there is no high-voltage enhancement for the textended cycling, the dual-salt electrolyte under high stack pressure pure LiDFOB and it performs poorly, much as in the full cells withreaches 90 cycles at 80% capacity retention (Supplementary Fig. 7). lower upper cut-off voltage. These results provide further evidenceThe lithium in the dual-salt LiDFOB/LiBFcells is close packed that the LiDFOB/LiBFcombination is a more practical electrolyte and dendrite free for both low- and high-pressure cells after one charge (Fig. 2f,h) and very flat after 50 cycles (Fig. 2g,i-m). In fact,

the quality of the lithium shown for the dual-salt LiDFOB/LiBF Li morphology and cell performance at increased pressure electrolyte under 1,200Pa shown in Fig. 2i represents the flattest Figure 2a shows capacity retention versus cycle number for targed most dendrite-free lithium after 50 cycles in a non-aqueous liq single-salt M LiPF₆ (orange squares) and dual-saltØ.6iDFOB uid electrolyte of which the authors are aware. Figure 2j-m shows 0.6 M LiBE (blue circles) electrolytes under varying applied pressume at this dual-salt electrolyte under 1,2000 results in a smooth Cells with 1M LiPF₆ constrained under low pressure (-KPEa) have lithium mosaic comprised of densely packed lithium domains up very poor capacity retention (orange, closed squares). Previtous0 m in diameter. In addition to these images taken at the top of reports have demonstrated the ability of increased stack pressurcharge with the maximum amount of lithium plated, images were improve lithium-metal cycling efficiency 20.32-34 and here increas taken at an intermediary state of charge with most (~80%) of the ing the stack pressure of the LiRell to 1,200Pa (orange, open lithium stripped away to confirm that this highly desirable lithium squares) more than triples the number of cycles before the cells hosephology persists throughout the thickness of the plated lithium. 60% of the initial capacity. The test fixture used to apply pressur Stopplementary Fig. 8 shows that even when most of the lithium the pouch cells is shown in Supplementary Fig. 4. The applications tripped away the morphology still consists of largen 50at of mechanical pressure affects the lithium morphology, which calormains, revealing that the internal structure of the plated lithium reduce capacity loss in two ways: (1) less dendritic lithium formesconsistent with the surface morphology. This suggests that the less unusable electrically isolated metallic lithium, and (2) loweightly packed domains achieved with LiDFOB/LiB#ectrolyte surface-area lithium minimizes the reactions with electrolyte that der 1,200 Pa shown in Fig. 2j-m are in fact lithium columns. consume active lithium to form a solid electrolyte interphase (SES)milar smooth lithium morphology is seen on the first cycle for Scanning electron microscopy (SEM) images of lithium morphodells that only use LiDFOB but have the same that all total salt con ogy taken in the fully charged state (A) are shown in Fig. 2b-m. centration (Supplementary Fig. 9), which makes sense given the Comparable optical images are shown in Supplementary Fig. 6.s Friglar capacity retention for 1M2 cells cycled to 4\5 with these 2b,c shows that lithium metal plated in the Liefectrolyte under two electrolytes (Fig. 1c,d). For LiDFOB cells cycled to lower volt low pressure is dendritic and has high surface area. Increasing stagek (4.9/, 4.2V in Fig. 1c,d) or with lower salt concentration M[1 pressure improves capacity retention by initially resulting in a mdreDFOB in Fig.1b), it is expected that the poorer capacity retention compact lithium surface after one charge (Fig. 2d), and destroyinguld also result in worse lithium morphology. Demonstrating that the dendrite formation after 50 cycles (Fig. 2e). such high-quality lithium can be created with a liquid electrolyte

Figure 2f shows that the dual-salt LiDFOB/LiBelectrolyte may eventually eliminate any need for solid-state cells. results in a dendrite-free morphology even under low pressure, which is expected given the improved capacity retention show he anode electrolyte interphase in Fig. 2a (blue, closed circles). Even after 50 cycles, the morp signice the lithium morphology is greatly improved by changing only ogy remains mostly compact (Fig. 2g). Higher stack pressure **dhe** salt used in the electrolyte, the difference in SEI composition was

explored. Figure 3 shows results from surface analysis by X-ray photo accurately capture the trends in electrolyte composition with toelectron spectroscopy (XPS) of the negative electrode from another number, the composition at cycle zero is measured by NMR free pouch cells with three different electrolytes. Measurementary electrolyte extracted from a cell after filling and wetting. were made after one C/5 charge C/2 discharge cycle (B56/) Measurements made for subsequent cycles use the same method at 40°C and 75cPa stack pressure. Each spectrum correspondsatofor cycle zero. Supplementary Table 1 compares the composition an electrode formed in a different electrolyte: black4-L1iPF6, measured on cycle zero with the composition calculated from the blue—1M LiDFOB and green—0N6 LiDFOB 0.6 M LiBF₄. All mass of each component mixed into the electrolyte. For each elec electrolytes use an FEC:DEC (volume ratio 1:2) solvent mix. Trootyte, the salt concentration measured on cycle zero is higher than sampling depth with this technique is 2HD. In each region, spec the salt concentration measured just after formation (cycle 1). Some tra are normalized to the highest intensity and a Shirley-type bask that be consumed during the first charge cycle to form the initial ground is subtracted. Spectra are offset for clarity. Assignment Spf, which is also indicated by the presence of boron (for LiDFOB components by binding energy are from the NIST XPS databasened LiBF electrolytes) or phosphorus (for LiPeffectrolytes) on the electrode surface after formation (measured by XPS; Supplementary well as other research papers35.

The fluorine 1s spectra in Fig. 3a contain one component **el**/68**F**ig. 10). After formation, the cells with LiRFig.4a) maintain the assigned to lithium fluoride (LiF) and a second component at highseme salt concentration during cycling, despite the fact that they have binding energy that is broadly assigned to organic oxygen-, carbdees than 20% capacity remaining at cycle 20. Not much salt is con boron- and fluorine-containing components, which may be similar tourned in this system, and although the composition of the solvent the LiDFOB decomposition products proposed by Schedlbaue^e et **a**hifts to slightly higher FEC content (Fig. 4b) the amounts of electro The SEI formed with LiDFOB (green) has a higher ratio of organize measured at cycle 1 and cycle 20 are similar (Supplementary Fig. fluorine components relative to LiF, whereas the SEI formed wilt²). The primary cause of capacity loss in this system is probably not LiPF₆ has more LiF relative to organic components. The increasteent the consumption of lithium to form an SEI, since this would organic component may contribute to the improved lithium moralso consume electrolyte. Instead, these cells must lose most of their phology and cycling efficiency in the single-salt LiDFOB cells. The primary from the formation of isolated metallic lithium, which is SEI formed in the dual-salt LiDFOELiBF₄ electrolyte has a largelikely given the highly dendritic lithium morphology (Fig. 2b,c). contribution from both organic fluorine components and LiF. Otheln contrast, both LiDFOB and LiBEre consumed during cycling researchers speculated that large amounts of LiF in the SEI are favorucells that use single- or dual-salt electrolytes (Fig. 4c,e able for good lithium plating Note that only information about the relative composition of the SEI is known from these data, not the

absolute amount of LiF present. Here, the cells with the best capacity retention have an SEI composed of both organic components and LiF. Oxygen 1s and carbon 1s spectra are shown in Fig. 3b,c, respectively, to further highlight the different organic SEI components formed in the three electrolytes. Electrolyte salts react at both the negative and positive electrodes, as indicated by the presence of boron (for LiDFOB and LiBF₄ electrolytes) or phosphorus (for LiPeFectrolytes). B and P spectra are shown in Supplementary Fig. 10. Positive-electrode XPS analysis is shown in Supplementary Fig. 11.

Electrolyte consumption

Figure 4 shows NMR measurements of electrolyte composition during cycling for anode-free cells that started with three different electrolytes: 0.99 (1M) LiPF₆ (a,b), 0.9n (1M) LiDFOB (c,d) and 0.5 m (0.6 M) LiDFOB 0.5 m (0.6 M) LiBF(e,f). All electrolytes used FEC:DEC (44:56 weight ratio:2 volume ratio) solvent, and cycling conditions were the same as for the cells in Fig°C; 40/5 charge, C/2 discharge between 3a and 4.5/ at 75kPa.

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NMR measurements on cells that started with puMeL1DFOB electrolytes show that when LiDFOB is consumed a small amount of LiBF₄ is formed (Fig. 4c and Supplementary Fig. 14). Recall from Fig. 1c that, for cells with single-salt LiDFOB electrolyte, capacity retention versus cycle number improved with higher upper cut-off voltage. The best capacity retention was for the cells cycled up to 4.5V. It is likely that higher voltage increases the amount of₄LiBF formed, which then improves performance by turning the electro lyte into a dual-salt LiDFOB_iBF $_4$ composition.

In addition to cell failure due to complete consumption of the salt in the electrolyte, the capacity retention in anode-free cells may be affected by changing electrolyte transport properties as the salt concentration decreases. Not only will electrolytes that start with different lithium salts have different SEI compositions, but the elec trolyte transport properties will also be different. Previous research ers have shown that properties such as electrolyte diffusion can have a big effect on lithium morphology The transport properties of electrolytes used in this work have not yet been explored.

Conclusions

Anode-free pouch cells with zero excess lithium were tested with FEC:DEC-based liquid electrolytes using different lithium salts: LiPF₆, LiBF₄ and LiDFOB. Cells with a dual-salt LiDFOBBF 4 electrolyte had the best performance of all the electrolytes tested-80% of the original capacity was retained for 90 cycles, which is an impressive cycle life for cells with no excess lithium. All previous reports of anode-free cells with liquid electrolytes fall below 80% capacity retention by 40 cycles or fewers SEM images of the lithium revealed flat, mosaic-like lithium morphology comprised of densely packed lithium columns with large domains up to 50m in diameter, which are desirable to prevent the forma tion of isolated metallic lithium and to reduce the reaction rate of lithium with the electrolyte by minimizing the surface area. This highly desirable lithium morphology in the dual-salt electrolyte may be influenced by the type of SEI formed compared with other electrolytes. XPS was used to show a dramatically different compo sition of the anode SEI formed in LiPF

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accelerating voltage and 25 resolution). To prepare samples for SEM, cells were dissected in an argon-atmosphere glovebox and electrode pieces were rinsed with dimethyl carbonate (DMC) to remove residual salt. Dried samples were mounted on SEM stubs with conductive carbon tape. Samples were transferred from the glovebox to the scanning electron microscope in an argon-filled bag, and were briefly exposed to air for less thans 30 hen loading in the scanning electron microscope.

Electrode surface analysis. SEI composition was analysed by XPS. Cells were formed at 40°C by holding at 1.% for 24h, charging at C/5 to 4J₅ then discharging at C/2 to 3J₈ After formation, cells were fully discharged to about 0.2V before dissecting in an argon glovebox to harvest electrode samples. Each electrode piece was rinsed with ethyl methyl carbonate to remove any residual lithium salt. After drying, electrodes were mounted on XPS sample holders using ultrahigh-vacuum-compatible copper tape (3M). Electrodes were moved from the glovebox to the XPS system without exposing to air using a custom transfer suitcase. A SPECS spectrometer with a PHOIBOS 150 hemispherical analyser was used for XPS analysis with Mg K radiation (1,253.6 eV) under ultrahigh-vacuum conditions (2 10 ° mbar). See ref[®] for further details.

Electrolyte extraction. Electrolyte was extracted from cells in one of two ways. (1) Cells were cut open in a glovebox and filled with df anhydrous deuterated DMSO (d-DMSO, Sigma). The solvent was massaged into the jelly roll, and then the electrolyte/d-DMSO mix was collected for analysis by NMR. (2) Cells were cut open outside the glovebox and the jelly roll was moved to a perfluoroalkoxy alkane vial with 19 of DMC (BASF). Vials were sonicated for 10, mixed on a wrist-action shaker forhl, sonicated for 100in, mixed on a wrist-action shaker for 1h, sonicated for 100 in then mixed on a wrist-action shaker overnight. m00 of the DMC/electrolyte mix was added to abouth@.8 f anhydrous d-DMSO for NMR analysis. Method 1 gives the salt concentration and relative percentages of electrolyte components that were in the pouch cell. Method 2 is a total extraction method and gives the salt concentration and total mass of each electrolyte component present in the pouch cell. The cells in Fig. 4a-d were analysed using method 2, which gives the composition (shown in Fig. 4b,d) and total amount of electrolyte (shown in Supplementary Fig. 11). The cells in Fig. 4e,f were analysed using method 1, which gives the salt concentration and relative solvent composition.

Electrolyte analysis. Electrolyte samples prepared in d-DMSO (as described in the previous section) were analysed using liquid NMR on a Bruker AV500 spectrometer. Protorll() spectra were collected over the rangeport. Fluorine (1°F) spectra were collected with no background suppression over the range 200 to 0ppm. Peaks for each solvent component appear in the spectrum at 6.ppm, 6.5ppm and 4.ppm (FEC), 3.ppm (DMC), and 4.ppm and 1.ppm (DEC). Peaks for FEC and fluorine salts appear in the following chemical shifts: 123 ppm (FEC)(70 ppm (LiPF₆), 151 ppm (LiDFOB) and 148 ppm (LiBF₄). Peak assignments were confirmed from the and "F spectra of each pure component.

Peak areas from the spectrum were used to calculate the relative FEC:DEC composition. For electrolyte extracted by method 2 the amount of DMC present in the NMR sample was known, so the DMC signal was used as a standard to calculate the masses of FEC and DEC extracted from the pouch cell. The peak areas from the spectrum were used to calculate the salt amount relative to FEC, which was used with the information from the

elal8(le co(g t)6(o)4.0999999(e)]TJ2(t)-6(hi)12(um s)-6et)-5.9000001(h)4((l ext)-e)-5(c)-6.9000001(t)-5(r)13(o)-9(de p)12or

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Acknowledgements

This research was financially supported by Tesla Canada and NSERC under the Industrial Research Chairs Program. A.J.L. thanks the Nova Scotia Graduate Scholarebinespondence and requests for materials should be addressed to J.R.D. programme and the Walter C. Sumner Memorial fellowship for support. M.G. thanks the NSERC PDF Program. The authors acknowledge Dr J. Li (formerly of BASF) and Dr Dublisher's note: Springer Nature remains neutral with regard to jurisdictional claims in Xiong (formerly of Capchem) for providing chemicals used in the electrolytes, as well as

S. Trussler for expert fabrication of the parts used in this work.

Author contributions

R.W., M.G., A.J.L. and J.R.D. conceived the idea. R.W., M.G. and A.J.L. designed the experiments with the guidance of J.R.D.; R.W., M.G. and A.J.L. performed the electrochemical measurements with assistance from S.H. and C.M.; R.W. performed the NMR analysis; R.W. performed the XPS analysis with guidance from I.G.H; M.G. and A.J.L. performed the SEM analysis; A.J.L. performed the mechanical pressure measurements. R.W., M.G., A.J.L. and J.R.D. prepared this manuscript with input from all other co-authors.

Competing interest

Rochelle Weber is employed by Tesla Canada R&D.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/ s41560-019-0428-9.

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