An efficient combinatorial approach for the design and evaluation of surface coatings to improve lithium metal cycling efficiency is demonstrated. The reliability of a 64-electrode combinatorial cell was verified through lithium metal cycling in a range of electrolytes on unmodified Ni and Cu electrode plates with parallel verification using conventional Cu||Li coin cells. A 1M LiPF6 FEC:TFEC fluorinated electrolyte demonstrated the best performance with coulombic efficiencies of 98.3% and 97.6% in the combinatorial cell (cyclic voltammetry) and coin cell (galvanostatic cycling) respectively, compared to only 91.0% (CV) and 90.3% (galvanostatic) for a 1M LiPF6 EC:DEC control electrolyte. High throughput sputtering was used to deposit different thin film coatings of varying thickness on the 64-channel cell plates to probe the lithium cycling performance as a function of electrolyte and surface coating. Zn surface coatings with thickness between 400–900 nm proved most beneficial; significantly reducing the lithium nucleation potential and leading to more stable cycling at high coulombic efficiency (99.0% in the combinatorial cell with FEC:TFEC electrolyte). These findings not only highlight some useful strategies for improving lithium metal cycling efficiency, but also show the potential for more advanced combinatorial analysis to design superior anodes for lithium metal cells.

© The Author(s) 2018. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.04018jes]

Manuscript submitted July 26, 2018; revised manuscript received September 7, 2018. Published September 20, 2018.

There is a continual push to improve the energy density of lithium ion batteries, but this is becoming increasingly difficult as it is believed that many of the best electrode materials have been found and optimized. In certain applications, where high energy density is paramount, it may be necessary to move beyond lithium ion. Recent research efforts have focused on reviving the lithium metal anode as a path to higher energy density.1–3 With its high theoretical capacity (3860 mAh g−1) and low negative redox potential (−3.040V vs SHE), lithium metal is certainly an appealing anode material for high energy density cells. However, lithium metal suffers from dendrite formation during electrodeposition instead of plating as a smooth film.4,5 Dendritic deposits are also prone to disconnection and the formation of electronically isolated or “dead” lithium. All of these factors contribute to an impractically low (<90%) coulombic efficiency of lithium metal in conventional organic electrolytes and in primitive cell designs. These issues are only compounded as the current density and capacity of plated lithium are increased,4 making the design of commercially relevant lithium metal cells a significant challenge.

Many strategies have been proposed to inhibit lithium dendrites and increase cycling efficiency including solid state polymer or ceramic electrolytes,6–10 the application of mechanical pressure,11,12 increasing the anode surface area via a structured matrix or 3-D current collector;13–15 the addition of selected cations which inhibit dendrites via a self-healing electrostatic shield mechanism;16 highly concentrated solvent-in-salt electrolyte systems;17–23 the use of fluorinated solvents like FEC or other electrolyte additives for the in-situ formation of a protective SEI;24–26 and the application of an artificial SEI to lithium metal before cycling.27–29 These strategies have led to some promising results in terms of dendrite mitigation; however more work is needed to develop superior solutions which allow for the high coulombic efficiency (>99.8%) cycling of lithium metal at commercially relevant capacities and current densities with high voltage positive electrodes.

Recent studies have shown that the morphology and plating efficiency of metal anodes can be vastly improved by using nanostructured surface coatings on the anode current collector foil.28,29 For instance, Pint and coworkers have shown that a nanocarbon nucleation layer formed on Al current collectors allowed for the stable cycling of 0.25 mAh cm−2 of sodium metal at 0.5 mA cm−2 with a coulombic efficiency of 99.8%.30 The Cui group has also demonstrated coatings on Cu current collectors consisting of metals that alloy with lithium like Au, Ag, and Zn as well as hollow carbon nanospheres containing nanoparticles of these alloying metals.2,31 The metal nanoparticles provide preferential lithium nucleation sites while the carbon nanospheres offer stable encapsulation leading to 98% coulombic efficiency for lithium metal cycling in alkyl carbonate electrolytes. Nanostructured surface coatings seem to be a promising approach for improving lithium metal cycling, so it would be beneficial to study the impact of numerous surface coatings with different composition, structure, and thickness, on the plating/striping efficiency of lithium metal. This is a daunting task; however, the Dahn group has developed and optimized high throughput sputtering methods that can quickly produce libraries of thin films with different composition, structure, and thickness.32,33 These sputtered libraries can be directly deposited on a 64-channel electrochemical cell-plate and tested in a combinatorial (combi) electrochemical cell34 to probe the morphology and plating efficiency of lithium as a function of electrolyte and surface coating composition – 64 experiments at once. Herein, we demonstrate how this combinatorial approach can be used to effectively screen and evaluate anode surface coatings based on their benefit to lithium metal cycling performance. This first involved demonstrating the reliability of the combinatorial cell by testing different electrolytes with unmodified 64 channel control electrode cell plates and comparing the performance to that of conventional coin cells. Once verified, the combinatorial cell was used to evaluate cell plates modified with sputtered carbon and sputtered zinc, two materials that show promise as potential lithium nucleation layers. These materials were deposited on the cell plates at varying loadings to evaluate both the effect of the material and its thickness on lithium plating/striping efficiency. “Winning combinations” were also tested in conventional coin cells to confirm the results of the combi cell and evaluate the lithium morphology. These results will provide perspective on promising strategies for achieving high lithium cycling efficiency and demonstrate the
potential of the combinatorial approach for optimizing the design of anodes for lithium metal cells.

Experimental

Materials.—Reagents used for electrolytes include 1:2 w/w ethylene carbonate: diethyl carbonate (EC:DEC, BASF, purity 99.99%), 1:1 w/w EC:DEC (Shenzhen Capchem (China), purity 99.99%), fluoroethylene carbonate (FEC, BASF, purity 99.4%), bis(2,2,2-trifluoroethyl) carbonate (TFEC, HSC Corporation (China), >99%), lithium hexafluorophosphate (LiPF₆, BASF, purity 99.9%), lithium bis(fluorosulfonyl)imide (LiFSI, HSC Corporation, purity >99.98%), lithium perchlorate (LiClO₄, Alfa, purity 99.9%). It should be noted that DEC was used as an electrolyte solvent instead of alternative linear carbonates like DMC or EMC due to practical considerations associated with assembling and testing the large combinatorial cell. DEC evaporates much more slowly than DMC or EMC, therefore any concerns regarding potential electrolyte evaporation during assembly or extended testing are mitigated.

64-Channel cell plate.—The 64-channel electrochemical cell plates were made by Optima Technology Associates Inc. (Lewisberry, PA) and utilized a standard resin-based printed circuit board. Details on the design and fabrication of the plate are provided by Maghrabi et al. A labelled cell plate schematic is shown in Figure 1a. Each of the 64 electrodes consists of an external electrical contact, a circular contact pad where the surface coating is deposited, and a connecting lead. The diameter of each electrode pad is 5 mm which corresponds to an electrode area of 0.198 cm². Cell plates with both copper and nickel plated electrodes were utilized.

Sputter deposition of thin film coatings.—DC magnetron sputtering was conducted using a Corona Vacuum Coaters (Vancouver, Canada) model V-3T system. Details on this sputtering system are provided by Dahn et al. Two inch diameter graphite (Kurt J. Lesker Company, purity 99.999%) and zinc (Kurt J. Lesker Company, purity 99.99%) targets were used for sputter deposition. A “linear-out” mask was placed over the targets to obtain a linear variation in carbon or zinc thickness from right to left across the cell plate as it is shown in Figure 1a. Images of the sputtering chamber including the target positions and substrate table layout before the carbon run are shown in Figure S1. The cell plates are positioned on the substrate table along with Al foil weigh disks that were weighed (0.1 μg precision) before and after the sputtering run to determine the position dependence of the mass per unit area of the material deposited. Copper foil disks were also positioned on the sputtering table to be used as electrodes for testing in conventional coin cells after sputtering. The sample chamber was pumped down to a base pressure below 0.3 μT before the run. Sputtering was done at room temperature under an argon pressure of 1.6 mT. The thickness of the sputtered films was measured with a Veeco Dektak 8 Stylus Profilometer.
Assembly and electrochemical testing of the combinatorial cell.—Figures 1b and 1c show a labelled schematic of the combinatorial cell which is assembled in an Ar-filled glove box as follows. The cell plate is placed on the combinatorial cell base and approximately 0.6 mL of electrolyte is spread evenly over all the electrode pads. One microporous separator (Celgard 2300) is then centered over the electrode array followed by a blow glass microfiber (BMF, 3M) separator which is wet with an additional 0.3 mL of electrolyte. A lithium foil (0.25 mm thick) with an area slightly larger than that of the cell array is placed on top of the BMF. The cell top, fitted with a Kalrez (DuPont) O-ring is then aligned over the cell array via the guideposts and placed in position. The cell is then sealed via the four clamping bolts, while the pressure bolts are tightened to ensure an even pressure on the cell plate. All bolts were tightened with a torque wrench set to 25 lb-ft.

Cyclic voltammetry measurements were performed on the cell plate electrodes using a multi-channel pseudopotentiostat as described by Cumyn et al.36 Cells were cycled between 0.6 and −0.3V vs Li/Li+ at a rate of 0.167 mV s−1. The Zn modified electrodes were cycled between 0.6 and −0.3 V for the initial cycle, however all proceeding cycles were between 0.125 and −0.3 V, with a 90 minute potential hold at 0.125 V. The upper cutoff voltage was limited to avoid cycling of the Li-Zn alloy. All of these conditions were chosen such that the average plating current was close to 1 mA cm−2 and average plating capacity was approximately 1 mAh cm−2. For the “high-capacity” test on the Zn modified electrodes, the voltage limits were the same, however, the scan rate was reduced to 0.06 mV s−1 to achieve a plating capacity of approximately 3 mAh cm−2.

Assembly and electrochemical testing of coin cells.—Standard 2325 coin cells were assembled in an Ar-filled glove box. Each coin cell consisted of a bare or surface coated Cu electrode (1.27 cm diameter) and lithium foil (1.27 cm diameter, 0.25 mm thick) negative electrode with two layers of separator (Celgard 2300). Galvanostatic charge-discharge cycling was conducted on a Maccor cycling unit. 1 mAh cm−2 of lithium was plated and stripped at 1 mA cm−2 for all coin cell tests.

Scanning electron microscopy imaging (SEM).—SEM analysis of the plated lithium morphology was conducted using a Nano Science Phenom Pro G2 Desktop Scanning Electron Microscope with a backscattered electron detector. Lithium electrodes were removed from the coin cells in an Ar-filled glove box and rinsed with dimethyl carbonate and dried. The samples were transferred to the SEM in an Ar-filled transfer container. Brief (approximately 30 seconds) exposure to the air while loading into the SEM occurred. The images of samples were taken with accelerating voltage of 5 kV and current of 0.6 nA.

Results and Discussion

Evaluating lithium plating and stripping in the combinatorial cell.—Before the combinatorial cell can be used to screen different surface coatings, it is first necessary to confirm the reliability of this test vehicle for evaluating lithium metal cycling. Consistent behavior across all 64-channels is important for ensuring reliable conclusions. For this reason, an unmodified cell plate with 64 identical Ni electrode pads was first evaluated in a control electrolyte, 1M LiPF6 in EC:DEC (1:1 w/w). Figure 2 shows cyclic voltammograms (CVs) across the 64 combi cell channels corresponding to the first lithium plating and stripping cycle on each of the 64 unmodified Ni electrodes in control electrolyte. The 64 CVs appear quite consistent with an average plating current of approximately 200 μA (1 mA cm−2) and an average stripping current of approximately 250 μA (1.25 mA cm−2). There are some slight variations in current density, but overall the performance is fairly uniform after one cycle. The initial capacity of plated lithium for each electrode is approximately 200 μAh or 1 mAh cm−2.

To better demonstrate the lithium cycling behavior in control electrolyte, Figure 3 shows (a) selected CVs, (b) capacity, (c) plating resistance, and (d) coulombic efficiency of a representative combi cell electrode (#19) over 40 cycles. The data for all 64 channels is included in Figure S2. The CV profiles in Figure 3a are consistent with those of lithium metal plating/stripping.18,37 For cycle 1 (red curve), the onset of lithium plating occurs at approximately ~70 mV, which represents the lithium nucleation overpotential. As the potential is swept down to −300 mV and then back to 0 mV, the CV forms a loop with more negative current densities in the second portion of the sweep. This type of hysteresis behavior is common[38]; the lower current densities in the sweep from −300 to 0 mV are indicative of the lower overpotentials associated with growing lithium formations rather than the nucleation of new deposits. The second portion of the plating sweep from −300 to 0 mV is quite linear which means a simple ohmic relation can be used to extract a plating resistance (larger slopes in this portion of the CV are indicative of lower plating resistance). When the potential is swept above 0 mV, there is an obvious cathodic peak corresponding to lithium stripping. The CV in the control electrolyte is clearly unstable with repeated cycling; the curve shows slight increases in current density early on, but diminishes significantly by cycle 40. With this decrease in current density there is a clear decrease in the slope of the plating portion of the CV. Figure 3b tracks this plating resistance which increases linearly after cycle 4. This huge increase in plating resistance provides a nice illustration of the difficulties associated with lithium cycling in conventional carbonate electrolytes. Dendritic lithium growth combined with constant breaking/reforming of the SEI during stripping/plating leads to porous lithium deposits including electronically isolated or “dead” lithium. These thick and poorly conductive lithium formations result in higher plating resistance and consume active lithium leading to the death of lithium metal cells.

Figure 3c illustrates the channel capacity of lithium plating and stripping over 40 cycles in control electrolyte. It’s clear that the capacity inversely tracks the plating resistance. Since the voltage limits are fixed in the CV scan, as the resistance increases, the capacity that can be delivered at a given voltage decreases. This is analogous to the increase in voltage polarization that is monitored in lithium half cells cycled galvanostatically. Thus, for the combi cell, tracking the plating resistance and/or channel capacity is a good gauge of lithium cycling performance. The coulombic efficiency is also an important metric, which is shown in Figure 3d. Unsurprisingly, the coulombic efficiency is low (~91%) in the control electrolyte and after the 10th cycle the CE values becomes less stable jumping from high to low values. This unstable and low CE is consistent across the 64 channels of the combi cell as shown in Figure 4 (the percentage values in each panel indicate the average CE for that channel over 40 cycles).

There are some obvious deviations in the CE behavior from channel to channel. While most channels behave similarly in the early stages, beyond cycle 20 the CE becomes less stable with some channels dropping significantly. Since most of this variance appears only after extended cycling, it is taken as further evidence of the inconsistent dendritic lithium growth in the control electrolyte rather than inherent limitations of the combinatorial cell. 1M LiPF6 in EC:DEC is clearly not suitable for stable cycling of lithium metal, so alternative electrolyte systems must be explored.

Fluorinated solvents for lithium metal cycling.—Recent reports have detailed the benefits of fluorinated solvents, particularly FEC, for improving the coulombic efficiency of lithium metal cycling.23,24,39 For this reason, a fluorinated electrolyte consisting of 1M LiPF6 in FEC:TFEC was screened in the combinatorial cell, again using an unmodified cell plate with 64 identical Ni electrodes. FEC and TFEC are the fluorinated analogs of EC and DEC with very similar structures (Figure S3), so comparison of this FEC:TFEC electrolyte to control will provide insight as to the effect of solvent fluorination on lithium metal cycling. The CVs, plating resistance, and capacity over 40 cycles for all 64 combi cell channels in the fluorinated electrolyte are shown in Figure S4. Data from a representative channel (#19) including (a)
selected CVs, (b) plating resistance, (c) capacity, and (d) coulombic efficiency are shown in Figure 5 (the control data are also included for comparison). The CV data in Figure 5a illustrates a significant improvement in the stability of lithium metal cycling with the fluorinated electrolyte. While the control CV is reduced substantially by cycle 40, the FEC:TFEC CV shows very little change, with no obvious decrease in the cathodic peak or increase in the slope of the plating portion of the curve. In contrast to the dramatic increase in plating resistance observed for the control electrolyte, the fluorinated system shows a lower resistance to start which remains low over the course of cycling (Figure 5b). The average plating resistance across all 64 electrodes was 0.45 kΩ in the fluorinated electrolyte, close to 3 times smaller than the 1.25 kΩ average shown in the control electrolyte. This lower resistance may be attributed to the change in SEI composition with the fluorinated solvents. Fluorinated electrolytes have been shown to result in a LiF rich SEI that is thinner and more uniform than that formed with non-fluorinated carbonates.\textsuperscript{23,24} A thin, more uniform SEI with the high lithium ion conductivity of LiF can help to achieve less dendritic lithium growth. This can mitigate or at least delay the onset of porous lithium deposits and dead lithium, which helps to keep the plating resistance low.

Figure 5c shows the capacity of lithium plated and stripped over 40 cycles with these values reaching a maximum of approximately 225 μAh, or 1.1 mAh cm\(^{-2}\) which corresponds to a theoretical lithium thickness of just over 5 μm. With very little growth in the plating resistance, the cycling capacity in the fluorinated electrolyte remains fairly constant over 40 cycles. This stable cycling behavior is very consistent across all 64 electrodes of the combinatorial cell with fluorinated electrolyte (Figure S4b), which shows much less channel to channel variation as compared to the control. The improved consistency across all channels can be attributed to the more uniform lithium deposition exhibited in the fluorinated electrolyte. The coulombic efficiencies in the fluorinated electrolyte are also much higher and more stable than the control as shown in Figure 5d. The CE behavior for all 64 electrodes in the FEC:TFEC electrolyte is summarized in Figure 6. Much like the capacity data, the CE shows less channel-to-channel variation in the fluorinated electrolyte. The average CE across all 64 electrodes is 98.3% compared to only 91.1% for the control cell. The higher lithium cycling efficiency is again attributed to less dendritic lithium growth which translates to lower surface area and less consumption of active lithium for SEI formation. A thin LiF rich SEI enabled by the fluorinated solvents may also contribute to less lithium consumption and higher CE values.

**Evaluating the combinatorial cell against conventional lithium coin cells.**—The previous sections have demonstrated that lithium metal cycling can be effectively evaluated in the combinatorial cell and that performance is consistent across all 64 electrode channels, particularly in electrolyte systems that are optimized for lithium metal cycling. However, to confirm the reliability of the combi cell data, it is important to compare these results against data collected using a standard approach for evaluating lithium metal cycling, Cu/Li coin cells. A series of electrolytes (including the two discussed in detail in the previous sections) were evaluated in the combinatorial cell.
with unmodified Ni cell plates to assess lithium metal cycling performance. Selected electrolytes from this screening were also tested via galvanostatic lithium plating and stripping in Cu||Li coin cells for comparison.

Figure 7a summarizes the average lithium plating/stripping coulombic efficiency over 40 cycles across all 64 channels for each electrolyte screened in the combi cell. The lowest coulombic efficiencies (<90%) are demonstrated by the 1M salt electrolytes in the EC:DEC 1:2 solvent. Linear carbonates, like DEC, show very low lithium cycling efficiencies\(^40\) therefore it is no surprise that the solvent system with a higher fraction of these linear carbonates shows the lowest coulombic efficiency of the electrolytes tested. This low CE shown in the EC:DEC 1:2 solvent can be increased to 95.0% with the use of high salt concentration (3 M LiFSI). This confirms the results of others who have demonstrated the positive effect of high imide salt concentration on lithium metal cycling efficiency.\(^17,18\) Nevertheless, the highest coulombic efficiencies were achieved in fluorinated electrolytes containing a large fraction (50 wt%) of FEC. FEC clearly has a strong effect on lithium metal cycling performance; when the EC in 1M LiPF\(_6\) EC:DEC is completely replaced by FEC, the CE increases significantly from 91.1% to 97.6%. When the linear carbonate is fluorinated, the CE increases again, but only marginally to 98.3% for FEC:TFEC. It should be noted that a high salt concentration (3M LiFSI) electrolyte with FEC solvent was not screened in the combi cell. The issue of Al current collector corrosion by LiFSI can be enhanced with solvents containing large amounts of FEC.\(^41\) Since this electrolyte would not be viable for full cells, it was not part of the combi cell screening.
Figure 4. Lithium plating/stripping coulombic efficiency (CE) for each of the 64 combinatorial cell channels over 40 CV cycles on nickel electrodes in control electrolyte (1M LiPF$_6$ in EC:DEC).

The 1M LiPF$_6$ EC:DEC 1:2, EC:DEC 1:1, FEC:DEC 1:1, and FEC:TFEC 1:1 electrolytes were also screened in Cu||Li coin cells, with the lithium metal cycling efficiencies for each summarized in Figure 7b. Since the pseudopotentiostat used to test the combi cell does not operate galvanostatically, it is difficult to precisely control the plating/stripping current and capacity. The average plating capacity for the combi cell tests was approximately 1 mAh cm$^{-2}$ and the average plating current was approximately 1 mA cm$^{-2}$. In an effort to mimic these conditions for the Cu||Li coin cell tests, 1 mAh cm$^{-2}$ of lithium was plated and stripped at a constant current of 1 mA cm$^{-2}$. The same general trend shown in the combi cell is also demonstrated by the coin cell results. The control type electrolytes (EC:DEC 1:2 and 1:1) show low and very unstable cycling efficiency. The CE of the EC:DEC 1:2 electrolyte declines and becomes unstable after only 10 cycles, while the EC:DEC 1:1 does the same after about 25 cycles. The average CE for these electrolytes over 40 cycles was only 83.7% and 90.3% for the 1:2 and 1:1 EC:DEC respectively.

The significant improvement in lithium cycling efficiency with fluorinated solvents is also demonstrated in the coin cells. FEC:DEC and FEC:TFEC both show much higher and more stable CE values compared to the control, averaging 97.0% and 97.6% respectively. The CE values from the combinatorial cell are higher than those from the coin cells, but only slightly. There are many possible reasons for the small discrepancy. For instance, since the combi cell was cycled by sweeping the voltage, the plating current was not constant. With this protocol, the initial lithium nucleation and plating occurs at very low current densities which may help in nucleating larger lithium deposits. Additionally, due to the lack of current control, the stripping currents were slightly larger than the plating currents in the combi cell. Cycling protocols with higher stripping current densities have been shown to result in enhanced lithium cycling efficiency. Finally, due to channel availability, the coin cell tests were conducted at 40°C while the combi cell tests were done at room temperature. Due to these differences, the CE values from the combi and coin cells cannot be directly compared, however, the overall trends in performance are the same with both test methods, which confirms the reliability of the combi cell as a screening tool.

The coin cell data shows that beyond 60 cycles even the CE of the fluorinated electrolytes becomes unstable. This was also found in the combi cell as shown in Figure S5 which summarizes the CE of all 64 combi cells channels in FEC:TFEC over 70 cycles. By cycle 60, the CE for the majority of the channels has become unstable. These extended cycling results again demonstrate the agreement between the combi cell and conventional coin cells in terms of evaluating the important trends in lithium metal cycling performance. These results also show that the fluorinated solvents alone are not sufficient to achieve stable and high CE for extended cycling. Surface coatings may be needed to further enhance lithium metal cycling performance and with the reliability of the combinatorial cell confirmed, it can now be used to effectively screen these coatings.

Surface modification: sputtered carbon.—A 64-channel Ni electrode cell plate was modified with amorphous carbon via sputter deposition in order to evaluate the effect of a carbon nucleation layer...
on lithium metal cycling. The electrochemical reaction of this sputtered carbon (in bulk) with lithium has been previously reported by Fathi et al.43 The carbon was deposited in a linear wedge, that is, the mass and thickness of the carbon increase linearly along the width of the cell plate. During sputtering, the substrate plate is oriented such that the mass/thickness of carbon in a given column of electrodes is relatively constant. The mass and thickness of the sputtered carbon modifying each column of electrodes is summarized in Figure 8a, with the columns numbered 1 to 8 from left to right on the cell plate. The carbon coating is quite thin, ranging from only 50 to 460 nm, which corresponds to a mass loading ranging from 0.02 to 0.1 mg cm$^{-2}$.

Figure S6 (a) shows the first cycle CV for each of the 64 carbon modified electrodes in 1 M LiPF$_6$ in FEC:TFEC with Figure S6 (b) showing a magnified scale highlighting the features around 0 V vs. Li/Li$^+$. The carbon loading increases from right to left in the figure. In each CV, a small anodic peak appears just above 0 V, which increases in magnitude with carbon loading. This peak corresponds to the lithiation of the carbon which occurs before the onset of plating at approximately $-0.05$ V. Due to the low carbon loading this lithiation capacity is negligible compared to the approximately 1 mAh cm$^{-2}$ of lithium which is plated.

Figure 8b summarizes the average plating/stripping coulombic efficiency for each row of carbon modified electrodes along with the value for unmodified nickel electrodes over 80 cycles in 1M LiPF$_6$ FEC:TFEC. The CE vs. cycle number and average CE for each of the 64 channels is shown in Figure 8c. The sputtered carbon does not seem to have a strong effect on the lithium metal cycling efficiency. For the thickest carbon coatings (columns 1, 2, and 3) the average CE (98.5%) is slightly higher than the unmodified control (97.7%), but there is not a consistent trend throughout the plate. For the thinner

**Figure 5.** Comparison of lithium plating in control (1M LiPF$_6$ EC:DEC) and fluorinated (1M LiPF$_6$ in FEC:TFEC) electrolyte based on output from representative electrodes in each combinatorial cell including (a) CVs; (b) plating resistance; (c) plating/stripping capacity; and (d) coulombic efficiency over 40 cycles.
Figure 6. Lithium plating/stripping coulombic efficiency (CE) for each of the 64 combinatorial cell channels over 40 CV cycles on nickel electrodes in 1M LiPF₆ in FEC:TFEC fluorinated electrolyte.

coatings (columns 5–8), some show higher CE than the control while others show no difference. This makes it difficult to conclude if the higher average CE values are significant or just a result of variability in the data. Additionally, Figure 8c shows that much like the unmodified control, the CE for many of the carbon modified electrodes becomes less stable after 60 to 70 cycles.

The reason for these trends in performance of the carbon modified electrodes becomes clearer after examining SEM images of the sputtered carbon surface before and after lithium plating. Figure S7 shows the SEM images of (a) a pristine sputtered carbon coating and (b) a sputtered carbon coating after a single lithium plating and stripping cycle. The pristine coating appears as a uniform dense carbon film. However, after one cycle of plating and stripping the carbon coating has expanded, fractured, and been torn apart leaving behind a mixture of porous carbon and residual lithium. It seems that during lithiation the amorphous carbon expands then cracks. As the potential sweeps below 0 V lithium can then plate then cracks and further break up the coating, pushing the carbon aside. This process will repeat over subsequent cycles as the coating continually deteriorates. This can help to explain why the thicker coatings showed slightly better performance. Carbon may have some benefit as a nucleation layer and the thicker layers may prolong the time it takes for the coating to deteriorate. The sputtered carbon is clearly not an ideal surface coating for lithium plating. An alternative nucleation layer with superior performance and stability is required.

Alloy surface modification: sputtered zinc.—It has been shown that little to no overpotential is needed to nucleate lithium metal on alloying elements that also possess a definite solubility in lithium like Au, Mg, Zn, and Ag. This suggests these materials may serve as useful surface coatings for lithium metal batteries as lowering the energy barrier for lithium metal nucleation may aid in more uniform lithium deposition. From the materials listed above, Zn is inexpensive, has a relatively small alloying capacity/volume expansion, and can be easily deposited via sputter deposition. Zn thin films of varying thickness were evaluated as lithium nucleation layers by sputter depositing a linear wedge of Zn on a 64-channel cell plate and cycling in the combinatorial cell. The first cycle cyclic voltammogram of a representative Zn modified electrode is shown in Figure 9a along with the first cycle CV of an unmodified Ni electrode for comparison (the electrolyte is 1M LiPF₆ in FEC:TFEC). The Zn CV clearly differs from that of the unmodified electrode; the numbers 1, 2, and 3 adjacent to the CV curve highlight the three step process occurring during a full cycle on Zn, which is summarized in Figure 9b.

In step 1, as the potential decreases below 0.5 V, the Zn on the electrode surface begins to alloy with lithium. Figure 9c shows a magnified scale focusing on the reduction peaks in the alloying region. The Li₂Zn₅ alloy is initially formed, followed by the fully lithiated LiZn. As the potential decreases below 0 V there is a sharp increase in negative current density indicating the onset of lithium plating (step 2) on the alloy. The inset in Figure 9a shows that for the zinc
Figure 7. (a) Average lithium plating/stripping coulombic efficiency across 64 channels over 40 cycles for a series of electrolytes screened in the combinatorial cell (Ni cell plate); (b) coulombic efficiency vs. cycle number for lithium cycling (1 mAh at 1C) in selected electrolytes tested in conventional Cu||Li coin cells for comparison (average CE values over 40 cycles for each electrolyte are indicated beside each plot).

Figure 8. (a) approximate carbon mass loading and thickness for each column of electrodes on the cell plate; (b) summary of the average CE over 80 cycles for each column of sputtered carbon electrodes in comparison to the unmodified Ni electrode control; (c) Lithium plating/stripping CE over 80 CV cycles on a Ni electrode cell plate modified with a linearly increasing wedge of sputtered carbon in 1M LiPF₆ FEC:TFEC electrolyte.
In order to confirm the results of the combi cell, Zn sputtered Cu discs were used to construct Cu-Zn||Li coin cells. Figure 12a shows the coulombic efficiency of the Cu-Zn||Li coin cells for plating/stripping of 1 mAh cm$^{-2}$ of lithium at 1 mA cm$^{-2}$ in 1 M LiPF$_6$ FEC:TFEC electrolyte. The CE of unmodified Cu||Li cells in 1 M LiPF$_6$ FEC:DEC and 1 M LiPF$_6$ FEC:TFEC is included for comparison. Much like the results from the combi cell, the Zn modified anodes show higher and more stable coulombic efficiency than the unmodified electrodes. While the unmodified electrodes begin with lower CE and gradually increase, the Zn CE is high from the early stages of cycling with an average of 98.2% compared to 97.6% for the unmodified copper in the same electrolyte. Figure 12b shows the voltage vs. time profile for the initial plating/stripping cycles of the Cu-Zn||Li and Cu||Li coin cells. Nucleation occurs at lower potentials for the coin cells compared to the combi cell as the nucleation current is much larger in the coin cell.

The coating has a minimum thickness of just over 100 nm corresponding to a Zn loading of 0.1 mg cm$^{-2}$ for column 8. The thickness increases to a maximum value just less than 900 nm and 0.63 mg cm$^{-2}$ for column 1. The average CE over 100 cycles for each column is summarized in Figure 10b. Column 5 of the cell plate was masked during sputtering to allow for an unmodified Ni electrode control column for comparison. The CVs, capacity, and plating resistance for each electrode modified with the linear wedge of Zn as well as the control column are shown in Figure S8. The zinc mass loading and thickness increase from right to left on the cell plate and the values for each column are summarized in Figure 10b.

Inspection of the zinc modified combinatorial cell plate after cycling provided a nice visualization of the impact of the zinc coating on lithium plating. Figure 11 shows the Zn modified cell plate with the unmodified control column (a) before and (b) after 100 plating cycles. After cycling, the control electrodes look much different from the rest. In the control column, lithium has grown out from the electrode pad and onto the cell plate. These unconstrained lithium deposits likely become electronically isolated preventing them from being completely stripped. As cycling continues this issue becomes more severe as indicated by the unstable CE values of the control electrodes after 50 to 60 cycles. The Zn electrodes, however, show much more constrained and uniform lithium deposition corresponding to their stable CE throughout cycling. The electrodes with the thinner Zn coatings in the rightmost column show some growth of deposited lithium out onto the cell plate, but much less than the control. These results suggest that Zn is acting as an effective nucleation layer. By lowering the energy barrier for nucleation the Zn alloy surface may allow for more nucleation events and more uniform lithium growth.

In order to confirm the results of the combi cell, Zn sputtered Cu discs were used to construct Cu-Zn||Li coin cells. Figure 12a shows the coulombic efficiency of the Cu-Zn||Li coin cells for plating/stripping of 1 mAh cm$^{-2}$ of lithium at 1 mA cm$^{-2}$ in 1 M LiPF$_6$ FEC:TFEC electrolyte. The CE of unmodified Cu||Li cells in 1 M LiPF$_6$ FEC:DEC and 1 M LiPF$_6$ FEC:TFEC is included for comparison. Much like the results from the combi cell, the Zn modified anodes show higher and more stable coulombic efficiency than the unmodified electrodes. While the unmodified electrodes begin with lower CE and gradually increase, the Zn CE is high from the early stages of cycling with an average of 98.2% compared to 97.6% for the unmodified copper in the same electrolyte. Figure 12b shows the voltage vs. time profile for the initial plating/stripping cycles of the Cu-Zn||Li and Cu||Li coin cells. Nucleation occurs at lower potentials for the coin cells compared to the combi cell as the nucleation current is much larger in the coin cell.

Figure 9. (a) Initial cyclic voltammogram of lithium plating/stripping on a sputtered Zn modified electrode and unmodified Ni electrode (the inset shows a comparison of the nucleation potential on each electrode); (b) illustration of the cycling protocol for the zinc electrode including alloying, lithium plating, and lithium stripping without significant dealloying; (c) magnified CV illustrating the reduction peaks corresponding to the initial alloying of the zinc electrode.
Figure 10. (a) Lithium plating/stripping CE over 100 CV cycles on a Ni electrode cell plate modified with a linearly increasing wedge of zinc in 1M LiPF₆ in FEC:TFEC electrolyte (column 5 was masked during sputtering and kept as an unmodified control); (b) summary of the average CE over 100 cycles for each column of sputtered zinc electrodes in comparison to the unmodified Ni electrode control; (c) approximate zinc mass loading and thickness for each column of electrodes on the cell plate.

cell. However, the nucleation overpotential (the initial well or voltage minimum before the stable plating potential) is much lower for the Zn electrodes both on the initial and subsequent cycle. Thus, the coin cells seem to confirm the benefit of zinc as a nucleation layer.

In all of the tests described above, lithium has been plated to a capacity of approximately 1 mAh cm⁻² or 5 μm. For commercially relevant, high energy density, lithium metal cells, the cycled lithium capacity should be closer to 3 mAh cm⁻² or 15 μm. In order to test the effect of zinc in a more practical scenario, a 64-channel Cu cell plate was modified with a linear wedge of zinc and cycled against lithium with an average plating/stripping capacity of approximately 3 mAh cm⁻². The parameters of the Zn wedge were identical to those previously discussed. The Zn coating increased in thickness from 100 to just under 900 nm from the rightmost to leftmost column of the plate with column 5 left as an unmodified control. The CE of all 64-channels over 100 cycles in 1 M LiPF₆ FEC:TFEC is summarized in Figure S9. Even under the more aggressive test parameters the benefit of the Zn coating is still apparent. The CE values for all the channels in the unmodified control column become unstable and drop after about 60 cycles. With the higher capacity of cycled lithium, some of the electrodes with a thin Zn coating, particularly those with the thinnest coating in column 8 also show unstable CE after 60 to 70 cycles. However, the electrodes with thicker Zn coating (columns 1–3) seem to maintain their performance under the aggressive conditions with fairly stable CE values averaging around 98.8 to 99.0%. These results are encouraging as they suggest that the benefit of the Zn nucleation layer can be extended to cells with practically relevant capacities.

**Lithium surface morphology.**—To augment the quantitative CE analysis, Scanning Electron Microscopy (SEM) was used to qualitatively examine the effect of electrolytes and surface treatments on the morphology of the plated lithium both initially and after extended cycling. For the SEM analysis, 1 mAh cm⁻² of lithium was plated at 1 mA cm⁻² in Cu/Li half cells. The lack of uniform pressure in conventional coin cells can make the accurate comparison of plated lithium samples difficult. Pressure has a strong influence on the morphology of plated lithium and the pressure applied to the edges of the coin cell electrode is generally higher than the pressure at the center. As a result, for this analysis, similar spots at both the center and edge of the plated lithium electrode were compared for each of the samples. Figures 13a1 and 13a2 show the morphology of lithium in 1M LiPF₆ EC:DEC control electrolyte after the first plating cycle. At the center of the electrode (a1) the lithium is very porous with small features and obvious rod-shaped dendritic growth. Under the higher pressure at the electrode edge (a2) the lithium morphology appears slightly less porous, but there is still clear evidence of mossy, dendritic lithium. With extended cycling the morphology of the plated lithium only worsens, becoming even more porous. After the 50th plating cycle in control electrode, the majority of lithium growth at the both the center (a3) and edge (a4) of the electrode is in the form of needle-shaped dendrites with diameters of approximately 200 nm.

Figure 11. Sputtered zinc modified combinatorial cell plate before (a) and after (b) 100 CV cycles of lithium plating and stripping; column 5 from the left was masked during sputtering to give an unmodified control column.
Figure 12. (a) Coulombic efficiency vs. cycle number comparing lithium cycling (1 mAh at 1C) in Cu-Zn|Li coin cells to unmodified Cu|Li coin cells in fluorinated electrolytes; (b) voltage vs. time profiles for the Cu-Zn|Li and Cu|Li coin cells over the first two lithium plating and stripping cycles.

Figure 13. (a1-d1; a2-d2) SEM images of lithium morphology after the first plating cycling (1 mAh cm\(^{-2}\) at 1 mA cm\(^{-2}\)) in control electrolyte on Cu (a1 and a2) and in fluorinated electrolyte on Cu (b1 and b2), sputtered carbon (c1 and c2), and sputtered zinc (d1 and d2). The images on the left (a1-d1) were taken from the center of the electrode and those on the right (a2-d2) were taken from the edge of the electrode; (a3-d3; a4-d4) Lithium morphology after extended cycling (1 mAh cm\(^{-2}\) at 1 mA cm\(^{-2}\)) in control electrolyte on Cu (a3 and a4) and in fluorinated electrolyte on Cu (b3 and b4), sputtered carbon (c3 and c4), and sputtered zinc (d3 and d4). The images on the left (a3-d3) were taken from the center of the electrode and those on the right (a4-d4) were taken from the edge of the electrode.
to 1 μm. This type of lithium growth corresponds to the low (~90%) CE values shown for the control cells.

With the fluorinated electrolyte, there is a significant improvement in lithium morphology after the 1st plating cycle (13 b1 and b2). At the center of the electrode (b1) the lithium is still porous but the features are much larger (5–15 μm) compared to the control which means less surface area. This low surface area is desirable as it suppresses side reactions between lithium and the electrolyte leading to higher coulombic efficiency. With the higher pressure at the edge of the electrode (b2) the porosity and surface area are even smaller with the appearance of columnar type lithium deposits, the desired morphology for lithium metal anodes. The large difference in morphology between the center and edge of the electrode here highlights the influence of pressure and the importance of reporting images from multiple electrode regions. At both the center and edge, the morphology in 1M LiPF6 FEC:TFE electrolyte appears far superior to the control. This improvement over the control morphology is also demonstrated after extended cycling (13 b3 and b4) in fluorinated electrolyte. After the 75th plating cycle, the lithium features have become much smaller and there is an obvious increase in surface area, however, compared to the control, the overall porosity still appears to be lower and there is much less needle-like dendritic growth.

The effect of the sputtered carbon surface coating after 1 plating cycle in fluorinated electrolyte is shown in Figures 13c1 and 13c2. As mentioned, the sputtered carbon coating is expanded and broken during lithiation and plating. At both the center (13c1) and edge (13c2) of the electrode there is clear evidence of sputtered carbon fragments amongst the plated lithium. After the 75th plating cycle the much finer lithium deposits have plated around and underneath fragments of the broken surface coating at the center of the electrode (13c3). Due to the deterioration of the coating, it’s not surprising that after cycling, the lithium morphology on the carbon coated samples does not appear much different than that shown on bare copper in the same electrolyte.

The lithium morphology on the sputtered Zn after 1 plating cycle is shown in Figures 13d1 and 13d2. Additionally, Figure S10 shows the sputtered Zn coating after the lithium has been stripped off the electrode. Unlike the sputtered carbon electrodes, there is no evidence of coating fragments after either plating or stripping, which suggests the Zn coating has remained intact. At the center (13d1) of the sample, the lithium morphology appears slightly more compact and less porous than that shown on the Cu electrode in the same electrolyte. Under sufficient pressure at the edge (13d2) of the Zn electrode, the lithium shows the desired columnar type morphology similar to that shown on the Cu. After the 75th plating cycle the lithium growth at the center and edge of the Zn electrode again appears to be slightly denser and less porous than the growth on the Cu. This noticeable improvement in morphology combined with the improved CE shown in both the combinatorial and coin cell tests demonstrate the benefit of the Zn nucleation layer.

Conclusions

A combinatorial electrochemical approach was demonstrated as an effective technique for evaluating lithium metal cycling performance as a function of electrolyte type and the electrode surface coating. With unmodified Ni electrode cell plates, the combinatorial cell showed consistent lithium plating/stripping behavior across all 64-channels. From a variety of electrolytes screened in the combi cell, it was determined that a fluorinated solvent system (1M LiPF6 FEC:TFE) showed the best performance with stable cycling and an average lithium cycling efficiency of 98.3% over 40 cycles compared to only 91.0% for the non-fluorinated 1M LiPF6 EC:DEC control electrolyte. Galvanostatic cycling in conventional Li batteries, the thicker Zn coating increased the CE from 97.6 to 98.2% in FEC:TFE electrolyte and resulted in more stable cycling. These results not only reveal some promising strategies for improving lithium metal cycling efficiency, but they also outline the framework of a new combinatorial approach for the design and evaluation of anodes for lithium metal cells.

ORCID

J. R. Dahn https://orcid.org/0000-0002-6997-2436

References

1. D. Lin, Y. Liu, and Y. Cui, “Reviving the lithium metal anode for high-energy batteries,” Nat. Nanotechnol., 12, 194 (2017).
2. G. Zheng, S. W. Lee, Z. Liang, H. W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu, and Y. Cui, “Interconnected hollow carbon nanospheres for stable lithium metal anodes,” Nat. Nanotechnol., 9, 618 (2014).
3. X.-B. Cheng, R. Zhang, C.-Z. Zhao, and Q. Zhang, “Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review,” Chem. Rev., 117, 10403 (2017).
4. A. Aurbach, Y. Gofer, and J. Langzam, “The Correlation Between Surface Chemistry, Surface Morphology, and Cycling Efficiency of Lithium Electrodes in a Few Polar Aprotic Systems,” J. Electrochem. Soc., 136, 3198 (1989).
5. F. Shi, A. Pei, A. Vailionis, J. Xie, B. Liu, J. Zhao, Y. Gong, Y. Cui, and T. E. Mallouk, “Strong texturing of lithium metal in batteries,” (n.d.).
6. Y.-L. Lu, M. Tikker, R. Mohanty, K. Hendrickson, L. Ma, and L. A. Archer, “Stable Cycling of Lithium Metal Batteries Using High Transference Number Electrolytes,” Adv. Energy Mater., 5, 1402073 (2015).
7. R. Khurana, J. L. Schaefer, L. A. Archer, and G. W. Coates, “Suppression of Lithium Dendrite Growth Using Cross-Linked Polyethylene/Polyethylene oxide) Electrolytes: A New Approach for Practical Lithium-Metal Polymer Batteries,” J. Am. Chem. Soc., 136, 7395 (2014).
8. B. Xu, W. Li, H. Duan, H. Wang, Y. Guo, H. Li, and H. Liu, “Li3PO4-added garnet-type Li10La2Zn12TeO3S2 for Li-dendrite suppression,” J. Power Sources, 354, 68 (2017).
9. K. (Kelvin) Fu, Y. Gong, B. Liu, Y. Zhi, S. Xu, Y. Yao, W. Luo, C. Wang, S. D. Lacey, J. Dai, Y. Chen, Y. Mo, E. Wachsmann, and L. Hu, “Toward garnet electrolyte-based Li metal batteries: An ultrafast, highly effective, artificial solid-state electrolyte/metallic Li interface,” Sci. Adv., 3, e1601659 (2017).
10. K. F. Yu, G. Yong, J. Dai, A. Gong, X. Han, Y. Yao, C. Wang, Y. Wang, Y. Chen, C. Yan, Y. Li, E. D. Wachsmann, and L. Hu, “Flexible, solid-state, ion-conducting nanowire with 3D garnet nanofiber networks for lithium batteries,” Proc. Natl. Acad. Sci. U. S. A., 113, 7094 (2016).
11. D. P. Wilkinson, H. Blom, K. Brandt, and D. Wainwright, “Effects of physical constraints on Li cyclability,” J. Power Sources, 36, 517 (1991).
12. T. Hirai, “Influence of Electrolyte on Lithium Cycling Efficiency with Pressurized Electrode Stuck,” J. Electrochem. Soc., 141, 611 (1994).
13. C.-P. Yang, Y.-X. Yin, S.-F. Zhang, N.-W. Li, and Y.-G. Guo, “Accommodating lithium into 3D current collectors with a submicron skeleton toward long-life lithium metal anodes,” Nat. Commun., 6, 5058 (2015).
14. Q. Yun, Y.-B. He, W. Lv, Y. Zhao, B. Li, F. Kang, and H.-Q. Yang, “Chemical Dendroyling Derived 3D Porous Current Collector for Li Metal Anodes,” Adv. Mater., 28, 6932 (2016).
15. Q. Li, S. Zhi, and Y. Lu, “3D Porous Cu Current Collector/Li-Metal Composite Electrode for Stable Lithium-Metal Batteries,” Adv. Funct. Mater., 27, 1604622 (2017).
16. F. Ding, W. Xu, X. Chen, J. Zhang, Y. Shao, M. H. Engelhard, Y. Zhang, T. A. Blake, G. L. Grafi, X. Liu, and J.-G. Zhang, “Effects of Cesium Cations in Lithium Deposition via Self-Healing Electrostatic Shield Mechanism,” J. Phys. Chem. C., 118, 4043 (2014).
17. J. Qian, B. D. Adams, J. Zheng, W. Xu, W. A. Henderson, J. Wang, M. E. Bowden, S. Xu, J. Hu, and J. G. Zhang, “Anode-Free Rechargeable Lithium Metal Batteries,” Adv. Funct. Mater., 26, 7094 (2016).
18. J. Qian, W. A. Henderson, W. Xu, P. Bhattacharya, M. Engelhard, O. Borodin, and J. G. Zhang, “High rate and stable cycling of lithium metal anode,” Nat. Commun., 6, 6362 (2015).
19. B. Lin, W. Xu, F. Yan, S. T. Kim, M. H. Engelhard, X. Sun, D. Mei, J. Cho, C.-M. Wang, and J.-G. Zhang, “Stabilization of Li Metal Anode in DMSO-Based...
