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Article

Chemical Compatibility of Battery Electrolytes with Rapid Prototyping Materials and Adhesives

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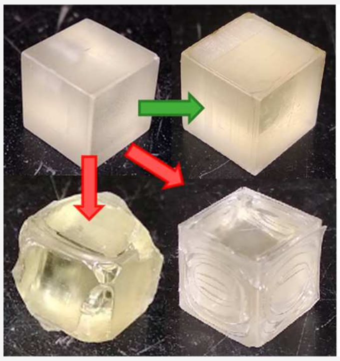
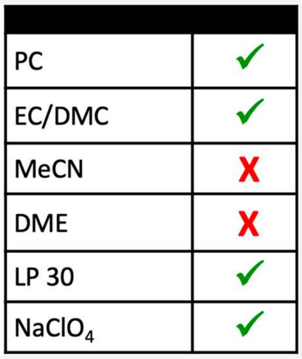
ABSTRACT: Custom electrochemical cells are necessary for fundamental in situ characterization experiments and applied transport studies of next-generation batteries. Limited data on the chemical compatibility of nonaqueous battery electrolytes and engineering materials frustrate experimental progress across laboratories. In this work, we evaluate the compatibility of epoxy-based adhesives and 3D printing resins with nonaqueous battery electrolytes. Materials compatibility requires not only mechanical and chemical stability but also the absence of electroactive dissolution products. We show that some adhesives can generate electroactive products that may cause experimental artifacts. The combined findings guide the material selection process for experimental electrochemists and offer a new protocol for future materials compatibility testing to capture previously overlooked effects.





PC	✓
EC/DMC	✓
MeCN	✗
DME	✗
LP 30	✓
$NaClO_4$	✓

1. INTRODUCTION

Decades of coordinated research and development have led to the commercial success of lithium-ion batteries. However, further improvements in cost, density, safety, and lifetime are still needed to reach the full potential of lithium-ion and "beyond lithium" in grid-scale and vehicle applications. Advanced characterization is key to mechanistic understanding that enables improved materials and devices. However, in situ, in operando, and combined online-electrochemical techniques almost always demand custom experimental setups due to variation between characterization tools and laboratory environments. Material selection for such setups is made challenging by limited published chemical compatibility data for battery electrolytes with engineering materials. Open data on chemical compatibility would prevent researchers across laboratories from repeating experimental errors to greatly improve the pace of scientific progress.

Hardware/fixtures surrounding electrochemical cells for in situ characterization must satisfy demanding design criteria including: chemical and electrochemical stability; resistance to leaks of electrolyte, oxygen, or moisture; and avoiding interference, e.g., transparent to specific wavelengths.[1,2] Techniques requiring transparency often employ Kapton, quartz, or borosilicate windows that necessitate an additional adhesive, commonly epoxy-based, to create a leakproof seal.[3,4] Epoxies can also be used as an insulating layer to control the geometry or surface area of an active material,[5,6] and to offer structural support to otherwise brittle or flexible materials.[7,8] They are further used as insulating or adhesive layers in microelectrodes where electroactive materials are embedded in epoxy and then polished flat[9,10] and as sealants for microelectrode arrays[11] and microbatteries.[4]

The capacity of additive manufacturing (3D printing) for rapid prototyping and complex geometries can greatly facilitate cell design for in situ characterization.[12] 3D printing can fabricate and prototype novel electrode geometries[13,14] as well as testing apparatus, including cell holders[15] and novel flow cells.[16,17] The rapid prototyping capabilities of 3D printing are of particular value to flow cells, enabling optimization of flow geometries without the time and expense of retooling. The wide range of polymer chemistries accessible by additive manufacturing affords researchers many options for material selection, each with advantages and potential disadvantages. Among additive manufacturing technologies, fused deposition has popularity for its low cost and ease of setup. However, printed thermoplastics such as polylactic acid and acrylonitrile butadiene styrene are limited by thermal compatibility and poor layer resolution that can result in high porosity and electrolyte leakage.[18] Stereolithography uses ultraviolet (UV) light to cure a photopolymer, often acrylate-based, layer-by-layer. It benefits from a much finer layer and spot resolution but suffers from a more limited palette of useable resins.

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Despite their importance, materials selection and compatibility for both adhesives and 3D resins are largely determined on an ad hoc basis. To the best of our knowledge, very few studies on material compatibility thus far have been presented. In one notable example, Channon et al. reported 24 h stability data for two UV-cured resins in several common solvents, but none that are ordinarily used in battery applications.[19] There is a clear need for easily accessible data on material compatibility between common engineering materials and nonaqueous battery electrolytes.

In this work, we present a study of materials compatibility in four common aprotic solvents and two battery electrolytes: propylene carbonate (PC), a common solvent for sodium ion batteries; ethylene carbonate−dimethyl carbonate (EC:DMC), the industry standard for lithium ion batteries; acetonitrile (MeCN), widely used for redox flow battery and cyclic voltammetry applications; and dimethoxyethane (aka monoglyme, DME), which has shown promise in beyond-lithium-ion batteries including lithium−sulfur, solvates, lithium metal, and magnesium ion. We evaluate compatibility of UV-cured polyurethane acrylate resin for 3D-printing applications and common adhesives capable of room-temperature cure. The effectiveness of these materials to resist chemical decomposition by nonaqueous electrolytes is presented here in the form of four-week-long storage tests and electrochemical sensing of dissolved products.

2. EXPERIMENTAL SECTION

2.1. Fabrication. Selected adhesives were Hysol 9462 (Loctite), 5-ton epoxy (Devcon), Gorilla 5 min epoxy (Gorilla Glue, Inc.), MarineWeld (JB Weld), and 406/19 (Lord Corp). Adhesive compositions are based on the manufacturer-supplied safety data sheets. All candidates are two-part adhesives with an epoxy resin and curing agent. Gorilla Glue, Hysol, Devcon, and MarineWeld have similar formulations with a bisphenol A-epichlorohydrin-based polymer and an aliphatic polyamine curing agent, a standard for most epoxies. The first three use an alicyclic polyamine, whereas MarineWeld uses a chain polyamine. Devcon, Hysol, and MarineWeld employ additional additives in the curing agent to increase cure rate and hardening. In contrast, Lord involves a proprietary combination of methyl methacrylate and epoxy-based resins, which results in a faster cure rate. Fillers such as silica and titanium dioxide can be used to improve performance, including cure rate, adhesion, modulus and chemical resistance.[20,21] In this study, Lord and Hysol both contain silica, whereas MarineWeld contains TiO_2.

Samples were mixed and cured at room temperature according to manufacturer specifications. For additive manufacturing, a clear 405 nm UV Resin (Anycubic) was printed at a 50 μm layer height with an LCD-based 3D printer (Anycubic, Photon). After rinsing printed cubes in isopropyl alcohol, the cubes were tested as printed ("green") or cured under a 405 nm UV lamp using a custom-built reflective chamber. 3D printed samples are referred to as UV followed by the cure duration in minutes, where UV 0 refers to the green resin.

Polytetrafluoroethylene (PTFE) and Viton fluoroelastomers were used as controls for null and high swelling cases, as PTFE is known to have excellent chemical resistance and Viton has poor compatibility with esters and polar organic solvents.

2.2. Soaking. Solvents were propylene carbonate (98%, Sigma-Aldrich), acetonitrile (99.5%, Beantown Chemical), 1,2-dimethoxyethane (≥99.0%, Honeywell), ethylene carbonate (98%, Sigma-Aldrich), and dimethyl carbonate (99%, Beantown Chemical). EC and DMC were mixed in a 1:1 weight-by-weight solution. All solvents were dried for a minimum of 72 h over 4 Å molecular sieves.[22] EC and DMC were mixed in a 1:1 weight-by-weight solution. Electrolytes were 1 M sodium perchlorate (98%, Sigma-Aldrich) in PC and as-formulated LP 30 (Gotion), which reports 1 M $LiPF_6$ in 50:50 vol:vol EC: DMC.

Samples were soaked for 24 h, 1 week, and 4 weeks and weighed at each interval. Prior to weighing, samples were dried to remove excess solvent. Any physical changes such as swelling, delamination, or fracturing in solvent were observed by optical inspection. Mechanical durability was evaluated by applying mild and moderate applied forces using the tip of a pair of tweezers. Mild and moderate forces were calibrated on a scale to approximately 50 ± 10 g and 250 ± 50 g, respectively. Samples that deformed under pressure were deemed "softened", whereas samples that disintegrated in the solvent or broke apart under mild pressure were deemed "failures". Three replicates were tested for each material−solvent combination.

2.3. Electrochemistry. The electroactivity of dissolution products was evaluated via voltammetry. Five-hundred milligram epoxy samples were soaked for 1 week in 15 mL of LP 30. Samples were then removed from vials, and the remaining electrolyte was added to an electrochemical cell with Li reference and Pt wire counter electrodes separated by fine mesh glass frits (Chemglass) and a glassy-carbon working electrode in a rotating-disk electrode (RDE) ensemble (Pine). Cyclic voltammetry of the electrolyte was performed on the RDE between 1.5 and 4 V vs Li/Li^+ and at 0, 400, 900, and 1600 rpm rotation rates. All voltages presented in this work are given vs the Li/Li^+ reference.

3. RESULTS

3.1. Soak Tests. *Propylene Carbonate.* Both green and cured UV resin showed excellent stability in PC with less than 0.1% weight change over 4 weeks, on-par with PTFE. All adhesives underwent some degree of swelling within PC, indicated by weight increases as shown in Figure 1a. Hysol showed a slower initial increase, but after 4 weeks, Hysol, Lord, and MarineWeld all swelled by 5.5−7%. As summarized in Table 1, the Lord epoxy also softened after 1 week but still maintained mechanical integrity over the full testing interval. Devcon and Gorilla Glue both increased by approximately 11% over 4 weeks, but Gorilla Glue exhibited mechanical failure. Samples disintegrated as early as 1 week into testing. As expected, Viton swelled immediately in the PC, as shown in Figure 1b. Its weight increased by 80%, and it was easily damaged with handling after 24 h of soaking. Consistent with expectations, PTFE showed very small changes, increasing by less than 0.5% over the course of 4 weeks in all solvents.

Ethylene Carbonate/Dimethyl Carbonate. Because they are both composed of carbonate esters, EC:DMC showed similar trends to PC but exhibited more limited compatibility. All resins swelled to some degree with EC:DMC, as shown in Figure 2, and these increases were more significant than with PC. Although the 3D printing resin appeared stable in PC with minimal weight changes, the green material showed weight changes of 12% after 4 weeks and developed cracks at the surface, as seen in Figure 3c. As summarized in Table 1, postprint curing greatly improved stability, reduced the weight

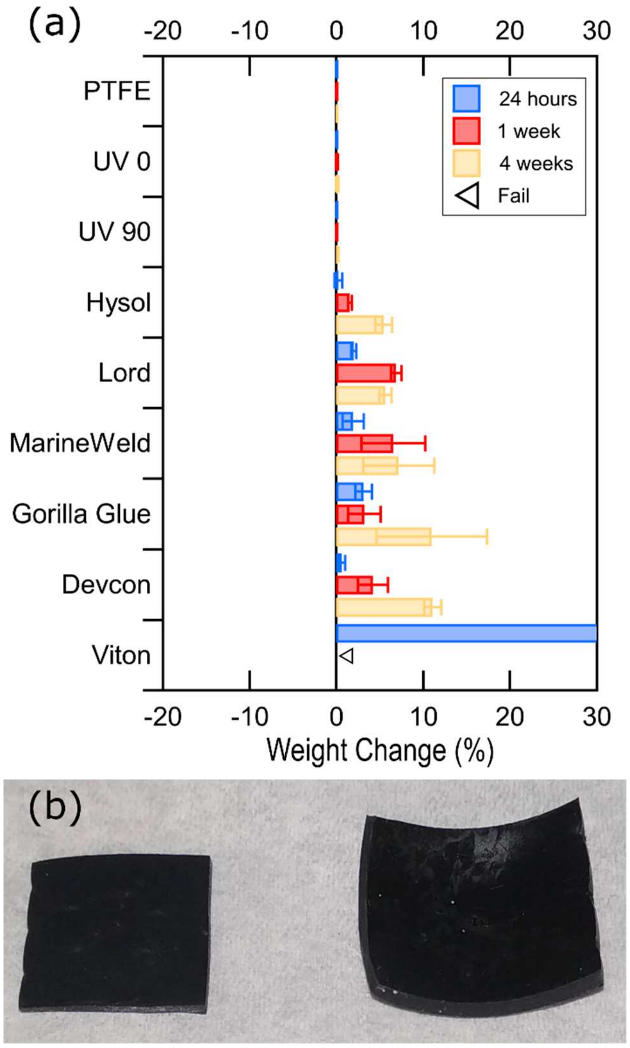

Figure 1. (a) Average weight change for materials in propylene carbonate (PC) after 24 h, 1 week, and 4 weeks in solution. Inset shows exceptional weight change for Viton. (b) Viton before and after soaking.

Table 1. Summary of Compatibility between All Materials and Solvents/Electrolytes[a]

material	PC	EC/DMC	MeCN	DME	LP 30	PC/$NaClO_4$
PTFE	A	A	A	A		
3D resin (green)	A	B	D	D		
3D resin (30 min)		A	C	B		
3D resin (90 min)	A	A	B/C	B	A	A
Loctite Hysol	B	B	B	B	C	B
Lord 406/19	C	C	C	C	C	C
JB Weld	B	C	A	B	C	C
Gorilla Glue	C	D	C	D		
Devcon	B	C	D	D		
Viton	D	D	C	C		

[a] A = less than 2% change over 1 month, no significant change in properties; B = 2−10% change over 1 month, with mild to no mechanical degradation; C = greater than 10% change and/or mechanical degradation in 1−4 weeks; D = significant changes or failure within 24 h.

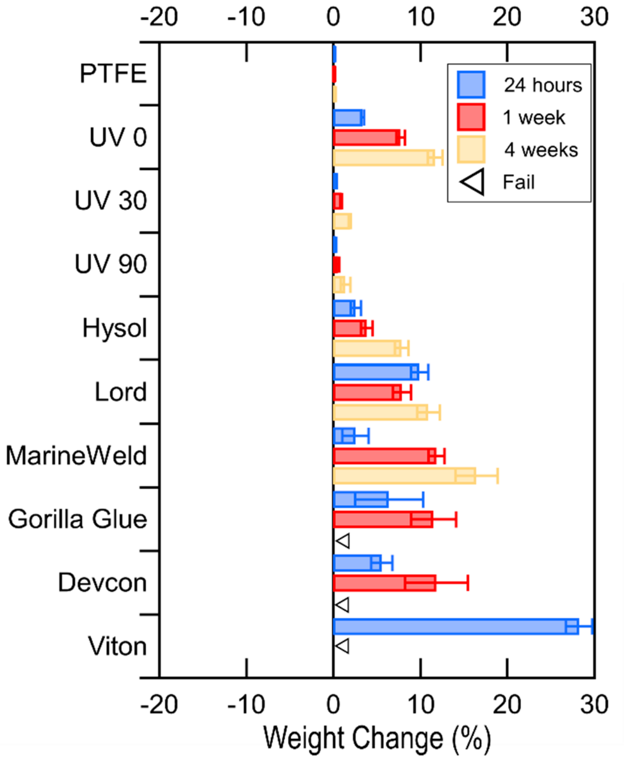

Figure 2. Average weight change for materials in 1:1 ethylene carbonate:dimethyl carbonate (EC:DMC) after 24 h, 1 week, and 4 weeks in solution.

gain to less than 2%, and prevented crack formation. Hysol showed the lowest weight gain of all adhesives over 4 weeks of exposure. The weight gain remained under 8%, whereas the other adhesives exceeded 10%, although rates of change varied between all the materials. The Lord and Hysol epoxies softened after 24 h and 1−4 weeks, respectively, but both still maintained mechanical integrity over the full testing interval. MarineWeld developed a crumbly texture and disintegrated after 4 weeks. Gorilla Glue epoxy remained rigid but cracked and broke apart easily after 1−7 days of testing in EC:DMC, in a more accelerated failure mechanism compared to PC. Devcon swelled at a similar rate to Gorilla Glue, but remained stable after 1 week; however, at 2 weeks, it showed signs of bending and breakage. Viton swelled immediately in the EC:DMC, increasing by 28% and becoming easily damaged with handling after 24 h. Materials that can last on the order of weeks in PC may fail in the order of days in EC:DMC and more significant weight changes exceeding 10% can be expected. As with PC, the use of Viton as a gasket material should be avoided.

Dimethoxyethane. DME caused weight loss for many of the materials and a high degree of mechanical failure, as shown in Figure 3a and Table 1. The green 3D printing resin underwent shrinkage and significant geometric deformation after 24 h, as seen in Figure 3b, whereas the cured resin showed increased weight. After 4 weeks, the 30 min-cured resin showed the formations of cracks and material peeling at the surface, as shown in Figure 3c, but no loss in mechanical strength or integrity. Increasing the cure time to 90 min did not significantly decrease the weight change, 5.6 vs 6.2% on average, but did reduce the formation of cracks on the cube surface. UV curing results in additional cross-linking of acrylate chains, and extended curing beyond the manufacture recommendations may be needed to maintain the stability of UV-cured resins in 3D printed parts for certain solvents, as the

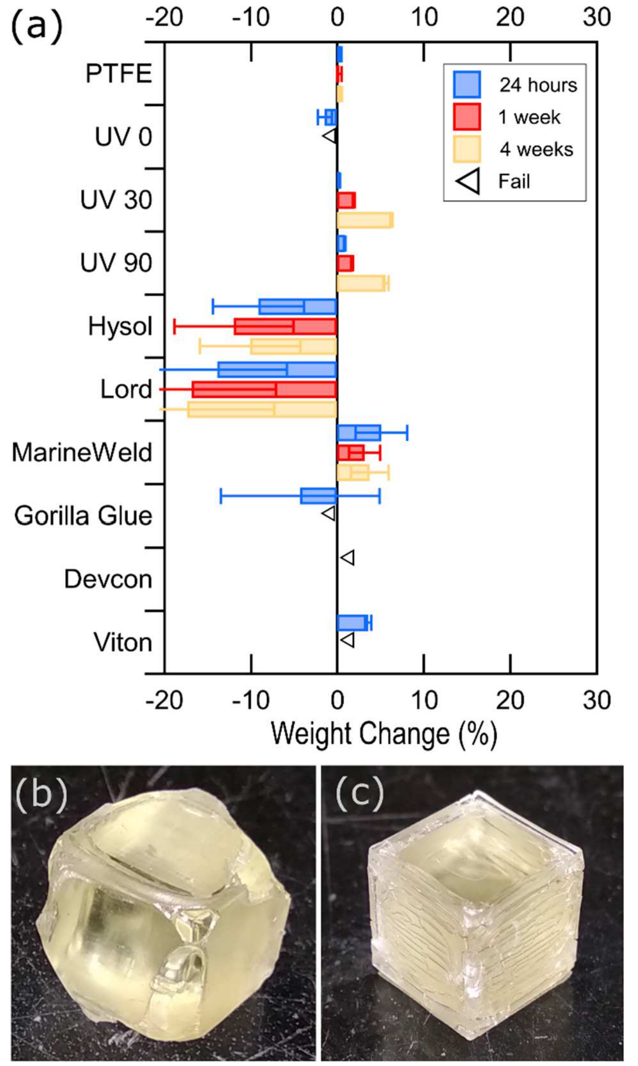

Figure 3. Average weight change for materials in dimethoxyethane (DME) after 24 h, 1 week, and 4 weeks in solution. (b) Deformation of uncured resin after 24 h. (c) Crack formation on cured resin after 4 weeks.

required degree of cross-linking must be optimized for any build geometry or application. Modification to the resin formulation may also improve stability. Commercially available high-temperature resins have been shown to improve chemical resistance over baseline formulations in some solvents, including acetonitrile.[19] MarineWeld showed the best stability of any adhesive and was the only epoxy to swell rather than shrink. It showed an initial change of 5% in the first 24 h and remained stable over 4 weeks of testing without changes to texture or mechanical stability. Hysol and Lord both showed severe weight losses greater than 10% over 4 weeks but remained rigid and mechanically stable throughout testing. Gorilla glue and Devcon epoxy, on the other hand, both failed within 24 h. The deterioration of the Gorilla glue samples made accurate measurement more difficult, resulting in very high deviation for weight change, whereas the Devcon softened and completely broke apart in the solvent, preventing any measurement. These epoxies should be avoided for applications with wetted contact in ether-based solvents. Viton showed less swelling with DME than other solvents and maintained integrity after 24 h but disintegrated after 1 week of exposure. Caution should be used when employing Viton in seals and frequent checks or replacement may be necessary.

Acetonitrile. MeCN showed similar compatibility trends to DME, as summarized in Table 1. The green 3D printing resin increased in weight by less than 1% but showed significant geometric deformation after 24 h and was removed from testing. The cured resin increased in weight by 10% over 4 weeks, as shown in Figure 4, and showed the formations of cracks at the surface after 4 weeks of soaking. Additional curing did not change the rate of mass changes but did reduce the severity of crack formation. Hysol and Lord underwent 2.5 and 5.3% mass loss, respectively, over 4 weeks but remained mechanically stable throughout testing, although Hysol softened after 1 week of testing. Devcon completely broke apart during the first 24 h in the solvent, whereas Gorilla glue increased by 3.8% and failed after 1 week, having exhibited both mechanical failure and softening. Viton changed by less than 1% and maintained good mechanical integrity after 24 h, but underwent significant mechanical degradation following 1 week of exposure, a clear sign that weight change alone is not a sufficient metric for evaluating compatibility.

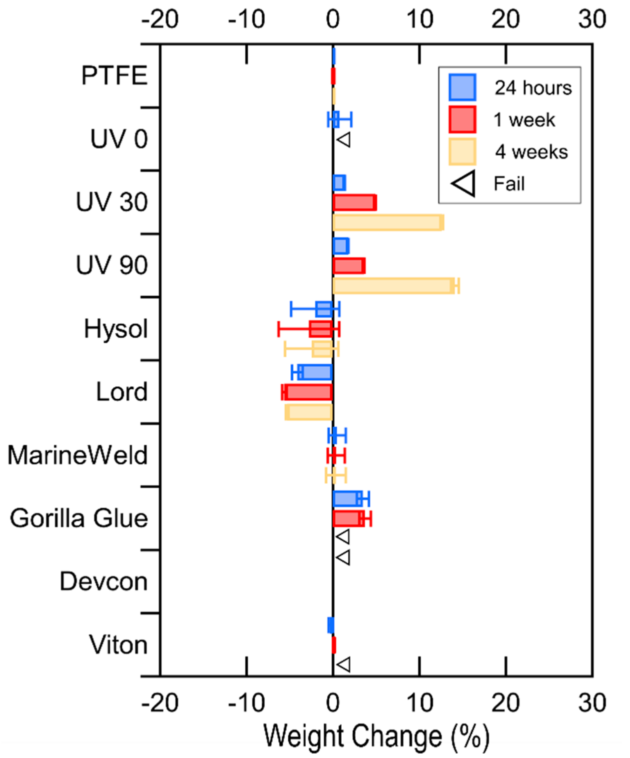

Figure 4. Average weight change for materials in acetonitrile (MeCN) after 24 h, 1 week, and 4 weeks in solution.

Electrolytes. Because electrolyte salts can have additional interactions with resin chemistry, soak tests were conducted in characteristic sodium and lithium-ion battery electrolytes. On the basis of solvent compatibility, the 90 min cured UV resin, Hysol, Lord, and MarineWeld were tested. Comparison of PC and 1 M $NaClO_4$ in PC showed comparable weight changes over the first week and an additional 2−5% increase versus neat PC after 4 weeks, as shown in Figure 5a. As summarized in Table S1, no adhesive underwent failure, but Lord softened within 24 h of soaking in sodium-based electrolyte as compared to 1 week in neat PC and MarineWeld softened after 4 weeks. Comparison of LP 30, which uses EC:DMC as a

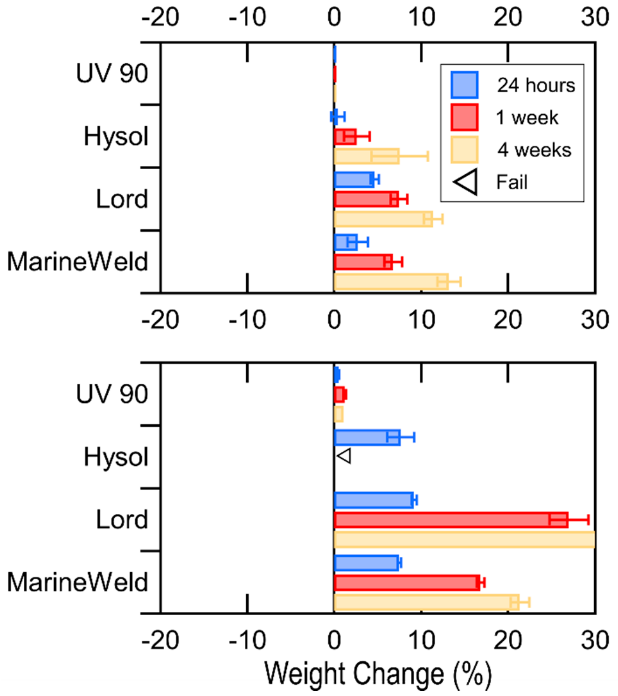

Figure 5. Average weight change for materials after 24 h, 1 week, and 4 weeks in (a) 1 M Sodium Perchlorate in PC and (b) LP 30.

solvent, to neat EC:DMC showed a trend of greater than 5% additional weight change for the adhesives at each time step, as shown in Figure 5b. Hysol showed the worst compatibility in LP30; it softened significantly and broke after 1 week compared to after 4 weeks in neat EC:DMC, and was the only material with increased physical or mechanical degradation in LP30 compared to neat EC:DMC, as summarized in Table S1. The UV resin displayed similar changes in both electrolytes compared to the neat solvents, showing promise for UV cure-based 3D printing of novel architectures as long as cure times are optimized. Decreased stability in the presence of $LiPF_6$, but not $NaClO_4$, is consistent with the known instability of the PF_6 anion.[23,24] Regardless of the mechanism, differences between salts and neat solvents highlight the specificity of chemical compatibility for battery applications.

3.2. Electrochemistry/Electroactive Product Formation. For any wetted materials in contact with electrolyte, chemical stability is as important as mechanical stability. Cyclic voltammetry was performed in neat LP30 and LP 30 after soaking Lord, Hysol and UV resin. We found that Lord epoxy produced an electroactive product that was reduced at approximately 2 V, as seen in Figure 6a. The reduction current was consistent with a mass-transfer limited process, as shown by the linear relationship between current and square root of the rotation rate, as seen in Figure 6b. The linearity of the Levich plot strongly supports the presence of a soluble product leached or generated from the epoxy during soaking. The presence of such products should deter the use of Lord in applications with extended wetted contact and sensitive electrochemical measurements, especially at low potentials.

4. DISCUSSION

The results of weight changes and material degradation are summarized in Table 1 and Table S1. Materials with an A represent excellent stability (<2% change). B represents good short-term stability but diminished long-term stability (<10% change over 4 weeks) and some softening or mechanical degradation. C represents significant deformation and caution needed, with more than 10% change and/or mechanical degradation in 1−4 weeks. Material-solvent combinations with a D rating exhibited massive deformation or failure within 24 h and are not recommended. Weight gains are indicative of solvent uptake, whereas weight losses are indicative of material dissolution. For applications with short contact periods (<24 h) or minimal wetted contact areas, materials that scored B or C could be acceptable, whereas cells intended for long-term testing or repeated exposure should be limited to materials with A or B scores. The target application will also determine the tolerance to minor swelling or deformation is acceptable. For instance, in microfluidic devices where high dimensional precision is of utmost importance, geometric variations like swelling are not acceptable, whereas cells for in situ spectroscopy may tolerate such deformation. Although trade-offs will still need to be evaluated on a case-by-case basis, the compatibility data presented here better inform that decision-making process.

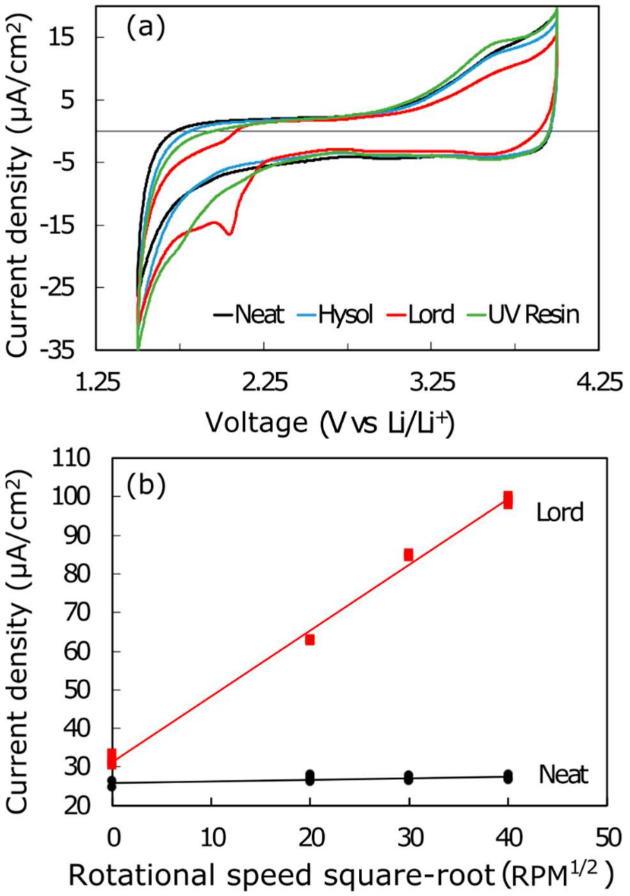

Figure 6. Electroactive product analysis for LP 30 electrolyte exposed to select materials for 1 week. (a) Cyclic voltammetry between 1.5 and 4 V at 0 rpm, and (b) Levich analysis of current at 1.5 V at 0, 400, 900, and 1600 rpm.

Here we show the promising stability of UV-sensitive 3D printing resins for applications with electrochemical testing of nonaqueous chemistries, especially in PC. Optimization of cure increased the durability in all solvents. This points to the significant impacts of postprint curing on materials compatibility in 3D printing, and different geometries of printed parts may require additional cure-time optimization. Improved durability may also be achieved through the use of altered resin formulations, some of which are already available from manufacturers for other technical applications, such as high-temperature operation.

The poor performance of Gorilla Glue, which does not include any additives, suggests that adhesives with additional hardeners and fillers will have improved chemical resistance, but the specific combination will still be system-dependent. This study also highlights that material compatibility is not transferable across nonaqueous solvents. For instance, Devcon exhibited moderate stability in carbonate solvents, but failed immediately in both MeCN and DME. Additionally, differences between neat solvents and electrolyte salts add another layer of specificity to compatibility requirements.

Mass changes and mechanical stability are not the only relevant compatibility parameters for electrochemical devices: the nature of degradation species must also be studied and considered. Evidence of electroactive dissolution products from at least one common adhesive suggests that this overlooked phenomenon can cause misleading results or unintended contamination.

5. CONCLUSIONS

Before mechanistic understanding of materials degradation can be achieved, materials compatibility with nonaqueous battery electrolytes must be quantified and benchmarked. A priori understanding of material compatibility can accelerate the development of novel reactor designs for many battery technologies. Here, we present the manner in which many common engineering materials exhibit unacceptable stability in nonaqueous battery electrolytes and solvents through mechanical degradation and the introduction of electroactive products into sensitive systems. The strong performance of acrylate-based 3D-printing resins in nonaqueous battery solvents is exciting because additive manufacturing enables ultrarapid prototyping and fully custom cell geometries. Furthermore, optimizing UV cure-time can improve chemical stability. Furthermore, although mechanical degradation is easily observed, generation of electroactive products is also possible and may cause experimental artifacts. It is important to screen for such effects in systems with sensitive electrochemical measurements. Future device fabricators may use the findings presented here to guide their material selection and as a launching point for understanding the interactions between engineering materials and nonaqueous solvents.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c02121.

Tables summarizing compatibility for all materials and solvents (PDF)

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Notes

The authors declare no competing financial interest.

Biographies

Sophia Lee is a PhD Candidate in the Department of Chemical and Biological Engineering at Drexel University, studying interfacial phenomena and degradation mechanisms in nonaqueous batteries. They are an NSF Graduate Research Fellow and received a S.B. in Chemical Engineering from the Massachusetts Institute of Technology in 2012. Prior to graduate school, Sophia worked as a research engineer commercializing flow batteries for grid scale energy storage.

Oliver C. Harris recently earned a Ph.D. in Chemical and Biological Engineering from Drexel University. His thesis explored failure mechanisms in Li-ion batteries. Dr. Harris has been honored as a recipient of the 2019 Koerner Family Award and the Drexel Graduate College Blue Doctoral Fellowship. Prior to Drexel, Oliver worked as a senior consultant developing and implementing energy-efficiency, renewables, and energy-storage programs for government agencies and utilities.

An Nguyen is currently completing his B.S. in Mechanical Engineering and Mechanics at Drexel University. His interests include product development, device design, and entrepreneurship.

Maureen Tang joined the faculty of Chemical and Biological Engineering at Drexel University in 2014. She received her BS in Chemical Engineering from Carnegie Mellon University in 2007 and her PhD from the University of California, Berkeley, in 2012. While at Berkeley, she received a NSF Graduate Research Fellowship, an NSF East Asia Pacific Summer Fellowship, and the Daniel Cubiciotti Student Award of the Electrochemical Society. Dr. Tang completed postdoctoral work at Stanford University and research internships at Kyoto University, the University of Dortmund, and DuPont. She is the recipient of a 2018 NSF CAREER award, the 2019 College of Engineering Early Career Research Award, and a 2018 Award for Excellence in Peer Review from the ACS PRF. Her research at Drexel focuses on mechanistic analysis of electrochemical reactions and systems.

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■ ABBREVIATIONS AND PHYSICAL PARAMETERS

CV, cyclic voltammetry
DMC, dimethyl carbonate
DME, dimethoxyethane
EC, ethylene carbonate
MeCN, acetonitrile
PC, propylene carbonate

PTFE, polytetrafluoroethylene
RDE, rotating disk electrode
UV, ultraviolet
j, current density, μA/cm^2
ω, rotation rate, RPM
V, voltage, V
Δ, weight change, %

REFERENCES

(1) Bak, S. M.; Shadike, Z.; Lin, R.; Yu, X.; Yang, X. Q. In Situ/Operando Synchrotron-Based X-Ray Techniques for Lithium-Ion Battery Research. *NPG Asia Mater.* **2018**, *10*, 563−580.

(2) Niemöller, A.; Jakes, P.; Kayser, S.; Lin, Y.; Lehnert, W.; Granwehr, J. 3D Printed Sample Holder for In-Operando EPR Spectroscopy on High Temperature Polymer Electrolyte Fuel Cells. *J. Magn. Reson.* **2016**, *269*, 157−161.

(3) Ghanty, C.; Markovsky, B.; Erickson, E. M.; Talianker, M.; Haik, O.; Tal-Yossef, Y.; Mor, A.; Aurbach, D.; Lampert, J.; Volkov, A.; Shin, J. Y.; Garsuch, A.; Chesneau, F. F.; Erk, C. Li^+-Ion Extraction/Insertion of Ni-Rich $Li_{1+x}(Ni_yCo_zMn_z)_wO_2$ ($0.005 < x < 0.03$; y:z = 8:1, w≈1) Electrodes: In Situ XRD and Raman Spectroscopy Study. *ChemElectroChem* **2015**, *2*, 1479−1486.

(4) Wang, J.; Eng, C.; Chen-Wiegart, Y. C. K.; Wang, J. Probing Three-Dimensional Sodiation-Desodiation Equilibrium in Sodium-Ion Batteries by in Situ Hard X-Ray Nanotomography. *Nat. Commun.* **2015**, *6*, 7496.

(5) Yan, Y.; Crisp, R. W.; Gu, J.; Chernomordik, B. D.; Pach, G. F.; Marshall, A. R.; Turner, J. A.; Beard, M. C. Multiple Exciton Generation for Photoelectrochemical Hydrogen Evolution Reactions with Quantum Yields Exceeding 100%. *Nat. Energy* **2017**, *2*, 17052.

(6) Chatterjee, S.; Griego, C.; Hart, J. L.; Li, Y.; Taheri, M. L.; Keith, J.; Snyder, J. D. Free Standing Nanoporous Palladium Alloys as CO Poisoning Tolerant Electrocatalysts for the Electrochemical Reduction of CO2 to Formate. *ACS Catal.* **2019**, *9*, 5290−5301.

(7) Czyzewski, J.; Burzyński, P.; Gawel, K.; Meisner, J. Rapid Prototyping of Electrically Conductive Components Using 3D Printing Technology. *J. Mater. Process. Technol.* **2009**, *209*, 5281−5285.

(8) Zestos, A. G.; Nguyen, M. D.; Poe, B. L.; Jacobs, C. B.; Venton, B. J. Epoxy Insulated Carbon Fiber and Carbon Nanotube Fiber Microelectrodes. *Sens. Actuators, B* **2013**, *182*, 652−658.

(9) Bowyer, W. J.; Clark, M. E.; Ingram, J. L. Electrochemical Measurements in Submicroliter Volumes. *Anal. Chem.* **1992**, *64*, 459−462.

(10) Baranski, A. S.; Fawcett, W. R.; Gilbert, C. M. Use of Microelectrodes for the Rapid Determination of the Number of Electrons Involved in an Electrode Reaction. *Anal. Chem.* **1985**, *57*, 166−170.

(11) Li, D.; Batchelor-Mcauley, C.; Chen, L.; Compton, R. G. Band Electrodes in Sensing Applications: Response Characteristics and Band Fabrication Methods. *ACS Sens.* **2019**, *4*, 2250−2266.

(12) Ambrosi, A.; Pumera, M. 3D-Printing Technologies for Electrochemical Applications. *Chem. Soc. Rev.* **2016**, *45*, 2740−2755.

(13) Maurel, A.; Grugeon, S.; Fleutot, B.; Courty, M.; Prashantha, K.; Tortajada, H.; Armand, M.; Panier, S.; Dupont, L. Three-Dimensional Printing of a LiFePO4/Graphite Battery Cell via Fused Deposition Modeling. *Sci. Rep.* **2019**, *9*, 18031.

(14) Wei, X.; Li, D.; Jiang, W.; Gu, Z.; Wang, X.; Zhang, Z.; Sun, Z. 3D Printable Graphene Composite. *Sci. Rep.* **2015**, *5*, 11181.

(15) Singer, A.; Zhang, M.; Hy, S.; Cela, D.; Fang, C.; Wynn, T. A.; Qiu, B.; Xia, Y.; Liu, Z.; Ulvestad, A.; Hua, N.; Wingert, J.; Liu, H.; Sprung, M.; Zozulya, A. V.; Maxey, E.; Harder, R.; Meng, Y. S.; Shpyrko, O. G. Nucleation of Dislocations and Their Dynamics in Layered Oxide Cathode Materials during Battery Charging. *Nat. Energy* **2018**, *3*, 641−647.

(16) Arenas, L. F.; Walsh, F. C.; de Leon, C. P. 3D-Printing of Redox Flow Batteries for Energy Storage: A Rapid Prototype Laboratory Cell. *ECS J. Solid State Sci. Technol.* **2015**, *4*, P3080−P3085.

(17) Snowden, M. E.; King, P. H.; Covington, J. A.; MacPherson, J. V.; Unwin, P. R. Fabrication of Versatile Channel Flow Cells for Quantitative Electroanalysis Using Prototyping. *Anal. Chem.* **2010**, *82*, 3124−3131.

(18) Ponce De Leon, C.; Hussey, W.; Frazao, F.; Jones, D.; Ruggeri, E.; Tzortzatos, S.; Mckerracher, R. D.; Wills, R. G. A.; Yang, S.; Walsh, F. C. The 3D Printing of a Polymeric Electrochemical Cell Body and Its Characterisation. *Chemical Engineering Transactions* **2014**, *41*, 1−6.

(19) Channon, R. B.; Joseph, M. B.; Macpherson, J. V. Additive Manufacturing for Electrochemical (Micro)Fluidic Platforms. *Electrochem. Soc. Interface* **2016**, *25*, 63−68.

(20) Ragosta, G.; Abbate, M.; Musto, P.; Scarinzi, G.; Mascia, L. Epoxy-Silica Particulate Nanocomposites: Chemical Interactions, Reinforcement and Fracture Toughness. *Polymer* **2005**, *46*, 10506−10516.

(21) Garg, A. C.; Mai, Y. W. Failure Mechanisms in Toughened Epoxy Resins-A Review. *Compos. Sci. Technol.* **1988**, *31*, 179−223.

(22) Williams, D. B. G.; Lawton, M. Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants. *J. Org. Chem.* **2010**, *75*, 8351−8354.

(23) Zaban, A.; Zinigrad, E.; Aurbach, D. Impedance Spectroscopy of Li Electrodes. 4. A General Simple Model of the Li−Solution Interphase in Polar Aprotic Systems. *J. Phys. Chem.* **1996**, *100*, 3089−3101.

(24) Campion, C. L.; Li, W.; Euler, W. B.; Lucht, B. L.; Ravdel, B.; DiCarlo, J. F.; Gitzendanner, R.; Abraham, K. M. Suppression of Toxic Compounds Produced in the Decomposition of Lithium-Ion Battery Electrolytes. *Electrochem. Solid-State Lett.* **2004**, *7*, A194.