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Factors That Control the Formation of Dendrites and Other Morphologies on Lithium Metal Anodes

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Lithium metal is a promising anode material for next-generation rechargeable batteries, but non-uniform electrodeposition of lithium is a significant barrier. These non-uniform deposits are often referred to as lithium “dendrites,” although their morphologies can vary. We have surveyed the literature on lithium electrodeposition through three classes of electrolytes: liquids, polymers and inorganic solids. We find that the non-uniform deposits can be grouped into six classes: whiskers, moss, dendrites, globules, trees, and cracks. These deposits were obtained in a variety of cell geometries using both unidirectional deposition and cell cycling. The main result of the study is a figure where the morphology of electrodeposited lithium is plotted as a function of two variables: shear modulus of the electrolyte and current density normalized by the limiting current density. We show that specific morphologies are confined to contiguous regions on this two-dimensional plot.

Keywords: dendrite, lithium metal, electrolytes, limiting current, rechargeable batteries

INTRODUCTION

There is growing interest in the nature of electrodeposition at lithium metal electrodes due to the current focus on increasing the energy density of rechargeable lithium batteries (Girishkumar et al., 2010; Balsara and Newman, 2013). However, many fundamental challenges must be addressed before lithium electrodes can be deployed in practical devices (Aurbach et al., 2000, 2002). One of the main challenges is the nucleation and growth of protrusions during battery charging (Selim and Bro, 1974; Besenhard and Eichinger, 1976; Epelboin, 2006), which limits the battery lifetime and compromises safety (Yamaki et al., 1998; Aurbach et al., 2002). These protrusions are often referred to as “lithium dendrites.” Strictly, the word “dendrite” implies a branched structure; we propose to not use this term as many non-dendritic morphologies have been reported in the literature.

Lithium metal protrusions have been observed in electrodeposition and cycling experiments conducted in a wide array of electrolytes (Arakawa et al., 1993; Brissot et al., 1998; Ren et al., 2015). We focus on three classes of electrolytes: those based on organic liquids, organic polymers, and inorganic solids. The lithium ions are present in both liquid- and polymer-based electrolytes due to the addition of a suitable salt. In contrast, lithium ions are an integral part of the crystal structure of inorganic solid electrolytes. The passage of current results in salt concentration gradients in liquid- and polymer-based electrolytes (Chazalviel, 1990). On the other hand, these concentration gradients are absent when current flows through inorganic solid electrolytes. In principle, polymer

electrolytes can also be single ion conductors if the anion is covalently linked to the polymer chain (Bouchet et al., 2013). Compared to polymer electrolytes with added salt, there is little information about dendrite morphologies obtained in polymeric single-ion conductors (Cao et al., 2019; Dai et al., 2019). We have thus chosen to only discuss liquid and polymer electrolyte systems with added salt. Our objective is to identify the parameters that control the nature of lithium electrodeposition in liquid electrolytes, polymer electrolytes, and ceramic electrolytes.

The morphology of electrodeposited lithium is affected by many factors, such as current density, salt concentration where lithium is plating, tip radius of the protrusion, temperature, pressure (Yamaki et al., 1998; Gireaud et al., 2006) solid electrolyte interphase (SEI), and the ion transport and mechanical properties of electrolyte (Barton and Bockris, 1961; Diggle et al., 1969; Jana and García, 2017). While we have focused on the anode and the electrolyte, it is well-known that spontaneous reactions between lithium metal and all known electrolytes result in the formation of an SEI layer (Peled, 1979), which plays a central role in stable cycling (Tarascon and Armand, 2001; Meyerson et al., 2019). We have also glossed over the fact that liquid electrolytes are often contained within porous separators that are necessary for battery operation. The observed morphologies are grouped in six different classes described in **Table 1**. Important features of the lithium morphology are summarized in **Table 2**.

Whiskers emanating from the anode represent the simplest morphology of lithium protrusions. These are generally long and thin structures, with widths of about 1 μm and lengths ranging from 10 to 100 μm (see first entry in **Table 2**). Panel a in **Table 1** shows a scanning electron microscopy (SEM) image of whiskers. A schematic of whiskers is shown next to the SEM image in Panel b (**Table 1**). In this schematic, we represent the whiskers connected directly to the anode without an intervening SEI layer (Aurbach et al., 2002). We hypothesize that this must be the case; we are not aware of any direct support for our hypothesis. The whiskers are covered by an SEI layer (Peled, 1979; Aurbach et al., 1987) and surrounded by the electrolyte. Panel c in **Table 1** shows an SEM image of mossy lithium and a schematic of this morphology is shown in Panel d (**Table 1**). This electrodeposited lithium presents solid interconnected pebbles with electrolyte filling gaps and pores. Panels e,f in **Table 1** present lithium dendrites. Dendrites are thin-branched, fractal objects. Lithium globules are presented in Panels g,h (**Table 1**). These objects are found in confined regions, unlike whiskers, mosses and dendrites which tend to form across the entire electrode. Globules are nucleated at an impurity particle in the electrode. Panels i,j in **Table 1**, show lithium trees emanating from the electrode. Unlike mosses that are irregular in shape, the lateral size of trees increases with increasing distance from the electrode. Panels k,l

TABLE 1 | Name, experimental visualization, and schematic of common morphologies of electrodeposited lithium. Images of whiskers, mosses, dendrites, globules, trees, and cracks are reproduced with permission from (a) Steiger et al. (2014), (b) Qian et al. (2015), (c) Bai et al. (2016), (d) Harry et al. (2015), (e) Brissot et al. (1998), and (f) Cheng et al. (2017).

Morphology	Image	Schematic
Whiskers		
Moss		
Dendrites		
Globules		
Trees		
Cracks		

in **Table 1** show lithium deposition through cracks in ceramic electrolytes. In this case, lithium protrusions grow through grain boundaries and result in cracking of the electrolyte. Typical sizes and aspect ratios of the protrusions described above are given in **Table 2**.

There have been many attempts to model the growth of metallic protrusions during electrodeposition from different electrolytes (Barton and Bockris, 1961; Diggle et al., 1969; Monroe and Newman, 2005; Voss and Tomkiewicz, 2006; Mayers et al., 2012). In the case of liquid- and polymer-based electrolytes,

Abbreviations: DEC, Diethyl carbonate; DMC, Dimethyl carbonate; EC, Ethylene carbonate; Li, Lithium metal electrode; LiClO₄, Lithium perchlorate; LiF, Lithium fluoride; LiFSI, Lithium bis(fluorosulfonyl)imide; LiPF₆, Lithium hexafluorophosphate; LiTFSI, Lithium bis (trifluoromethanesulfonyl) imide; LLZO, Li₇La₃Zr₂O₁₂ ceramic electrolyte; PC, Propylene carbonate; PEO, Poly(ethylene oxide); SEI, Solid electrolyte interphase; SEM, Scanning electron microscopy; SEO, Poly(styrene) – b – poly(ethylene oxide); SiC, Silicon carbide.

TABLE 2 | Name, description, characteristic width, and aspect ratio of electrodeposited lithium morphologies.

Name	Description	Width (μm)	Height (μm)	Aspect ratio (length/width)
Whiskers	Objects with minimal branching and kinks surrounded by excess electrolyte	0.1–5	10–100	100
Moss	Interconnected pebble-like objects with electrolyte within gaps and pores	10–50	–	1
Dendrites	Branched, fractal structures	1–20	100–600	10
Globules	Collections of compact globules nucleated on an impurity particle	20–150	20–150	1–2
Trees	Object with a narrow stem and a branched top	At the bottom 10–50 At the top 50–500	100–500	1–3
Cracks	Object growing through grain boundaries or structural weakness in the inorganic solid electrolyte	1	–	5

TABLE 3 | The three categories of electrolytes covered in this review, with their description, order of magnitude of ionic conductivity, κ , order of magnitude of the salt diffusion coefficient, D , characteristic range of steady-state current fraction, ρ_+ , and characteristic mechanical behavior at the temperature of interest.

Electrolyte	Description	Mechanical behavior	Order of magnitude of κ [S.cm ⁻¹]	Order of magnitude of D [cm ² .s ⁻¹]	Order of magnitude of ρ_+
Liquid	Salt dissolved in traditional carbonate-based liquid electrolyte (e.g., EC, PC, DMC)	viscous	10 ⁻²	10 ⁻⁶	0.3–0.4
Polymer	Salt dissolved in a neutral polymer (e.g., PEO, SEO)	elastic	10 ⁻⁴ –10 ⁻³	10 ⁻⁸ –10 ⁻⁷	0.05–0.2
Inorganic solid	Solid ceramic with lithium ions in the lattice (e.g., LLZO)	solid	10 ⁻⁴	–	1

the passage of current results in depletion of salt at the cathode where lithium is being deposited. The current density, i , at which the salt concentration at the cathode approaches zero is defined as the limiting current density, i_L . The depletion of salt has been implicated in lithium protrusion nucleation and growth (Chazalviel, 1990; Bai et al., 2016). However, lithium protrusions have been observed to nucleate and grow at current densities far below the limiting current (Rosso et al., 2001; Xu et al., 2014; Jana and García, 2017). The nucleation and growth of lithium protrusions is also affected by the modulus and other mechanical properties of the electrolyte (Monroe and Newman, 2003, 2005; Barai et al., 2017). The importance of limiting current has been recognized in the literature (Chazalviel, 1990; Bai et al., 2016; Barai et al., 2017; Maslyn et al., 2018).

In this review, we demonstrate that the lithium protrusion morphology obtained in different classes of electrolytes are mainly functions of two parameters: (1) current density normalized by the limiting current density and (2) modulus of the electrolyte. We present literature results for lithium protrusion morphology as a function of these two parameters on a “morphology diagram.” Each morphology is roughly restricted to contiguous regions on this diagram.

METHODS

The classes of electrolytes covered in this review are given in **Table 3**. The first column in **Table 3** provides a description of these classes and gives typical examples. The second column describes the mechanical behavior of the electrolyte. The liquid and inorganic solid electrolytes are relatively simple from the mechanical point of view. Polymers on the other hand are

neither simple solids nor simple liquids. They exhibit both viscous and elastic properties depending on temperature and time-scale of observation. Additionally, **Table 3** includes the orders of magnitude of relevant electrochemical properties: conductivity, κ , salt diffusion coefficient, D , and steady-state current ratio, ρ_+ . Conductivity is measured by ac impedance, salt diffusion coefficient is measured by restricted diffusion, and the steady-state current ratio is measured in lithium-lithium symmetric cells.

The steady-state current fraction deserves some clarification. This approach for characterization of electrolytes was pioneered by Bruce, Vincent, and Evans (Bruce and Vincent, 1987; Evans et al., 1987). In this approach, a fixed dc potential is applied to the symmetric cell and current is recorded as a function of time. At early times, the salt concentration in the electrolyte is uniform (as it is when the cell is at rest) and the current obtained under these circumstances is dictated by conductivity alone. We ignore contribution from interfacial impedance in this description; this is discussed extensively in the literature (Bruce and Vincent, 1987; Evans et al., 1987). We refer to the current obtained in the absence of concentration gradient as i_Ω . The passage of time results in the establishment of salt concentration gradients, which, in turn, lead to a reduction of current. The ratio of the final steady-state current obtained in such an experiment, i_{SS} to i_Ω is defined as the steady-state current fraction ρ_+ (Gray and Bruce, 1995; Galluzzo et al., 2019). In the literature this fraction is often called the transference number, t_+ . It is known however that ρ_+ equals t_+ for the case of dilute electrolytes that are thermodynamically ideal (i.e., when the salt activity coefficient is unity). Since practical electrolytes are never dilute, it is our understanding that the transference number is different from ρ_+ in all of the electrolytes covered in this study. Nevertheless,

the steady-state current fraction is an important characteristic of electrolytes. The analysis presented in this paper makes extensive use of this characteristic.

DISCUSSION

The systems chosen for this study are listed in **Table 4**. Each class of electrolytes is presented using a different color background: blue for liquid electrolytes listed first, red for polymer electrolytes listed second, and yellow for inorganic solid electrolytes listed third. The liquid electrolytes are alkyl-carbonate-based systems used in lithium-ion batteries. The alkyl carbonates of interest include ethylene carbonate (EC), dimethyl carbonate (DMC), diethylene carbonate (DEC), and propylene carbonate (PC). The salts dissolved in these liquids include bis (trifluoromethanesulfonyl)imide lithium salt (LiTFSI), lithium perchlorate (LiClO₄), and lithium hexafluorophosphate (LiPF₆). The second class is polymer electrolytes, which are composed of a neutral polymer, such as poly(ethylene oxide) (PEO) or block copolymer poly(styrene)-*b*-poly(ethylene oxide) (SEO). The salt dissolved in these polymers is usually LiTFSI or lithium bis(fluorosulfonyl)imide (LiFSI). The last class is inorganic solid electrolytes, which can be either classical crystalline solids with lithium ions in the lattice, such as Li₇La₃Zr₂O₁₂ (LLZO) or glassy solids, such as 80Li₂S-20P₂S₅.

The importance of limiting current has already been discussed above. However, this parameter is seldom measured directly by experiment. We thus use a simple expression for the limiting current taken from (Monroe and Newman, 2003),

$$i_L = \frac{2c_bDF}{(1 - \rho_+)L} \quad (1)$$

where c_b is the salt concentration in the conducting phase, F is the Faraday's constant, and L is the distance between the two electrodes. We have taken the liberty of replacing the transference number in equation (23.5) in Monroe and Newman (2003) by ρ_+ . Equation 1 only applies to electrolytes containing added salt. It does not apply to single ion conductors.

In **Table 4**, we provide values for the parameters required to calculate i_L . For completeness we provide values for conductivity, though this parameter is not used in our analysis. The first entry in **Table 4** is the classical lithium-ion battery electrolyte. The formation of lithium protrusions in this electrolyte was studied using two different kind of cells: lithium-lithium symmetric cells and a half cell with carbon as the cathode. Protrusions were obtained after cycling the cells, indicated in the cycling/deposition column by 'C'. The electrochemical parameters were obtained from references (Valøen and Reimers, 2005; Dahbi et al., 2011) as indicated in the first entry in **Table 4**. In many of the entries in **Table 4**, electrochemical characterization data was obtained from different references, as is the case for the first entry. In such cases, the reference is provided below the parameter. In cases where electrochemical characterization data were presented along with lithium protrusion characterization, no references are provided

next to the characterization data. The parameter L , is the distance between the electrodes. In the case of composite cathodes like the carbon (graphite particles) used in the first entry, we ignore salt concentration gradients that occur within the electrolyte contained inside the pores of the composite cathode. In addition, when the cell has two different electrodes, one of the electrodes is always lithium metal and we are only concerned with electrodeposition of lithium on the lithium metal electrode. The second entry in **Table 4** is similar to the first entry except that the cell was not cycled. The formation of lithium protrusion was studied after one-directional electrodeposition, indicated in the cycling/deposition column by 'D'. In the third entry in **Table 4**, the copper cathode is electrochemically inactive. Lithium metal is deposited onto this cathode, which is similar to a lithium metal electrode after sufficient passage of current. Other entries related to liquid electrolytes in **Table 4** include surfaces treated with specific chemicals [e.g., copper treated with lithium fluoride (LiF) and lithium treated with silicon carbide (SiC)]. A majority of the liquid electrolytes studies reported in **Table 4** were conducted on lithium-lithium symmetric cells.

In many systems reported in **Table 4**, the parameters needed to estimate i_L were not reported in the lithium electrodeposition studies. We have relied on literature to estimate parameters in these cases. The deposition experiments for liquid electrolytes were conducted in the vicinity of room temperature (20°C to 30°C). We have not accounted for temperature variation between different studies. The values of i_L reported in **Table 4** vary from 0.06 to 380 mA.cm⁻². While many parameters affect i_L , the wide range of i_L values are largely due to differences in L (see Equation 1). We posit that the differences in mechanical properties of liquid electrolytes are small, and therefore not relevant. We thus do not report the modulus of these systems in **Table 4**.

The work on lithium electrodeposition through polymers is restricted to PEO homopolymers and PEO containing block copolymers. The electrodeposition experiments are conducted at elevated temperatures (e.g., 90°C), due to poor ion transport in the vicinity of room temperature. The electrochemical parameters reported in **Table 4** are applicable at the temperature at which the electrodeposition was performed. In polymer electrolytes the values of i_L range from 0.001 to 4 mA.cm⁻². The in-phase shear modulus, G' , of the polymers in the low frequency limit is also reported in **Table 4**. At the temperatures of interest, PEO homopolymers are rubbery liquids and in the low frequency limit G' is proportional to ω^2 , where ω is the frequency. In other words, the shear modulus of PEO homopolymer is negligible at low frequencies. On the other hand, SEO block copolymers exhibit a frequency independent G' in the low frequency limit. This solid-like behavior is due to the presence of the glassy polystyrene domains. The values of G' reported for these systems is thus non-negligible.

The last set of entries in **Table 4** pertain to inorganic solid electrolytes. In these systems Li⁺ is the only mobile ion and thus $\rho_+ = 1$. The limiting current in these systems cannot be calculated using Equation (1) (Monroe and Newman, 2003). The shear moduli of these materials are 4 orders of magnitudes larger than those of polymeric solids in **Table 4**.

TABLE 4 | Properties of electrolytes and cells used to study lithium electrodeposition covered in this review.

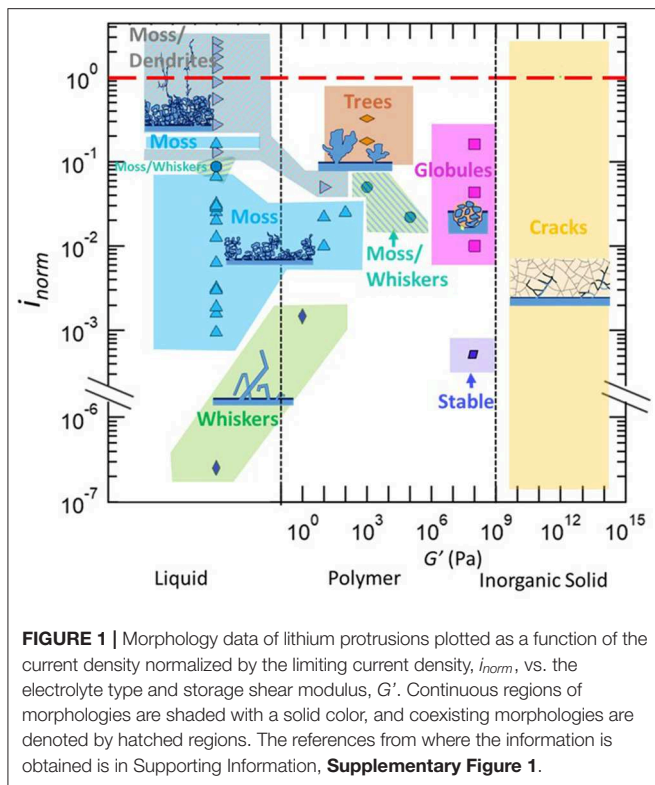
Electrolyte	G' (Pa)	c_b (mol.L ⁻¹)	κ (S.cm ⁻¹)	D (cm ² .s ⁻¹)	ρ^+	L (cm)	i (mA.cm ⁻²)	i_L (mA.cm ⁻²)	Type of cell used	Cycling/ Deposition	References
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.1	1	8	Li/Li and Li/graphite	C	Kim and Yoon, 2004
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	1.0 × 10 ⁻⁶	0.38	0.03	1.09 to 50	20	Li/Li	D	Bai et al., 2016
LiPF ₆ PC:DMC ratio 1:3	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.013	4	120	Li/Cu	D	Crowther and West, 2008
LiPF ₆ EC:EMC ratio 3:7	–	1.2	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	2	380	Li/Li ₄ Ti ₅ O ₁₂	C	López et al., 2009
LiClO ₄ in PC	–	0.25	5.4 × 10 ⁻³ Werblan and Balkowska, 1993	2.2 × 10 ⁻⁶ Nishikawa et al., 2006	0.29 Mauro et al., 2005	0.0025	5	75	Li/Ni	D	Nishikawa et al., 2010
	–	1		1.3 × 10 ⁻⁶ Nishikawa et al., 2006			5	177			
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	0.5	316	Li/Cu and Li-LiF/Cu	D	Zhang et al., 2017
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	0.74 to 0.2	316	Li/Cu and Li/W	D	Steiger et al., 2014, 2015
LiPF ₆ in EC:EMC	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	0.3	316	Li/Li and Li/SiC	C	Sun et al., 2016
(LiPF ₆), (LiTFSI), or LiFSI in DME, or DOL and PC	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	0.2 to 8	316	Li/Li and Li/Cu	C	Qian et al., 2015
LiPF ₆ in EC:DEC	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0015	0.5	527	Li/Li and Li/graphene sheet	C	Bobnar et al., 2018
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0025	1	316	Li/Li	D	Zachman et al., 2018
LiPF ₆ EC:DMC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.2	0.64	395	Li/Li	C	Eastwood et al., 2015
LiPF ₆ or LiTFSI EC:DMC or EC:PC ratio 1:1	–	1	1.0 × 10 ⁻² Dahbi et al., 2011	2.5 × 10 ⁻⁶ Valøen and Reimers, 2005	0.39 Valøen and Reimers, 2005	0.0695	1 to 50	11.4	Li/Li	D	Gireaud et al., 2006

(Continued)

TABLE 4 | Continued

Electrolyte	G' (Pa)	c _b (mol.L ⁻¹)	κ (S.cm ⁻¹)	D (cm ² .s ⁻¹)	ρ ⁺	L (cm)	i (mA.cm ⁻²)	i _L (mA.cm ⁻²)	Type of cell used	Cycling/Deposition	References
LITFSI and SEO (240–260)	10 ⁸ Harry et al., 2014	1.59	5.5 × 10 ⁻⁴ Villaluenga et al., 2018	4.70 × 10 ⁻⁸ Villaluenga et al., 2018	0.05 Pesko et al., 2018	0.003	0.175	4	Li/Li	C at 90°C	Harry et al., 2014, 2015, 2016; Schausser et al., 2014
LITFSI and PEO 30	10 ⁹ Stone et al., 2012	0.095	1.5 × 10 ⁻³ Pesko et al., 2018	3.5 × 10 ⁻⁸ Pesko et al., 2018	0.085 Pesko et al., 2018	0.2	0.1 to 0.5	0.0035	Li/Li and Li/Cu	C at 90°C	Dollé et al., 2002
LITFSI and PEO 300	10 ⁸ Stone et al., 2012	0.095	1.5 × 10 ⁻³ Pesko et al., 2018	6.00 × 10 ⁻⁸ Pesko et al., 2018	0.085 Pesko et al., 2018	0.0035 0.01	0.06 0.06	0.343 0.12	Li/Li	D at 90°C	Rosso et al., 2006
LITFSI and PEO 30	10 ⁹ Stone et al., 2012	0.095	9.7 × 10 ⁻⁴	3.5 × 10 ⁻⁸ Pesko et al., 2018	0.085 Pesko et al., 2018	0.2	0.2	4	Li/Li	C at 80°C	Brissot et al., 1998
LITFSI and PEO 60	10 ⁹ Stone et al., 2012	0.95	1.0 × 10 ⁻⁵	6.00 × 10 ⁻⁸ Pesko et al., 2018	0.085 Pesko et al., 2018	0.02	0.05	0.6	Li/Li	D	Hirano, 2010
LITFSI and SEO (115–172)	10 ⁸ Harry et al., 2014	1.59	5.5 × 10 ⁻⁴	7.37 × 10 ⁻⁸	0.045 Pesko et al., 2018	0.004	0.02 to 0.64	4	Li/Li	D at 90°C	Maslyn et al., 2018
LITFSI and PEO 30	10 ⁹ Stone et al., 2012	0.095	9.1 × 10 ⁻⁴ Pesko et al., 2018	3.50 × 10 ⁻⁸ Pesko et al., 2018	0.085 Pesko et al., 2018	0.1	0.95	0.007	Li/Li	D at 80°C	Brissot et al., 1999, 2001
β-Li ₃ PS ₄	10 ¹² Baranowski et al., 2016	–	1.6 × 10 ⁻⁴ Liu et al., 2013	–	1	0.3	0.01 to 5	–	Li/Li	C/D	Porz et al., 2017; Seitzman et al., 2018
LLZO	5 × 10 ¹⁰	–	2.0 × 10 ⁻⁴ Shao et al., 2016	–	1		0.015 to 0.50	–	Li/Li	C/D/C	Ren et al., 2015; Cheng et al., 2017; Porz et al., 2017)
80Li ₂ S-20P ₂ S ₅	2 × 10 ¹⁰ Kato et al., 2018	–	2.8 × 10 ⁻⁴ Sakuda et al., 2010	–	1		0.05 to 20	–	Li/Li	C	Nagao et al., 2013

We report shear modulus, G', the ionic conductivity, κ, diffusion coefficient, D, the current ratio, ρ₊ number or best estimated transference number, the applied current density, i, the measured or calculated limiting current, i_L, the distance between the electrodes, L, the type of cell cycled, if the lithium was unidirectional electrodeposited (D) or cycled (C) and the reference. The number next to the polymer electrolytes refers to the number averaged molecular weight of the polymer in kg.mol⁻¹.



There are many studies of lithium protrusion morphology in novel electrolytes such as ionic liquids and organic-inorganic composite electrolytes. We do not include them due to the unavailability of the necessary electrochemical characterization data.

Since theory suggests that the limiting current plays an important role (Chazalviel, 1990; Monroe and Newman, 2003; Bai et al., 2016; Barai et al., 2017; Maslyn et al., 2018), we define a normalized current density as the experimental current density over the limiting current density.

$$i_{norm} = \frac{i}{i_L} \quad (2)$$

Where i is the applied current density.

In **Figure 1**, we present results of lithium electrodeposition experiments that were listed in **Table 4**. The modulus of the electrolytes is given on the abscissa and the normalized current density is given on the ordinate. A red dashed line indicates where the applied current density to the cell equals the limiting current. All of the protrusion morphologies listed in **Table 1** occupy contiguous regions in **Figure 1** and are shaded in different colors with the corresponding cartoon for visual clarity. The vertical dashed lines in the figure distinguish the three different kinds of electrolytes considered in this review (**Table 3**):

- (1) **Liquids.** In liquid electrolytes with negligible moduli, whiskers (green) are obtained in the regime $i_{norm} = 10^{-7}$. At this low normalized current density, the driving force for

lithium ion reduction is not sufficient to induce branching in the projecting structures. It is important to note that in this particular study, lithium electrodeposition was carried out without a separator. Increasing i_{norm} in liquid electrolytes results in the formation of mossy lithium (blue). This morphology is obtained in the range $10^{-3} < i_{norm} < 7 \times 10^{-2}$. In most studies mossy lithium was observed in coin cells where the electrolyte is contained in a porous separator. The spring in the coin cell does exert pressure on the cell components including the interface between lithium metal and the porous separator. It is possible that the mossy lithium seen at low values of i_{norm} are compacted whiskers due to the pressure exerted on them by the separator. Some evidence for this is presented below. Increasing i_{norm} to 0.08 results in coexistence of mossy and whiskers (hatched green and blue). Further increase of i_{norm} to 0.3 results in dendrites that grow on the top of the mossy deposit (hatched gray and blue). The cross-over from mossy to dendritic deposits occurs over a range of i_{norm} values, from 0.08 to 0.3. In this regime we see two isolated pockets: one where moss and whiskers coexist and one where only moss is observed (see **Figure 1**). There are no examples in **Table 4** where lithium dendrites are seen to grow directly from the planar anode.

- (2) **Polymers.** Low modulus polymers ($G' < 10$ Pa) exhibit behavior similar to liquids at low values of i_{norm} . At $i_{norm} = 0.001$, whiskers are seen in a cell that does not contain a separator. Note that at this value of i_{norm} , mossy lithium deposits have been observed in liquid cells with separator (see **Figure 1**). This suggests that some of the mossy deposits seen in liquid electrolytes may be due to the pressure exerted by the separator. Increasing i_{norm} to 0.01 results in the formation of moss, which is seen in the range between 0.01 and 0.04. At higher normalized current densities, coexisting moss/dendrites are seen. With higher modulus polymers ($G' = 10^3$ Pa) and higher normalized current densities, coexisting moss/whiskers are seen for $0.02 < i_{norm} < 0.05$. At higher normalized current densities, $i_{norm} \geq 0.2$ trees are observed (orange). Increasing the modulus of polymers to 10^8 Pa results in stable lithium deposition at $i_{norm} = 0.005$. While the current used under these conditions are too low for practical applications, it is important to note that whiskers are obtained at the same normalized current density in both liquids and polymers with $G' < 10$ Pa. Increasing i_{norm} to 0.01 results in the formation of globular protrusions. This morphology is seen up to $i_{norm} = 0.2$.
- (3) **Inorganic solids.** The three inorganic solid electrolytes in **Table 4** include crystal and glassy solids. In all cases failure due to the passage of current induces cracking (yellow) in the electrolyte. While lithium protrusions grow through grain boundaries in crystals, it is postulated that they grow through mechanically weak portions of glasses. In a recent study it was shown that grain boundaries in crystalline lithium ion conductors exhibit higher electronic conductivity than the bulk crystal (Han et al., 2019). This is one explanation for the observation of the growth of lithium protrusion in grain boundaries.

CONCLUSION

We have surveyed the literature on electrodeposition of lithium through a variety of electrolytes: liquids, polymers, and inorganic solids. We have focused on the morphology of lithium protrusions that often emerged in these experiments. We show that these morphologies are governed by two parameters: shear modulus of the electrolyte and current density normalized by the limiting current density. The main result of this work is **Figure 1** where we plot the lithium protrusion morphology as a function of these two parameters. The different morphologies appear in contiguous regions in this figure, analogous to a phase diagram.

AUTHOR CONTRIBUTIONS

LF, GS, and JM compiled information from the literature. LF, GS, JM, and NB wrote the manuscript.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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SYMBOLS

- c_b – Salt concentration (mol.L^{-1})
 D – Salt diffusion coefficient ($\text{cm}^2.\text{s}^{-1}$)
 F – Faraday constant (96485 C.mol^{-1})
 κ – Ionic conductivity (S.cm^{-1})
 ω – Frequency (rad.s^{-1})
 G' – Shear modulus
 ρ_+ – Steady-state current fraction
 i – Applied current density (mA.cm^{-2})
 i_L – Limiting current density (mA.cm^{-2})
 i_Ω – Current obtained in the absence of salt concentration gradient (A)
 i_{norm} – Normalized current density
 i_{SS} – Steady-state current (A)
 L – Distance between the electrodes (cm)
 t_+ – Transference number.