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Smart interfaces in Li-ion batteries: near-future key challenges

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Smart interfaces in Li-ion batteries: near-future key challenges

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Abstract

The recent impressive growth of Li-ion batteries (LIBs) production infrastructures is related to the surge of electric automotive industry. However, the current performance of LIBs is limited by the intrinsic capacity of graphite anodes, the use of organic solvents and by the limited wettability of the separator. In this review, we aim at demonstrating the grade of advance that can be expected for the performances of Li-ion batteries in the short term (roughly, 5-10 years) thanks to introduction of smart materials and interfaces. This temporal limit reflects the need of maintaining the current production chain of LIBs and optimizing the relative investments.

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Keywords

Lithium, batteries, wettability, deep eutectic solvents, Li anodes, Li metal, room temperature ionic liquids.

1. Introduction

The world energy scenario is a highly discussed topic mostly because of its strict relation with carbon dioxide emissions and thus to global warming. As depicted in **Figure 1a**, energy production, still mostly relying on fossil fuels, also leads to health emergencies that are detectable in the short term. For example, the World Health Organization estimates that 4.2 million deaths occur every year because of the exposure to outdoor air pollution (https://www.who.int/health-topics/air-pollution, accessed on 14 August 2021). According to the International Energy Agency, the global energy demand is growing worldwide, except for 2020, when the COVID-19 emergency led to a decrease of the energy demand with respect to 2019 (https://www.iea.org/reports/global-energy-review-2021?mode=overview accessed on 09 March 2022).

It is worth noting that, in 2020, the share of energy from renewable sources used in transport in Europe reached the 10% target (https://www.eea.europa.eu/data-and-maps/daviz/share-of-renewable-energy-9#tab-chart_9 access on march 2022) but reaching the goals set by the European Green Deal (zero net emissions of greenhouse gases by 2050) will require further, intensive efforts.

The sustainable exploitation of renewable energy sources demands for suitable energy conversion and storage technologies, aimed at buffering and compensating for the oscillatory and localized productivity of solar, wind and all other natural supplies. This in turn guarantees a decreasing use of fossil fuels, followed by reduced carbon dioxide emissions and by the saving of raw chemicals to be used in the chemical industry.

While the use of energy vectors, such as hydrogen, is rising as the most promising strategy for mid-large facilities, also by adapting natural gas infrastructures, energy storage for the medium-small scale almost completely relies on lithium-ion batteries (LIBs). LIBs real price dropped by about 97% since their introduction in the market, in 1991 [1], as show in **Figure 1b**, and notwithstanding the rapid growth of Li price [2]. This decrease, that is comparable to the one of photovoltaic panels, is at the bases of the boom of electric micro-mobility and certainly plays an enormous role in the advance of portable devices and of electric (or hybrid) automotive market up to the utility (grid) scale (few megawatt-hours, MWh, to hundreds of MWh).

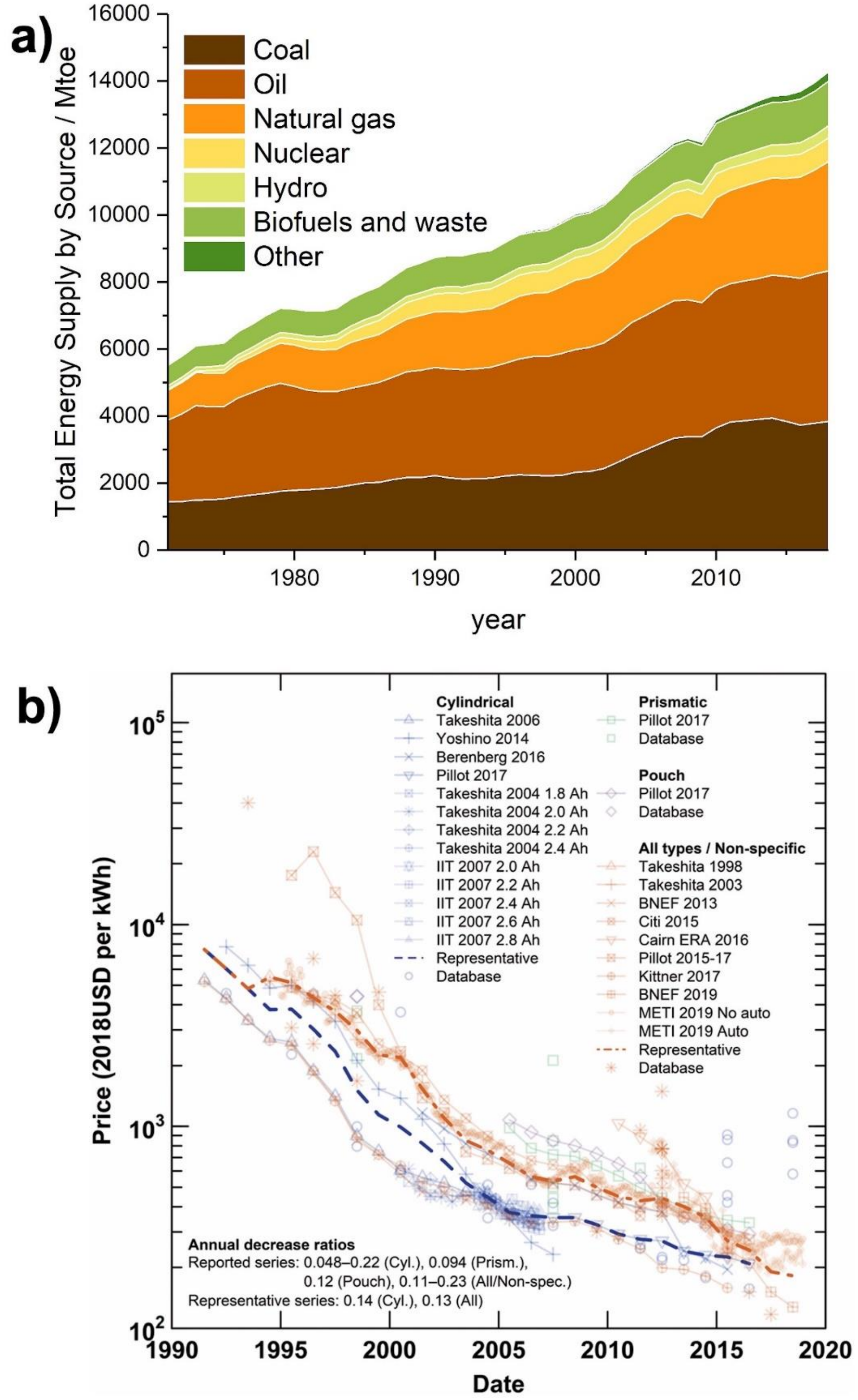

Figure 1. a) Energy production shares (1990-2019), based on International Energy Agency, IAE, data from IEA (2022) [Energy Supply by Source], https://www.iea.org/data-and-statistics (accessed on date 21 February 2022), All rights reserved; as modified by the Authors of the present paper and, (b) price of LIBs per kWh (1990-2019) Reproduced from ref [1] with permission from the Royal Society of Chemistry

The Nobel Prize 2019 in Chemistry, awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino "*for the development of lithium-ion batteries*", clearly witnesses the fundamental importance of Li-ion batteries in human beings' daily life.

Still, we can ask ourselves a rather compelling question: are we witnessing the midlife crisis, the swan song or rather a "rebirth" of Li-ion batteries?

The success of LIBs in portable devices follows their high energy/power density (in J m^{-3} and W m^{-3}) and specific energy/power (in J kg^{-1} and W kg^{-1}), together with their flexible exterior dimensions and design, and their robustness (temperature range of operation, cyclability etc.). Particularly important, for electric vehicle (EV) applications, is the specific capacity (in Ah g^{-1}), that regulates the travel distance and that can be calculated by equation 1:

$$specific\ capacity = \frac{nF}{M_{\mathrm{w}}} \qquad (1)$$

where n is the number of exchange electrons, F the Faraday constant and M_{w} the molecular weight.

The market is constantly asking for better batteries, with increased specific capacities, yet longer lasting and safer. This is needed to increase EV autonomy. In ref. [3], the main strategies for future batteries were listed, and include the search for novel LIB electrode materials, 'bespoke' batteries for a wider range of applications, the development of new electrolytes, the introduction of new anion redox chemistries (Li air, Li-sulphur) [4–6], the use of other cations (Na, Mg, Ca, Al) and the possibility of decoupling electrochemistry and storage, *i.e.*, redox flow batteries. The transition towards these technologies will unavoidably require a deep renovation of production infrastructures [7].

In the most recent years, Li-metal batteries were also the focus of important publications, because of their high potentialities (increase of energy density) but with all the limits related especially to the possible growth of Li dendrimers and ensuing anode-cathode short circuit.

Among all these possible strategies, the technologies most likely to be introduced at the industrial level are new electrode materials, in particular anodes, modified separators, and new solvents. This can be easily understood considering the current scenario of LIBs fabrication.

In fact, we are witnessing an impressive growth of LIBs industrialization, particularly relevant in the automotive industry. For example, as declared in the Tesla website [https://www.tesla.com/Gigafactory, accessed on May 2021], the production of EVs requires the entire world's supply of LIBs and led to the installation of new battery production facilities, the so-called "Gigafactory" (the first one reaching a productivity equivalent of roughly 20 GWh y^{-1}), aimed to compensate this lack.

This opens serious questions, including the availability of the requested supplies (of Li, Ni and Co, *in primis* [8]) and the need of proper recovery and recycling of the various battery components [2], which will likely lead to a deep renovation of the battery market.

However, an intermediate step will serve in transition, to further improve the LIB performances, yet not requiring any revolution in the production plants.

In this review, we – the Milan school of electrochemistry at which Prof. Sergio Trasatti belonged for over 30 years – offer a critical perspective on some of the most striking technical aspects which can allow the survival of LIBs, and particularly on those that will likely play a role soon (5-10 years) without shaking up the current production chain. Developing suitable smart interfaces will extend the specific capacity of LIBs mostly by coupling the design of new anode materials (**Section 4**) with an improved wettability of the anode and of the separator (**Section 3**). The possible substitution of the electrolyte can also play a crucial role.

For what concerns this last aspect, different technologies have been proposed, including polymers. ionic liquids (ILs) and, more recently, deep eutectic solvents. However, the first technology will likely require a deep modification of the productive processes and still possess important drawbacks (see below), thus we will review the most important outcomes on the other two (**Section 2**).

We believe that the most likely advance from LiBs could be the (re)introduction of Li-metal batteries, an industrial technology already adopted for primary batteries (that represented the predecessor of LIBs and that are still in use[9]) but that suffers from charge/discharge cycles mostly because of the formation of dangerous dendrites. It is now evident that a rational design of a smart interface can overcome this limit, thus allowing a dramatic increase of specific capacitance compared to LIBs (**section 5**).

2. Lithium battery electrolyte issues and related advanced media tools

The performances of lithium batteries are of course strictly related not only to cathode and anode material and morphology, but also to the electrolyte nature and properties.

In particular, requirements for an ideal lithium battery electrolyte, particularly considering Lithium-ion batteries, but also Lithium metal ones, for which adoption of appropriate electrolytes is a determining condition to become as above mentioned a key asset in the near future, are [10–15]:

A) Charge transport properties: high ionic conductivity; in particular, very efficient transport of Li^+ cations in their shuttling between electrodes in charge/discharge processes, which should not become rate determining respect to the electrode processes in which they are involved (*e.g.* solid-state diffusion intercalation processes).

B) Interphase-related issues: good contact/wettability of the electrodes (also considering porosity), low resistance of the electrode|electrolyte interface. Moreover, ability to promote on the graphite intercalation anodes the formation of a passivation layer (SEI, "solid electrolyte interface", which will be specifically dealt with at paragraph 5, being a key issue for Li-ion batteries, and an even decisive one for Li-metal ones), conducting for Li^+ ions but not electrons, and of soft/elastic/self-healing and thus beneficial nature during the battery cycle life, that is, with low tendency to defect formation during deposition/dissolution cycles; also, particularly in the perspective of lithium metal batteries, preventing dendrite growth and anode exfoliation[1], and thus preserving capacity and cycle life, preventing dangerous short circuits from dendrite material getting through the separator [15]; actually the former transition from Li-metal to Li-ion batteries was also prompted by the intrinsically better properties of the SEI in the Li-ion case [13,16], and the possible return to the Li-metal strategy with related advantages is deeply connected to the possibility of improving/controlling SEI features [13,15,16].

C) Electrochemical stability: Wide potential window, consistent with the large potential differences involved in lithium batteries, in the 3-5 V range depending on the electrode choice, implying high electrochemical stability of the electrolyte on both the oxidation and reduction sides in order not to interfere with the battery anodic and cathodic processes.

D) Safety issues: chemical stability in a wide temperature range (allowing battery operation both at high and low temperatures), low vapor pressure, low or null flammability, ensuring safe operation particularly in the rapidly growing electric and hybrid vehicle industry; features enabling to avoid leakages.

E) Sustainability issues: Reasonable cost; environment-friendly nature.

Of course, above issues A, B and C are strictly related to the electrolyte solvation/coordination features, especially concerning Li^+ ion. In fact, such features can be determining both on electrolyte properties (solubility, ion mobility, conductivity, viscosity...) and on interphase features and processes (interphase structure, electrode reactions involving lithium ion or/and solvent, as well as SEI formation, morphology and properties) and thus dramatically affect the battery performance parameters and lifetime [10,11,17–27]. Accordingly, the key, very complex issue of solvation in lithium battery electrolytes, and the strictly related ones of conductivity, viscosity and ion diffusion

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[1] Li metal can react with solvents and Li salts in the battery electrolyte, forming a passive solid electrolyte interface (SEI) on the anode surface. When the latter cannot withstand volume changes in cyclic Li deposition/dissolution, defects can be generated in the SEI, corresponding to preferential Li^+ diffusion and higher local current density, with dendrite growth. Coulombic efficiency is reduced, and Li dendrite material can get through the separator, with short circuit dangers.[15]

coefficients and dynamics, have been dealt with in many studies and employing a very wide pool of techniques, including MD and DFT computations, electrochemical techniques, IR, FTIR/ATR, Raman, IR-DOS, SERS, X-ray diffraction, NMR, NOE, ESI-MS, inelastic neutron scattering, FM-AFM UV/Vis, thermal analyses, rheometry, fluorescence, EPR and the Moiré pattern method [19–26,28–65]

An early, very popular choice as commercial lithium battery electrolytes is represented by solutions of lithium salts, particularly $LiPF_6$ (on account of an overall favourable property combination; however, others have also been pointed out as possibly competitive, like *e.g.* LiFSI and LiTDI [26]), in organic carbonates (ethylene carbonate EC, diethyl carbonate, DEC, ethylmetyl carbonate, EMC, propylene carbonate PC and others, often in admixture to find a good property compromise) [10,14,66,67]. In such "traditional" solvent+supporting electrolyte systems, solvation modes can be discussed in terms of solvent-separated ion pairs, contact ion pairs, or aggregates [25,26], modulated by nature and concentration of the components; for example, optimized properties in carbonate electrolytes can be obtained by an appropriate balance of cyclic and linear ones [23,25]. Various additives, fluorinated carbonates and anion modulation have also been proposed to modulate properties and especially to improve SEI formation and safety [10,14,18,64]. Besides carbonates, other organic solvents/cosolvents, including sulfones, nitriles, and fluorinated solvents (particularly beneficial for SEI formation) have also been investigated [14,18,65]; a study on a single-Li^+ion conducting polymer (poly(allyl glycidyl ether-lithium sulfonate) dissolved in nonaqueous solvent DMSO showing improved performances respect to a simple Li salt has also been reported [68].

However, organic carbonate media (and in general liquid electrolytes based on organic solvents) suffer from intrinsic severe drawbacks. They have low stability on the anodic side, low flash point, flammability, possibility of leakages [10,11] and, particularly when employed in Li-S and Li/Na-air batteries, they can promote side reactions and dissolution of electroactive materials [12].

To improve lithium battery electrolyte features many approaches have been proposed, including:

(i) Solid electrolytes [69]. *Inorganic*: either crystalline/ceramic or amorphous [14], including Li^+-containing oxides (particularly perovskites), sulfides, hydrides, borates, phosphates, LIPON (lithium phosphorus oxynitride) also as thin film solid electrolyte for thin film batteries, LISICON lithium superionic conductors (similar to NASICON sodium ones) like *e.g.* $LiTi_2(PO_4)_3$) [14,69]. *Organic:* dry solid polymer electrolytes, particularly composite ones with integration into organic matrices like PEO, PAN, PMMA, PVC, PVDF, of ceramic fillers, either involved in ionic conduction, like Li_2N and $LiAlO_2$ or not, like Al_2O_3, SiO_2, MgO [12,67], and many more, very attractive also in the Li-metal perspective (recent exhaustive review in [70]); for example very

good performances in various setups were obtained with mechanically robust PI/PEO/LiTFSI polymer electrolyte [26,71]. Solid electrolytes have also been tested in Li-air, Li-S and Li-Br_2 cells. [14,21] However, solid electrolytes, in spite of eliminating leakage problems, having low flammability and resulting in higher anode stability, suffer from problems of little electrode contact and low ability to SEI self-repairing, and therefore require some “softening” [11,13], like in semisolid/gel/hybrid materials discussed below.

(ii) Lithium salts/cations in advanced liquid media ionic liquids ILs or deep eutectic solvents DESs, on which we will focus below.

(iii) Hybrid/semisolid/gel materials, most of which based on (*ii*).

ILs are molecular salts liquid below 100 °C (in particular, RTIL room temperature ionic liquids are liquid at 25 °C), often based on ammonium, phosphonium, (benz)imidazolium, pyridinium, piperidinium cations with long alkyl chains, combined with “soft” anions (*e.g.* BF_4, PF_6, and especially TFSI, bis(trifluoromethane)sulfonimide $(CF_3SO_2)N^-$, a very popular tool for melting point lowering) [10–13,66]. They have acquired great popularity on account of many advantages, including low volatility and flammability, tunable polarity, acidity and proticity, wide chemical and thermal stability in liquid form, and tunable functional properties [13], including viscosity and conductivity (they are considered “designer solvents”). From the electrochemical perspective, they are also attractive since they act as both solvent and electrolyte and on account of their good transport properties and wide electrochemical windows [10–13]; respect to traditional media they have peculiarities concerning charge transport, viscosity and solvation [11] as well as much higher structural order at the charged electrochemical interphase [11], locally resembling bulk liquid crystal properties, extending at a considerable distance from the electrode surface [72], and also holding in the presence of significant amounts of water [67].

Basically, IL-based lithium battery electrolytes can be obtained dissolving a lithium salt in an IL, possibly with the same anion; a typical example is 0.2-1 M LiTFSI in Pyr_{14}TFSI (N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide) [10,66]. The resulting media are quite attractive considering the above ideal feature check list for a lithium-ion or lithium-metal battery electrolyte, because:

- respect to solid electrolytes, they offer better electrode wettability and formation of good SEI layers, which can even form electrolessly [11,12,73]. On the other side, leakages are possible, although they are more viscous than other liquid electrolytes;
- respect to liquid electrolytes based on organic solvents, they are much safer, being of little or no volatility and flammability [10,12,66]; they offer a wider operating temperature range on account

of their good thermal stability in liquid phase with low melting point and very high boiling point [10,66]; moreover, unlike carbonate media, their electrochemical windows are wide on the oxidation side, too [11].

On the other side, with respect to classical solvent+electrolyte systems, IL-based ones can have lower conductivity ([10]; a favorable comparative case is instead reported in [44]), higher viscosity [8], as well as lower wettability of the electrode surface [8]; however, solid-state diffusion within electrodes is significantly more rate determining than diffusion of Li^+ even in viscous ILs [8], and electrode wettability could be enhanced by appropriately tuning electrode porosity [8].

Moreover, viscosity and conductivity in IL-based electrolytes are widely modulable by adding partner cosolvents/additives ([34,45,53]; see also below) and/or by appropriate molecular design [11,13,27] (and in this light development of new IL families is highly desirable). The system (LiTFSI in IL media with TFSI anion) is a favorite model subject for studies of Li^+ coordination, as a function of concentration, IL cation, and possible additives [28–34][39,40,42,43,46,55] which can determine different coordination regimes/modes. In general oxygen atoms provide most of the coordination points in Li^+ interaction with $TFSI^-$ anions [28–34], which is the predominant structural feature [36] although some Li^+ aggregates might also be present [35]. While in an aprotic IL the cation is preferentially coordinated by the anion, in a protic IL proton competition for $TFSI^-$ coordination can leave the Li^+ cations more free, resulting in higher conductivity and lower charge transfer resistance, implying the possibility to operate at higher discharge rate [10,36,37]. Changing the anion [44,55], or modulating the anion structure as in a $TFSA^-$/FSA^- study [39], can result in significant electrolyte property variations.

It is important to underline that Li^+ coordination and thus transport features are significantly different in ILs respect to the above organic media; they have been described in terms of a Li^+ hopping mechanism between ligand coordination shells, with related activation barrier [36].

For their attractive features IL-based electrolytes look promising for Na batteries, too [74,75].

Moreover their performances can be improved forming hybrid systems and/or implementing more advanced functions [10–13,66,74–77]:

- <u>ILs + molecular solvent mixed media</u>, for a reasonable compromise between safety and low resistance and viscosity; the mixture component ratio can vary widely; a small carbonate amount can result in very good performances (lower resistance and viscosity, better wettability without electrolyte flammability); on the other hand, small IL additions can act as flame retardant [11];

- in particular, redox-active ILs as additives in lithium battery liquid electrolytes acting as redox shuttles to prevent overoxidation and related dangers (in the event of an overcharge they are oxidized in place of the positive electrode active material) [76];
- "solvate ionic liquids" consisting of mixtures of Li salts in glymes strongly coordinating the Li^+ cations [19,42,48,51], which depending on concentration and molecular structures can have either ionic liquid or concentrated salt solution behaviour [48,51];
- ILs as components of gel electrolytes ("Ionogels" [78]). Gel electrolytes prepared from a polymer like PEO, PEG, PMMA plus a lithium salt typically require a carbonate plasticizer additive, resulting in better conductivity but also flammability [11,69]. The problem is solved filling the polymer matrix with ionic liquids instead [11,12,69,78]. Ionogels can also have the IL filled into an inorganic matrix (e.g. SiO_2) or even an hybrid inorganic/organic one [12,70], or consist of two ILs, one acting as matrix and one as plasticizer [11]. Ionogels can exhibit high elasticity and flexibility as well as transparency combined with high conductivity and non flammability [77];
- ionic liquid crystals ILC: supercooled ILCs [11] combine structuring of LCs and conductivity of ILs which can promote charge channeling along nematic structures;
- organic ionic plastic crystals, with the added bonus of plasticity [12,77];
- poly(ionic liquids) having no leakage problem and the possibility to form (poly)ionogels and "single-[Li^+]ion conducting electrolytes" [75], with high Li^+ transference numbers;
- IL-tethered nanoparticle hybrid electrolytes [12,66,78–81];
- ILs as wetting agents and/or SEI film promoters between solid electrolytes and electrodes;
- ILs as fillers of polymer frameworks to obtain solid electrolytes with good conductivity and mechanical properties [14,69];
- the issue of suitable separators in LIB operating with IL-based electrolytes has also been treated [82].

It is also worthwhile mentioning that, besides as advanced electrolyte components, ILs are precious tools in LIB technology development also [11,12],

- as components of electrodes as modulable, multifunctional binders (particularly PILs) *e.g.* between less conducting cathode materials like $LiFePO_4$ and graphite;
- for fabrication of porous carbons through facile one-step thermolysis of ILs (in particular, from cyano-functionalized anions N-doped carbons are obtained); IL-derived carbons can also be used as coatings of support materials besides as backbones;
- for IL-assisted synthesis of inorganic materials and inorganic/organic composites and for IL-mediated electrodepositions.

More recently, a new media class, deep eutectic solvents DESs [83], has been attracting increasing interest in the chemical [83–87] and electrochemical community [88–90], including the lithium battery (Li-ion, Li-Me, Li-S) field [15,48,91–118].

DESs are multicomponent, usually binary, systems resulting in eutectic formation at a much lower temperature than that predicted in ideal conditions, on account of strong specific interactions between their components (especially Lewis or Arrhenius acid/base ones). [83] They are defined as DESs even if the component ratio does not correspond to the eutectic composition, provided that their melting point be below the above ideal eutectic one [83]. They can be prepared by simply mixing their components, often of natural origin and of low cost.

Their attractiveness and competitivity respect to ILs stems from,

- advantageous properties similar to IL ones, including low or null volatility and flammability, good solubility and transport properties, wide modulability of functional properties ("designer solvent" features), and high structural order at the charged interphase, intermediate between ILs and normal double layer, also in the presence of significant water amounts [90].
- In addition, respect to ILs, much easier synthesis, lower cost and higher biocompatibility; DES can often consist of very common natural ingredients and therefore be completely biocompatible, available in large quantities, and with interesting functional properties (like *e.g.* chirality) [90].
- Specifically for application in LiB electrolytes, the lithium salt can be one of the two DES components, and if the partner is a non-electrolyte Li^+ can be the only cation in the medium, with high transference number. Instead with ILs usually lithium salts are dissolved in the IL; thus the anion can be the same but there are two cations; formulation of an IL with Li^+ as the only cation looks hard [114].

In this frame, various DES systems have already been successfully tested as electrolyte media in LiBs, most of them, but not all, based on amide+lithium salt binary systems.

- in 2013 DESs consisting of N-Methylacetamide combined with LiX, with X = TFSI, PF_6^-, NO_3^- anions were found to have wide liquid-phase ranges with very low eutectic points (between -50 and -80 °C), low vapor pressure, as well as high ionic conductivity, and performed well in preliminary LiB tests in (Lithium titanate or Activated Carbon |DES |$LiFePO_4$) setups. [101][112] The NMA: LiTFSI DES was also the object of a detailed investigation concerning intermolecular interactions between its components [113];

- in 2014 DESs consisting of alkyl sulfonamides with lithium perfluoroalkylsulfonimide salts exhibited room temperature conductivity similar to carbonate-based liquid electrolytes (although viscosity was much higher) and good cathode and anode cycling behaviour [114];
- in 2018 the system 0.5 M $LiPF_6$ in environmentally friendly and very cheap DES 3:1 ethylene glycol+choline chloride (about US$1 per kg and US$0.5 per kg, respectively) showed very good conductivity and good thermal and electrochemical stability [115];
- in 2019 the methylsulfonylmethane+lithium perchlorate+water ternary system was proposed as a safe, environmentally friendly, and low-cost "water-in-salt" electrolyte, with satisfying electrochemical stability window, and enabling high energy density and high capacity retention in $Li_4Ti_5O_{12}$|Electrolyte|$LiMn_2O_4$ cell tests [116];
- In the same year, an ε-caprolactam+acetamide DES was found to dissolve all sulfide and polysulfide species, effectively attenuating major problems affecting Li-S batteries (massive cathode volume changes and Li_2S_2/Li_2S precipitation, increasing polarization and decreasing cycle life), besides other favourable features [117];
- In 2020, a DES based on 4:1 2,2,2-trifluoroacetamide (TFA)+ LiTFSI with addition of 10% ethylene carbonate gave satisfactory performances in Li|Electrolyte|$LiMnO_4$ cell tests in terms of specific capacity and of cycling behaviour [118];
- Other binary or ternary DES systems with promising features for lithium batteries have recently been the object of preliminary physicochemical and electrochemical investigations, ranging from LiCl in choline chloride+urea [91] to LiCl or LiTFSI with various amides (comparing HBD containing and HBD free ones in terms of Li^+ coordination ability, and highlighting tetramethylurea/LiTFSI and 1,3-dimethyl-2-imidazolidinone/LiTFSI as most promising systems) [92], to $LiClO_4$+acetamide (focusing, again, on Li^+ solvation and transport issues) [48].

Compared to former cases of (solvent+lithium electrolyte) systems and of lithium salts in ILs, in the case of DES-based lithium electrolytes it is even more difficult to achieve a rationalization of the cell performance in terms of Li^+ solvation modes (as for a rationalization of the electrode|solution interphase structure, too). This is because of the system complexity (in terms of number of actors and of the variety of interactions to be simultaneously considered), of the enormous range of cases possible, and of the still small number and specific character of investigations available on the topic. [53] Most of them concern amide-based DESs. In the above cited early work on N-Methylacetamide cod with LiTFSI, $LiPF_6$ or $LiNO_3$, the authors assumed possible interaction of methylacetamide with both Li^+ (on the C=O side) and anion (on the NH side), resulting in microdomains [101]. Various Li salt-amide systems are also the object of a MD study in the more recent above cited work [92], confirming strong Li^+ coordination to C=O. In a MD+neutron scattering study performed on a ($LiClO_4$ + acetamide) DES, lithium ions were reported to prevailingly diffuse together with their first coordination shell, consisting on an average of about 3.2 acetamide molecules [48]. The effect of alkyl chain length, temperature, and anion on interaction and dynamics in alkylamide+lithium electrolyte systems was studied by a combination of MD and experimental techniques in [58]. MD studies also dealt with orientational jumps in acetamide+lithium salt systems with related anion modulation [60], and with the effect of an increasing water content on Li^+-acetamide interactions [62]. A study based on IR as well as physico/chemical and electrochemical characterizations investigated (LiTFSI+Trifluoracetamide) DESs, as such and upon modification with small EC additions [118]. A combined MD and NMR study on sulfonamide-LiTFSI systems provided formulation guidelines for significant property improvement [59]. A quite smaller number of studies involved non-amide Li-DES cases, such as *e.g.* structure perturbation upon addition of lithium salt of binary ethaline and decaline DESs [47], competition of urea with $TFSI^-$ in Li^+ coordination in LiTFSI/urea systems [62,63], ionicity evaluation in many DESs including some lithium-containing systems [50], and combination of carbonate-based lithium electrolytes with choline-based DESs [57].

As for ILs, also in the DES case a further evolution step as lithium battery electrolytes consists in the development of gel systems, called "eutectogels" (ETGs) by DES hybridization with inorganic or polymeric matrices, in analogy with the above IL-based "ionogels", eliminating leakage problems and of convenient mechanical properties [93–96].

A first ETG family was proposed in 2018, consisting in N-methylacetamide+LiTFSI DESs−silica composites, prepared over a broad range of compositions via a nonaqueous sol−gel route, of high ionic conductivity and thermal, chemical, and electrochemical stability, resulting in stable cycling Li/ETG/LiFePO4 cells over 100 cycles at C/10, and of lower cost than ionogels [93]. In 2020 the same group proposed to integrate the same kind of DES in a polymeric host, avoiding the heating required in case of inorganic matrices, resulting in partial amide loss, and resulting in better mechanical features; this ETG was obtained from a blend of acryloylmorpholine (monomer), ethylene glycol dimethacrylate (crosslinker) and 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), with a procedure involving UV irradiation the resulting ETG had very good conductivity, stability and mechanical properties, low flammability and by stable cycling results of Li/P-ETG/$LiFePO_4$ cells over 100 cycles at C/5 to 1C rates. [94] A N-methylacetamide+LiTFSI DES was also successfully combined in the same year by another group with a polymer matrix consisting of 2-hydroxyethyl acrylate (HEA) and polyethylene glycol methyl ether acrylate (MPEGA), resulting in ETGs of improved stability and performances in $Li_4Ti_5O_{12}$|ETG|$LiMn_2O_4$ cell tests respect to the corresponding liquid DESs, and also more water tolerant, a useful feature for application in ambient conditions [95].

Another recent approach concerned an ETG obtained by *in situ* polymerization (an attractive tool to optimize electrode|electrolyte interface features), in mild conditions and with nearly quantitative yield, from a molten mixture of monomer (2-(((2-oxo-1,3-dioxolan-4-yl) methoxy) carbonylamino))-ethyl methacrylate), a succinonitrile plastic crystal, and two lithium salts; also in this case good Li^+-conductivity and very good high-voltage stability in Li-metal battery with $LiCoO_2$ cathode were obtained [96].

A very attractive DES-based *in-situ* prepared and self-healing ETG for application as lithium-metal battery electrolyte has also been recently proposed, obtained by a facile *in situ* thermally initiated polymerization from comonomers 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)ethyl methacrylate and pentaerythritol tetraacrylate, integrated by a non-flammable DES electrolyte containing fluoroethylene carbonate (FEC) as an additive. The hybrid system displays nonflammability, high ionic conductivity and electrochemical stability, and dendrite free Li deposition; moreover, tested in LiB with $LiMn_2O_4$ cathode, such electrolyte also prevents manganese dissolution from the cathode, resulting in stable interface features, high capacity and a long cycle life even at high temperatures [15].

Finally, it is worthwhile mentioning that, similarly to ILs, also DESs have been successfully studied and tested for other tasks in LiB development. They show attractive potentialities:

- as media for the controlled synthesis of LiB cathode materials (spindle-like $LiMnPO_4$/C [97], $LiMnPO_4$/C Nanorods [98]];
- as media for the controlled synthesis of LiB anode materials (Porous Sn-Ni-Cu Alloy anode [99] porous carbon xerogels with expanded graphite [100] , morphology-controlled Sn powders [102]);
- as media for sustainable and efficient dissolution/recovery of cathode materials from exhausted LiB, especially cobalt, whose recycle could be of potential strategical/economical interest [103–111].

3. The separator-electrolyte interface: tailoring wettability for better Li-ion batteries

In the last decades, the separator in lithium-ion batteries (LIBs) has played a progressively significant role for the enhancement of cell performances [82,119]. Intuitively, separators are necessary to prevent the direct contact between the positive and negative electrodes, concomitantly guaranteeing the lithium ions transport [120]. As such, a promising separator should ideally exhibit excellent chemical/electrochemical/mechanical stability, high ionic conductivity as well as an almost complete wettability by the electrolyte solution. A smart design of these two interfaces (electrolyte|separator and electrolyte|electrode) could be at the bases of a significant improvement of the specific capacitance in LIBs and in Li-metal batteries. Nowadays, the most common separators are based on polyolefin membranes, such as polypropylene (PP, commercially available as Celgard 3501), polyethylene (PE, namely Solupor 7P03A), poly(ethylene terephthalate) (PET, known as Separion S240P30) or their composites [121,122]. However, bare polyolefin-based materials generally are poorly wettable and show limited electrolyte uptake, which leads to poor ionic conductivity of the electrolyte-containing separator and, in turn, to poor rate performances and faster deterioration of the LIB [82,122–124].

Focusing on wettability, to reduce the cell internal resistance in LIBs, the electrolyte should completely wet out both the electrodes and the separator. The wettability of porous materials can be modelled considering a capillarity-driven liquid movement [125]. While in liquid electrolyte cells electrode wetting is generally a minor issue [82], incomplete wetting of the separator can occur due to poor compatibility with the electrolyte, resulting in dry spot formation during cycling and uneven current distribution [119]. Moreover, at the same time, scarce wetting can cause both lithium extrusion and lithium degradation, giving rise to safety concerns and to a significant reduction of the battery life [82,126]. The speed of wetting plays a key role in electrolyte infilling, which is a known bottleneck in LIB manufacturing process that can take 12-24 h by application of a negative pressure [127,128].

Comparing the wetting properties of cell components is made more complex by the lack of standard methods. Typically, the wettability of separators and other cell materials is investigated by contact angle measurements, *i.e.*, by measuring the profile of an electrolyte drop deposited on a dry separator (**Figure 2a**) [129], allowing also the determination of the solid surface free energy [130,131]. However, contact angle accuracy is limited when the liquid is rapidly absorbed by the separator. It should also be noted that contact angle measurements refer to solid-liquid interactions at the separator surface, whereas the migration of the electrolyte into the separator porous structure is the real key aspect (**Figure 2d**). Contact angle measurements alone are not enough to predict imbibition rates: besides surface chemistry and electrolyte surface tension (which determine contact angle values), other parameters such as the electrolyte viscosity, solid porosity, pore size and interconnectivity play a crucial role in capillarity-driven imbibition phenomena [125]. Alternative methods have been proposed. For instance, l'Abee *et al.* [132] used a testing method from the textile industry based on the measurement of capillary forces (in terms of liquid height and liquid mass uptake) as a function of time during the upwards flow of liquid through a porous medium (**Figure 2e**). However, the accuracy of the wetting balance method (based on Lucas-Washburn equation) is limited by assumptions about the sample geometry (uniform porosity and pore cross-section) and other interfering phenomena (evaporation, inertia and gravity influences are neglected). As an alternative, Davoodabadi *et al.* measured imbibition rates of electrodes by direct visualization of the imbibition front during horizontal absorption in the absence of evaporation [125]. Other methods include impedance spectroscopy [133,134], and in situ X-ray and neutron imaging of the wetting front [135,136]. Besides experimental techniques, a computational method (namely lattice Boltzmann method, LBM) has been adopted to simulate the electrolyte transport into porous electrodes [137,138]: for instance, Jeon recently reported an in-depth study of the dynamic interaction between the liquid electrolyte and the electrodes surface showing the impact of pore-throat size distribution on the electrolyte wetting behaviour [138].

Several studies have shed light on the main physicochemical features that a promising separator should have for optimal wettability properties [82,124,127]. Among them, key roles are played by the materials porosity, pore size and surface chemistry [82,126,128,139–141]. In particular, pores blockage reduces the overall electrodes wetting, thus leading to an increase of the electrolyte resistance, concurrently decreasing the electrodes capacity. To increase the electrolyte distribution, the fine control of the material porosity and pore size results pivotal. Regarding the former, a too low porosity (below 40% as in PP, PE or PP/PE separators) can cause scarce imbibition and, as a result, it cannot guarantee a sufficient mass transport. Nevertheless, to improve the power density, this parameter needs to be around and not above 40-45%. A good balance may be the engineering of membranes having microchannels that can prevent the problem of pores blockage [137,139,142]. Porosity is also fundamental to keep enough electrolyte to assure an adequate ionic conductivity (that should range between 10^{-3} and 10^{-1} S cm^{-1}). Besides, it is believed that pores size should be smaller than the particles size of both the electrodes and, overall, in sub-micrometric range [82,124]. Furthermore, the separator morphology together with the pores distribution should be homogeneous in order to reach a uniform current distribution inside the battery [143].

Another parameter that can affect the final device performances is the tortuosity, which indicates the lithium ions mean path inside the separator pores structure; by increasing the winding degree, dendritic growths may be hindered to the detriment of a greater ionic resistance. For instance, several authors reported [82,122,141,143] that electrospun fibres-based separators exhibit pores size of about hundreds of nanometres and very high porosity (ca. 80%) with an improved air permeability, thus representing excellent candidates for LIBs.

The surface chemistry of separators also plays a key role in tuning the device operation. Apart from being inert and electrochemically/thermally stable under either reductive or oxidative conditions during battery cycling, surface chemistry significantly influences both the wettability by the electrolyte/solvent and the lithium ions migration [82,127,130,133,144,145]. Zhang *et al.* [146] recently reported the chemical modification of propylene-based separators with tannic acid (TA) and polyethyleneimine (PEI) through a layer-by-layer method, which allowed to prevent porosity decrease. They found that, by introducing TA and PEI, a decrease of electrolyte (the most commonly used one is $LiPF_6$ in the mixture of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate solvents [146,147]) contact angle of ca. 35° occurred (from around 45° to 10°), underlining the improved wettability. This is mainly due to the tailored surface chemistry of the separator, principally thanks to the presence of nitrogen atoms; these atoms can also weaken the electrostatic interactions between anions and cations, facilitating the ion pair dissociation and thus enhancing the ionic conductivity. As a result, the engineered cell with the TA/PEI-PP separator showed superior cycling performances and excellent C-rate values (**Figure 2b,c**).

Apart from tuning the separators chemistry and porosity, the type of electrolyte/solvent used is also fundamental to improve the wettability features. It should be noted that, electrolyte penetration and its spreading into porous materials is critically affected by the electrolyte viscosity and surface tension, respectively [148]. Hence, alongside with lowering the contact angles, higher surface tension and decreased viscosity are targeted to achieve electrolyte solutions with optimal wetting of the porous network [128]. For instance, higher salt concentrations were reported to unfavorably affect the electrolyte's wetting behavior, mainly by increasing viscosity [125].

Today's research attention has been turned towards the investigation of ionic liquids (ILs), as safer alternative electrolytes for Li-ion batteries especially because of their higher thermal stability. Deep eutectic solvents are emerging as a possible alternative (see previous section). One of the main shortcomings in using ILs is, up to now, their poor wetting of commercially available separators, *e.g.* polyolefin-based ones. Combining the common polymeric membranes with ceramic additives (together with suitable manufacturing processes) can dramatically enhance the final performances [149,150]. Several works have shown that the introduction of inorganic particles, such as alumina (Al_2O_3) [151], silica (SiO_2) [149], zirconia (ZrO_2) [150], titania (TiO_2) [152] or hydroxyapatite [123] into the polymeric separator matrix could remarkably enhance their thermal stability and wettability because of the high surface free energy. Ceramic-filled membranes show greater surface hydrophilicity thanks to the presence of hydroxyl groups on the nanoparticles. These inorganic materials also confer good thermal/chemical stability and thermal conductivity to the separators; this can also result in an improved battery safety and less heat dissipation. The manufacturing process used to produce ceramic-combined polymeric materials is based on either coating with the inorganic particles (such as by spraying, casting, or dip-coating) or filling them into the polymeric matrix (by simple dispersion). Some studies have shown a significant rise in the separator porosity (from around 40% to 55-70% depending on the ceramic used) with the addition of these inorganic materials [153–155]. Specifically, a blend of silica and alumina (50%-50%) resulted in the highest porosity (up to 80%) [82] and lowest variation in the interfacial resistance, ascribable to both the superior chemical compatibility and greater solid electrolyte interphase (SEI) chemical stability with respect to that of the pristine commercial separator.

Alongside with microporous separators (*e.g.*, polyolefin-based ones), the so-called nonwoven membranes (such as polyesters, polyimides, polyamides [156] or polybenzimidazole [121,157] usually prepared by electrospinning methods) are taking hold due to their highly interconnected pores structure and presence of open pores that also facilitate the ionic transport. It is worth noting the performance improvement by introducing ceramic fillers also in this class of separators, especially when ionic liquids are adopted as battery electrolytes. Specifically, the inorganic particles help in enhancing the final ionic conductivity. Novel poly(vinylidenefluoride) (PVDF)-based membranes exhibit very promising features in terms of ions conductivity (>2-3 mS cm^{-1} with respect to 0.23 mS cm^{-1} of pristine PVDF [82,158,159]) and IL electrolyte uptake and wetting (>400% with peaks of ca. 700% when Al_2O_3, SiO_2 or $BaTiO_3$ were added [82,160]), but its performances even get higher when combined to ceramic fillers as silica, alumina or barium titanate [82]. In addition, Li *et al.* [123] described a fresh alternative to polyolefin-made separators based on a cellulose network cross-linked to hydroxyapatite nanowires (HAP NWs, $Ca_5(PO_4)_3(OH)$) giving rise to a hierarchical highly flexible and porous structure. The as-prepared material exhibited nearly zero contact angle values and outstanding electrolyte uptake (more than 250%), mainly due to the combination of electrolyte affinity, elevated porosity and unique layered structure. Furthermore, both HAP NWs and cellulose possess abundant surface functional groups that can further enhance the separator mechanical properties through the occurrence of numerous interfacial interactions (as hydrogen bonds and/or van der Waals forces). Finally, in this direction, late works [161–163] are disclosing the potentiality of adding cellulose materials to microporous or nonwoven membranes; for example, when it has been combined to PVDF-*co*-hexafluoropropylene-based separator a significant decrease of IL contact angle down to ca. 9° was observed [82,164]. Once again, this can be probably due to the rise in the materials porosity, thus resulting in an increase of the electrolyte retention compared to the pristine membrane.

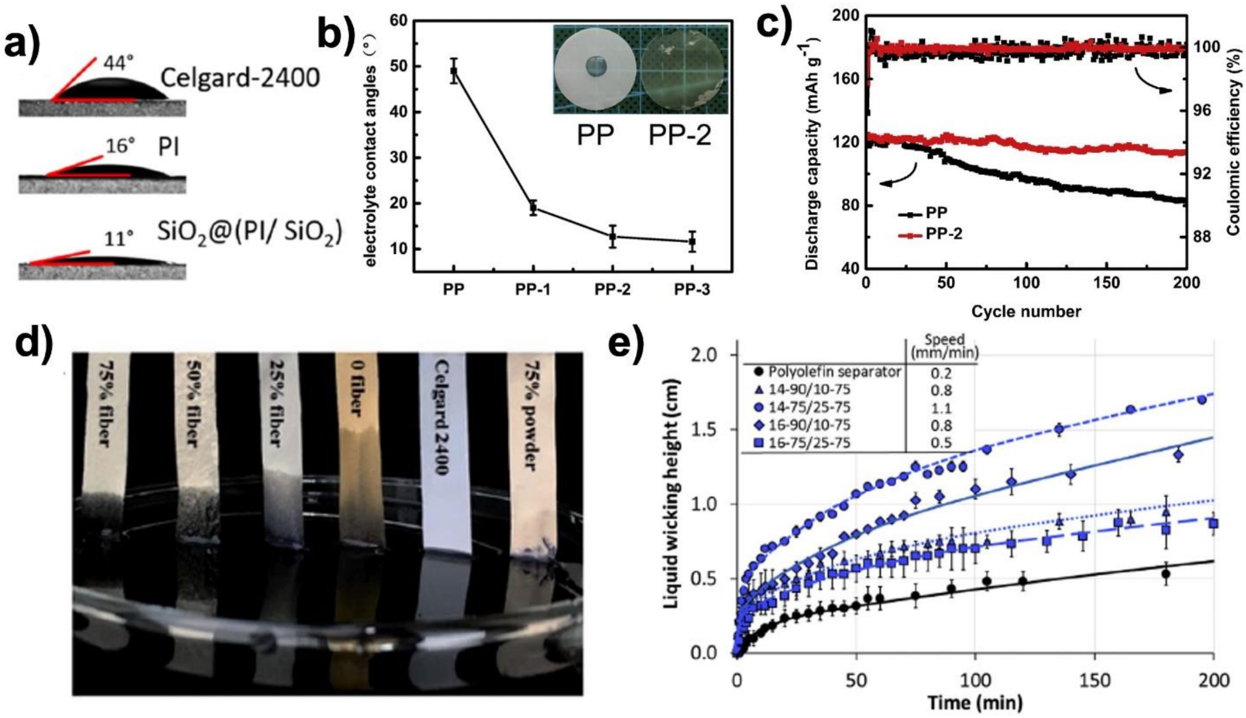

Figure 2. (a) Contact angle measurement by a carbonate-based electrolyte for Celgard-2400, polyimide (PI) and SiO_2@(PI/SiO_2) separators. Reproduced with permission [149]. Copyright xxx, yyy. (b) Contact angles of a carbonated-based electrolyte on polypropylene (PP) before and after modification with tannic acid (TA) and polyethyleneimine (PEI), with (c) relative cyclability and Coulombic efficiency of the TA/PEI-based PP battery at 1 C. Reproduced with permission [146]. (d) Immersion-height of a carbonate-based electrolyte on Celgard 2400 separator and on membranes with different ZrO_2 contents. Reproduced with permission [150]. (e) Liquid wicking height as a function of time of a carbonate-based electrolyte for polyolefin and para-phenylenediamine-polyetherimide separators. Reproduced with permission [132].

4. 2D carbon materials and beyond: the quest for a smart anode

Nowadays the most likely development in LIBs is related to the negative electrode [165]. In the early days of lithium batteries, lithium metal was used as negative electrode, but the formation of dendrites during cycling process has so far hampered its commercial diffusion, as it will be further discussed in Section 5. Consequently, several materials have been tested and proposed since then in which lithium ions, during the charge process, are stored with three possible mechanisms depending on their nature [165]:

a) insertion reaction mechanism,
b) conversion reaction mechanism,
c) formation of an alloy.

Focusing on insertion mechanism, the most eligible materials should quickly insert lithium without hindrance and be characterized by a very low redox potential versus lithium with a high specific capacity in terms of mAh g^{-1}.

The most archetypal material of this class is the commercial graphite, the so-called "soft carbon". Although this material has a significant crystallinity, the maximum level of lithium intercalation is Li:C=1:6, and its capacity is only 372 mAh g^{-1}. More than 90% of this capacity can be released below 0.5 V with a total cell voltage of more than 3.0 V [166]. The mechanism of insertion and the specific capacity dramatically change if a high surface carbon material, or a nanocarbon are considered [166]. In this case, being structures not clearly ordered and organized, intercalation does not happen, and the insertion of lithium ion might occur via surface adsorption or interactions with surface defects [166].

Considering the formation of LiC_2, carbon nanotubes (CNTs) can ideally reach 1116 mAh g^{-1}. They may accommodate lithium ions not only on the outer surface, but also in the inner part. In ref.[165] it is evidenced that Li^+ penetrates into CNT with two mechanisms, either through their crystal defects or through the ends of the tubes. Synthesis methods affect performance of these materials since their symmetry and diameter modify their lithium storage capacity [1,3]. In particular, their chirality affects the barrier for lithium ion diffusion, while their diameter influences the curvature of walls on which lithium condensates, with a direct proportionality between lithium capacity and CNT diameter [167]. Also, CNTs length affects lithium capacity, the shorter they are the higher the capacity, with a maximum predicted for $Li_{0.19}C$ [168], and a theoretical capacity of 424 mAh g^{-1}. In terms of other properties, they are characterized by high electrical conductivity, good structural stability, tuneable surface functionality, and excellent mechanical properties [165].

Similar properties are typical of another carbon material, graphene. This material can ideally be lithiated on both sides, giving a theoretical stoichiometry of LiC_3, with a capacity of 744 mAh g^{-1} [169]. Unfortunately, the high specific surface of this material, about 2600 m^2 g^{-1}, is a drawback, since provokes agglomeration of graphene sheets and a worsening of performance due to a reduction of capacity [165]. A solution may be the removal of oxygen functional groups, or a doping with metal and metal oxides, the latter case leading to an increase of Li insertion. Another strategy is the doping with heteroatoms. Nitrogen is a good candidate in this approach, since the difference in electronegativity between nitrogen and carbon induces change of charge density, and differences in their size introduce defects in the structure. These defects increase the mobility of lithium and, therefore the charge capacity of these materials [165].

Another solution could be the porous graphene, which is characterized by high conductivity and, thanks to 3D networking, high porosity compared to graphene [170]. However, it is noteworthy that, in graphene 3D structures, the crystallinity of the material is more important than the distribution of porosity or specific surface area because the former has a primary role in the diffusion of lithium [171]. Jung *et al.* highlighted that aerogel and xerogel graphene, with huge differences in specific surface area, have the same capacity of about 380 mAh g^{-1} at 1C [171]. Nevertheless, Ikram *et al.* reported that the doped porous graphene, synthesised by chemical vapour deposition, has a capacity of 2250 mAh g^{-1} under a current density of 50 mA g^{-1} (after 50 cycles) [172]. As for "simple" graphene a surface functionalisation and/or modification, with the introduction of functional materials, can boost performance of this material [170]. Multiple heteroatoms co-doping appears very promising, due to the synergistic effect among C atoms and dopants. Furthermore, a coupling of these heteroatoms-doped carbon-derivatives, graphene with other carbon nanomaterials (*e.g.*, carbon nanotubes), has attracted many interests, thanks to a synergistic effect among their properties [170]. Alongside these materials, in the last 20 years many authors have predicted that new carbon allotropes, not yet synthesised, could be very useful as anode in LIBs [173]. As reported in **Figure 3** [173], specific capacity varies varying the structure and the chemical complexity of the considered allotrope.

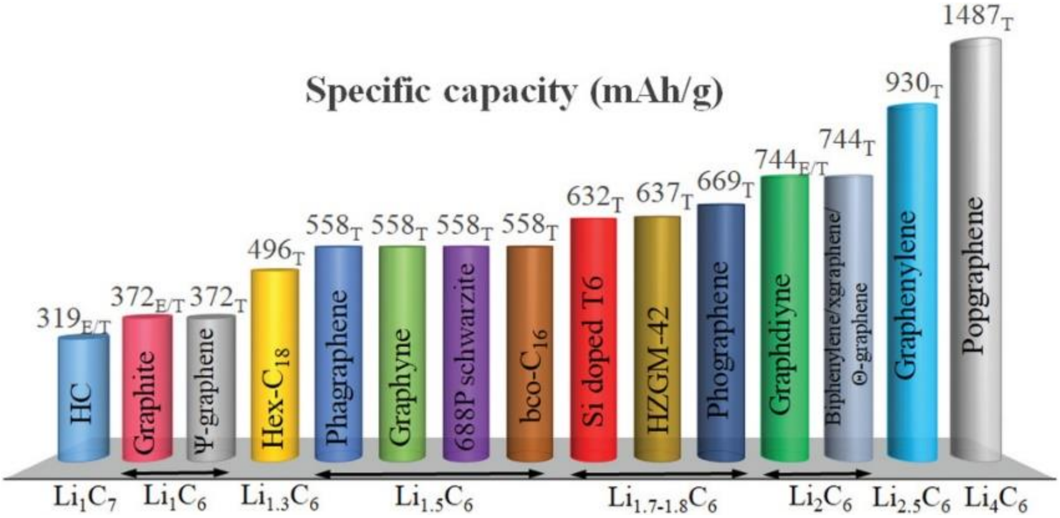

Figure 3. Specific capacity of various carbon-based anodes. Reproduced from ref. [173] with permission from John Wiley and Sons.

Notwithstanding these very promising results, it should be noted that criticisms have been raised concerning the use of CNTs and graphene as electroactive materials in LIBs anodes[174]: i) the high specific capacities exhibited during the first lithiation step is not completely released in the following delithiation process, with a huge loss of lithium ions, that are irreversibly consumed instead of being reversibly stored, and, therefore, with a lowering of Coulombic efficiency of the cell; ii) a graphene-based negative electrode delivers discharge capacities at a potential of 1–3 V (vs. Li/Li^+) rather higher compared to 0.3 V (vs. Li/Li$^+$) for a conventional graphite electrode, with a large voltage hysteresis in the charge/discharge curves. In the case of CNT electrode, a lack a voltage plateau is observed, together with large change in voltage during discharge, and a worsening of energy efficiency; iii) these materials often suffer from rapid capacity decay after a few cycles. Consequently, the capacity decreases, making them not competitive with graphite. Nevertheless, their use in LIBs could be beneficial, acting as a regulator, modifying the lithium storage behaviour of a specific electroactive material [174,175]. Moreover, they can also affect the lithium dendrite growth [174]. Sun et al. [176] analysed the reasons why graphene is a very promising charge regulator in negative electrodes for LIBs and concluded that its intrinsic properties, easy modification of its atomic structure, and the possibility of built a 3D network are the main aspects that should be considered.

Anode materials are not limited to carbon-based ones. Even considering their low cost and improving performances, we have to remind how EVs ask for higher energy density, specific energy and Coulombic efficiency, not provided by nowadays LIBs' anode materials [177–180], as evident from **Figure 4**.

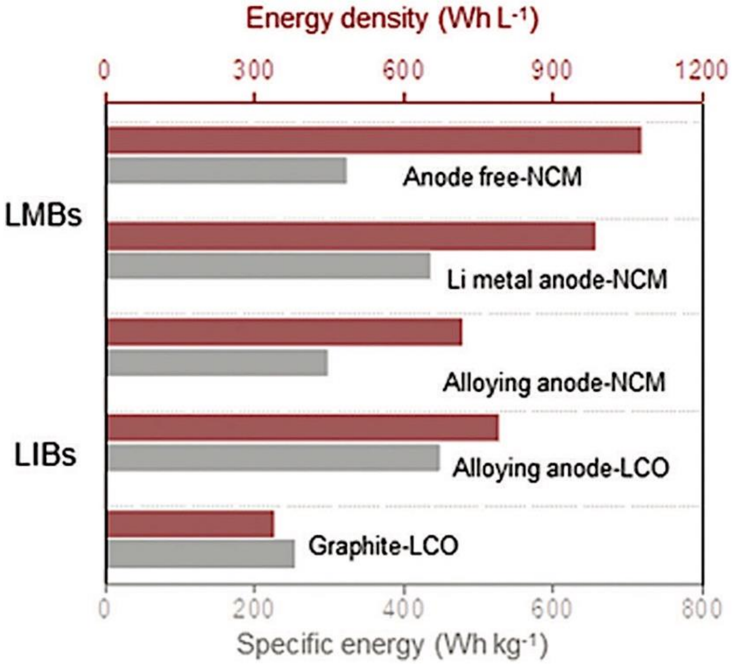

Figure 4. Specific and volumetric energy densities for typical and state-of-the-art Li-based batteries; LCO = Lithium Cobalt Oxide, NCM = nickel-rich trimetallic oxide. Reproduced from ref [180] with permission from the Royal Society of Chemistry.

Thus, materials with low molecular weight able to perform multi-electron reactions must be employed to increase the theoretical capacity. When LIBs are working, during discharging and charging cycles, kinetic problems arise, manly connected with the diffusion of Li inside the anode. During the discharge, Li must leave an electron and exit the anode material and the SEI to enter the electrolyte. Thus, the diffusion process can be considered the rate determining step (rds) for the LIB. On the contrary, during the charge, Li must enter the anode and diffuse towards the active sites where it recombines with an electron. Also in this case, the diffusion can be the rds of charging process. To increase the diffusion rate, one can either reduce the space in which Li ions must travel before recombination using nanomaterials or increase the diffusion coefficient of Li ions inside the anode, for example by distorting the crystal lattice.

Moreover, the anode materials for LIBs are still a big challenge due to the problems connected with stability, cyclability, Coulombic efficiency and safety. Recently, different supporting materials have been studied to promote efficiency and cyclability of LIBs [165]. The main problem is the optimization of all the aspects connected to the anode performance, which are strongly correlated. As mentioned, intercalation mechanism is involved not only in graphitic materials, but also in TiO_2 and other Ti-based anodes. This mechanism is highly active but provides very low specific capacity, leading also to a mechanical degradation of the anode due to the intercalation process: the periodic crystal lattice modifications are detrimental for the structural stability, also leading to a low energy and capacity density, not adequate for EV applications. In this optic, oxide-materials with low volume changes during expansion (intercalation)/expansion (deintercalation) cycles are under investigation. Nb_2O_5 is a noteworthy example [181,182] but, as most oxides, suffers for low electrical conductivity. A possible solution is to generate an intimate connection between the anode material and a good electrical conductor, for example by the growth of a doped carbon shell directly onto the oxide particles. [183]

A second approach, the "conversion reaction" leads to very high specific capacity thanks to a reversible reaction between Li and transition metal cations. Tarascon and his group [184] firstly defined this new mechanism and proposed the usage of different metal oxides. Using nanoparticles of transition metal oxides, TMO, with formula MO where M = Co, Ni, Cu or Fe, they prepared a composite material, MO + 10% of SP carbon black, with a specific charge of 700 mAh g^{-1} and 100% capacity retention after 100 cycles, presenting also a very high recharging rates due to the chemical reaction mechanism. The best performing TMO, characterized as positive electrode in an electrochemical cell whose negative electrode was Li sheet, is CoO, whose reversible "conversion reaction" with Li ion is:

$$CoO + 2Li^+ + 2e^- \rightleftarrows Co + Li_2O \qquad (1)$$

leading to the formation of metallic Co during the discharge cycle. This reaction mechanism causes the decomposition/amorphisation of CoO, with the formation of nanoparticles that remain unchanged in the subsequent cycles. This is made evident by a *I-E* curve of the first discharge cycle highly different from the following ones, because the crystalline structure collapses when CoO is completely reduced by the reaction with Li ions, forming metallic nanoparticles of about 1-5 nm dispersed in Li_2O. The reversibility of reaction (1) was proven using spectroscopic and magnetic techniques, which evidenced the importance of the nano-size of oxide precursor that can dramatically influence the electrochemical performance of the anode material in terms of specific capacity and cyclability. These performances are strictly connected to the above described “conversion mechanism” between Li ions and CoO. This mechanism relates to the lattice of these TMO, which present a rock-salt structure in which empty sites for Li ions are completely absent.

Starting from this seminal work, the “conversion mechanism” has been studied by many authors, with the aim to find the best TMO precursor to obtain high specific capacity and energy density and long-life span of the LIBs. While several reviews have been written on this topic [165,185,186], the reasons behind the high specific capacity and energy density observed in these materials are still unclear. Since the described seminal work of Tarascon, many different TMO have been synthesised and electrochemical characterized to be used as anode material in LIBs and Na ion batteries [187–191]. Many of these TMO, used as conversion-type anode, present a strong affinity for Li, thus leading to a formation of strong chemical bond during the lithiation process with the result of irreversible lithium incorporation. Finally, TMO as conversion-type anode are characterized by this general charge reaction:

$$\mathrm{M}_a\mathrm{O}_b + 2b\mathrm{Li}^+ + 2b\mathrm{e}^- \rightarrow b\mathrm{Li}_2\mathrm{O} + a\mathrm{M} \qquad (2)$$

and the possible irreversible formation of LiO_2 during the first lithiation process leads to a decrease of the initial Coulombic capacity for these materials.

The issue of low initial Coulombic efficiency is largely investigated and discussed and some solutions, not yet commercially available, have been already proposed [192,193]. In summary, the possible solutions are chemical or electrochemical treatments of LIBs’ electrodes to pre-lithiate the anodic and/or cathodic material, to reduce or completely avoid the capture of Li by the electrode. The chemical pre-lithiation processes can be carried out in lab scale but are not suitable for industrial production due to the toxicity and/or flammability of prelithiating agents, which cannot be adapted for the current technological applied to industrially prepare the electrodes. Electrochemical pre-lithiation is more suitable for an industrial application, also adding the possibility of accurately tuning the grade of lithiation process by controlling the electrode potentials or the current intensity. Even if largely studied, these methods introduce sacrificial Li in the LIBs, to increase the initial Coulombic efficiency of the batteries and are still under investigation to solve the weaknesses for their use in large-scale commercial applications.

A third approach is based on alloying reaction between Li and elements such as Si, Sb, Sn, Zn, In, Bi, and Cd [193–197]. In this case it is possible to reach higher specific capacity, up to more than 4200 mAh g^{-1} in the case of Si anodes [198], and a fast Li diffusion inside the alloy [199,200]. Several battery manufacturers are already using blended graphite and Si anode in commercial LIBs and full silicon-based anode technologies seem to be close to commercialization, such as Tesla 4680 cells. However, Si anodes suffers from a limited life span due to extremely high stress connected with alloying/dealloying cycles. Alloying process can lead to the anode's volume modification up to 300%, thus causing large strains of the crystal structure followed by partial pulverization [201]. Finally, the high production cost of these materials can represent a serious hindrance towards their effective application [202]. Numerous solutions have been proposed to solve these issues, as discussed in recent reviews [201][202]. Among them, 2D architectures, such as silicene – a Si allotrope similar to graphene, represent emerging candidates due to their fast ionic/electronic diffusion kinetics [203]. Silicene possesses ample channels for the adsorption and migration of Li ions, thus efficiently preventing volume change during the lithiation/delithiation processes that occur in crystalline silicon, leading to a longer lifetime.

In recent years, perovskite have become a very promising class of materials for LIB anodes, as they can reduce the volume expansion and the following destructive phenomenon strictly connected with alloying/dealloying processes, thus improving the performance of LIBs due to the ease insertion/deinsertion of Li in the structure. In 2016 Park and co-workers [204] proposed for the first time the use of a mixture composed by cubic perovskite $BaSnO_3$ nanoparticles and reduced graphene oxide (rGO) as anode material for high performance LIBs. Firstly, $BaSnO_3$ not only can incorporate Li alloying it with Sn, but also Ba can form Li-Ba alloys with high electrical conductivity, thus leading to a high theoretical reversible capacity [205]. The preparation of the composite anode materials is simple and clean, involving a co-precipitation and solid-state reaction method to synthesize cubic perovskites and Hummer's method to prepare rGO, see **Figure 5.** This composite anode presents a reversible specific capacity of 1200 mAh g^{-1}, very high compared to the pristine material, and excellent cyclability due to the presence of well electrical connected 2D graphene sheets, that activate the formation of Li-Ba alloy with high Li diffusion rates.

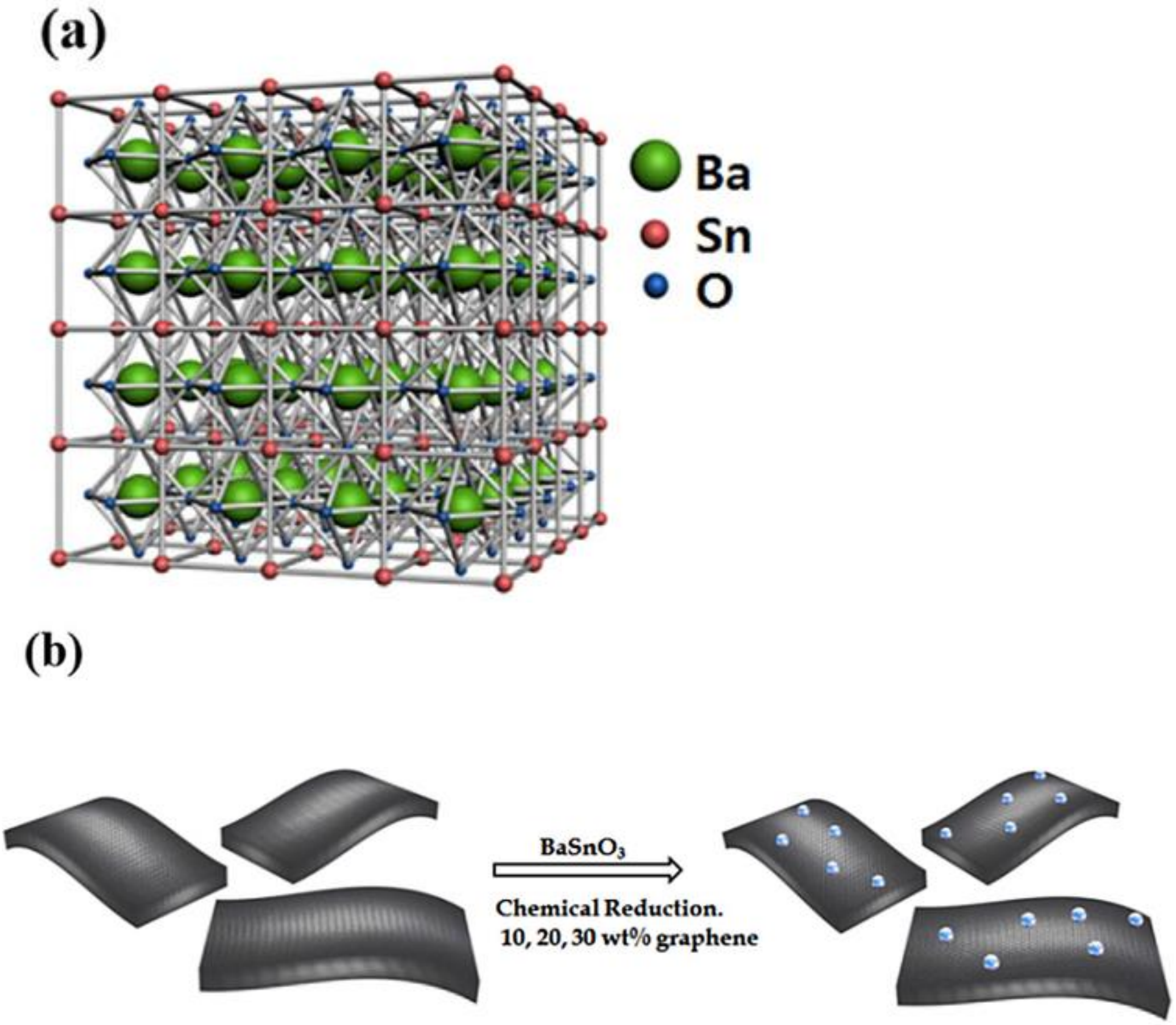

Figure 5. (a) Three-dimensional cubic crystal structure of the synthesised perovskite $BaSnO_3$. (b) Scheme of $BaSnO_3$ on graphene sheets. Reproduced from reference [204] with permission of Elsevier.

The importance of the presence of rGO, a good electronic conductor, was attributed to the need of the electrochemical activation of the “inert” BaO, thus promoting its reversible reduction to Ba [204]:

$BaO + 2\,Li^+ + 2e^- \rightleftarrows Ba + Li_2O$ (3)

which in turn increases the specific reversible capacity due to the possibility of the formation of Li-Ba alloy. This composite anode is very stable and present a very high-rate capability, higher than 1000 mA g^{-1}, also at C-rate = 10. This increased cyclability of LIB was accompanied to a low initial Coulombic efficiency of this conversion-type anode, which remained below 60%. In fact, the initial Coulombic efficiency of LIBs is strictly connected with the loss of Li atoms during the first discharge/charge cycle. During the first cycle, Li can be seized by both the SEI formation and the lithiation process. In the first case, Li is removed from the electrolyte, thus decreasing its concentration, because it remains stuck in the SEI structure. The amount of Li seized by the SEI formation can also increase with time because of the continuous SEI rupture and reformation, observed on materials with a very large volume variation for intercalating/deintercalating processes. The second effect is due to the irreversibility of the lithiation/delithiation anode processes occurring in the first charge/discharge cycle.

Finally, both conversion and alloying anodes are characterized by some problems that hinder their performances, as easy disaggregation, very low stability of SEI, and mechanical stress, due to large volume change during cycling. This can be really detrimental for the long life lasting of the devices, thus reducing their utilization by the final users [206]. To boost their widespread commercialization, it is necessary a better cycling stability, acting on the mechanical and chemical robustness of the SEI by designing suitable nanostructures able to interchange among different solid phase, avoiding any mechanical strain. Moreover, the right selection of electrode materials and surface modification can help in solving the problem [206].

5. Smart interfaces for Li metal anodes

In the last years there has been a renaissance of the usage of metallic Li metal as anode for LIBs. Lithium metal represents the holy grail of anode materials as it can provide the highest energy density for any given cathode, thanks to the highest capacity (around 3900 mAh g^{-1} and 2000 mAh cm^{-3} [198]) and the lowest working potential of 0 V (vs. Li^+/Li) among all anode materials. It can deliver an energy density of about 536 $Wh \cdot kg^{-1}$ in a $LiCoO_2/Li$ galvanic cell. According to its strong electrochemical activity, metallic Li reacts with liquid electrolytes forming a SEI. However, rechargeable lithium metal anodes are still far from commercialization, especially due to safety issues. In particular, the electrochemical formation and growth of dendritic structures during battery recharging represents a major concern since these structures can induce a cell short circuit, which can ignite any flammable liquid electrolyte. Other concerns of metallic Li anodes are the anode volume expansion and Li Coulombic efficiency.

Li dendrite growth has been related to SEI formation and stability [192]. A fragile SEI, due to different effects for which also the Li^+ diffusion in the electrolyte plays a key role, is the first reason of the dendrite growth. The two phenomena interact mutually: a fragile SEI allows for a facile dendrite growth, while the dendrite growth leads to a fragile SEI. Li et al. [192] analyzed and described deeply the interconnection between SEI stability and rate of dendrite growth, and concluded that the dendrite formation is strictly connected with Li^+ diffusion mechanism and Li^+ solvation sheath.

The formation and growth of dendrites has been related also to the poor wettability of bare lithium metal surfaces by the electrolyte. Chen *et al.* [207] proposed that a poor wetting leaves portions of the metal surface uncontacted, hence these regions do not contribute to Li stripping and plating during electrochemical cycling. Over many charge/discharge cycles, this unbalance leads to a rough Li surface (**Figure 6a**). In this respect, coating the Li surface with an Al_2O_3 coating deposited by atomic layer deposition (ALD) promotes the electrode wettability by both carbonate-based and ether-based electrolytes [207], leading to a uniform SEI layer and to a more efficient lithium stripping and deposition (**Figure 6b**). The complete electrolyte spreading observed upon ALD Al_2O_3-coating could eliminate voids in the lithium–electrolyte interface, providing a more uniform electric field over the electrode surface during cycling and a more uniform lithium flux and electrodeposition.

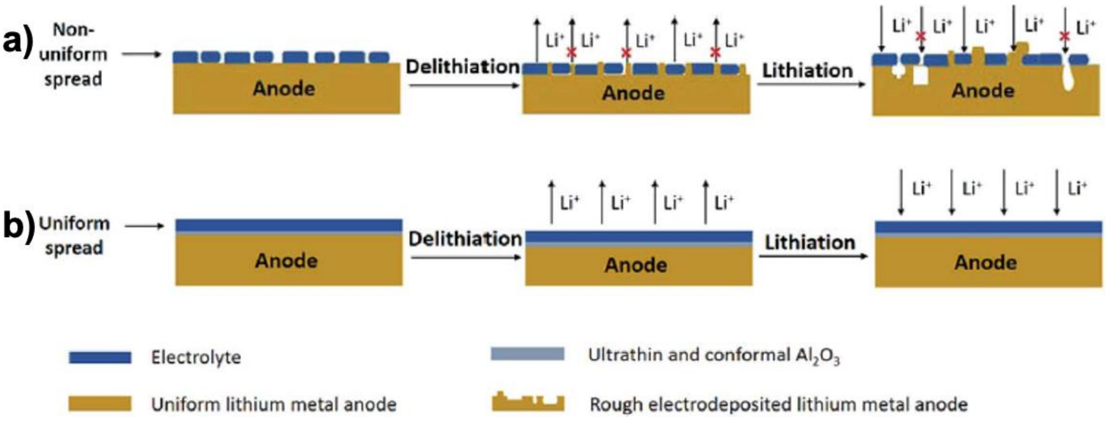

Figure 6. (a) Schematic of Li plating on lithium metal anodes on bare lithium surface, resulting in rough surfaces and (b) ALD Al_2O_3-coated lithium surface leading to a uniform and smooth layer. Reproduced with permission [207].

Then, Park and Goodenough [208] reported the modification of the Li metal surface with Li_3N as a strategy to suppress dendritic growth, which they explained using a wetting model (**Figure 7c**). Plating of lithium through a bed of Li_3N particles still causes the formation of Li dendrites at liquid the electrolyte/Li interface (**Figure 7a**). However, dendrites tend to wet the Li_3N particle, leading to the growth of a 3D lithium network.

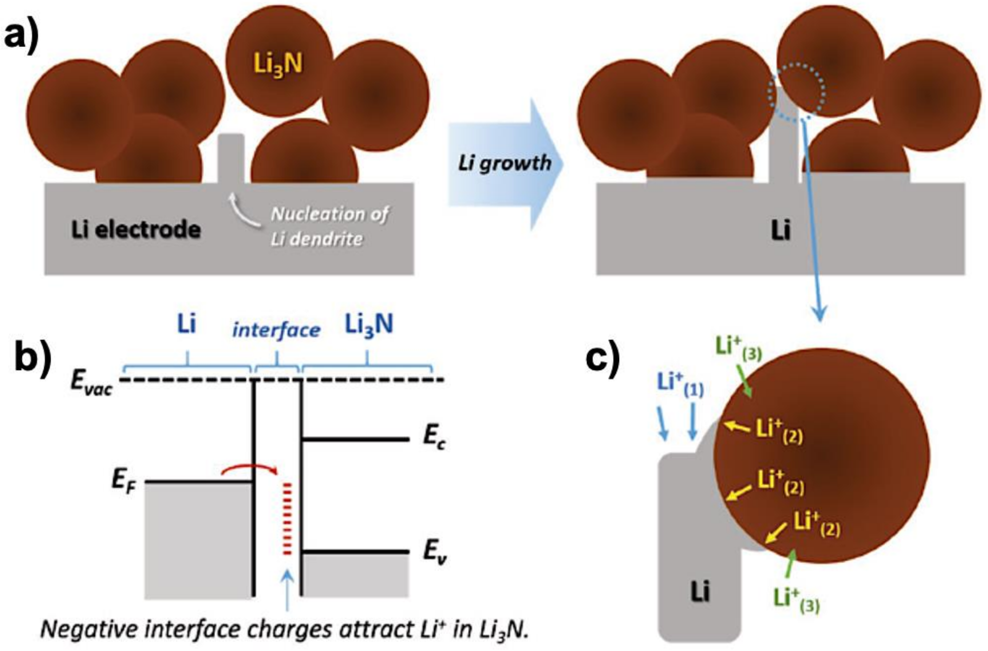

Figure 7. Schematic representation displaying (a) the nucleation of a Li dendrite and its growth through Li_3N particles network. (b) Energy band diagram at the Li_3N/Li heterojunction showing electron transfer at the interface. (c) A proposed Li wetting model in the presence of liquid electrolyte and Li_3N particles. Reproduced with permission [208].

Solid-state electrolytes (SSEs) have also been proposed to help in suppressing lithium dendrites formation even if there are still challenges to overcome: both the high interfacial resistance and the non-uniformity at Li/SSE interface can lead to Li dendritic growth [209,210]. Notably, voids formed at the interface can accumulate on cycling, thus provoking an increase of the local current density due to dendrite formation on plating, short circuit and cell death [211]. In addition, attempts made to reduce the non-uniformity of the interface, for example by densifying SSE [212], cannot entirely hinder dendrite formation. In the same way, lithiophilic materials (such as alumina [207], zinc oxide [213] or lithium nitride [208]) coated on SSEs, which can fill the energy gap between Li and SSE, are able to reduce the Li/SSE interfacial resistance but Li dendrites can still grow [209,210]. According to Ji et al. [210], to effectively suppress this undesired phenomenon, three criteria for the electrolyte and the formed interfaces should be fulfilled: *i*) they must be stable towards lithium, *ii*) they should possess high ionic and low electronic conductivities, and *iii*) they should have high interface energy against lithium so that its nucleation and growth inside the electrolyte are hindered. Cheng et al. [214] reported the case of Li_2O-Al_2O_3-P_2O_5-TiO_2-GeO_2 composite material reacting with Li that can effectively terminate the continuous Li dendrite propagation and growth, therefore resulting in a meta-stable interface which can afford a soft contact between Li-metal anode and SSE.

Conversely, a stable and rigid interface (such as $Li_{6.1}Ga_{0.3}La_3Zr_2O_{12}$/Li) will terminate the cell cycling earlier because of the increased interfacial resistance. Ye et al. [209] recently showed how a solid-state battery designed with a multilayer structure (a less-stable electrolyte sandwiched between two more-stable solid electrolytes) could prevent any lithium dendrite growth through well localized decompositions in the less stable electrolyte layer. In this way, every possible crack is filled by dynamically generated and well constrained decompositions, thus resulting in very stable cycling performances of the lithium metal anode coupled with a $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode, showing a ca. 80% capacity retention after 10,000 cycles at a 20 C rate. Suppression of dendrite growth can also depend on the mechanical properties of an SSE. This in turn requires a deeper knowledge of the morphology and stress-generation of growing Li dendrites, calling into action advanced characterization techniques. [215]

Notwithstanding these issues, SSEs do show some important advantages: they can replace conventional flammable non-aqueous electrolytes and, generally, they show a large electrochemical potential window (above 5 V) [216]. Solid-state electrolytes can either be inorganic (*e.g.* sulphides or oxides [217,218]) or polymer-based ones (such as polyethylene oxide, poly(vinylidenefluoride), polymethylmethacrylate, and so on [219,220]). Recently, for both classes, several authors have reported strategies to reduce the interfacial resistance promoting the wetting of the lithium anode by solid state electrolytes [217,218,220–224]. Particularly, they focused on the interface between lithium anode and garnet-type ceramic electrolytes [217,221,223–225]. Garnet-structured electrolytes, such as $Li_7La_3Zr_2O_{12}$ and $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$ (LLZTO), are believed to be promising for solid-state lithium ion batteries (SSLIBs) due to their good chemical stability against metallic lithium and high ionic conductivity [226], but their interfacial contact with Li metal is very poor, resulting in high interfacial resistance (10^2-10^3 ohm cm^2) and uneven current distribution [217]. Several strategies have been reported to improve the interfacial compatibility between Li metal and garnet electrolytes: thin layers of Al [217], Al_2O_3 [224], LiN_3 [218], or Ge [222], surface treatments with carbon [223], and garnet modification with polymers [225] or graphite [221] have been reported to promote the wettability between the garnet surface and the molten Li metal (from lithiophobic to lithiophilic), resulting in a better interfacial contact (**Figure 8**). Dong *et al.* [220] proposed a ‘‘universal’’ interfacial modification method based on a curable polymer-based electrolyte glue to address the issue of solid‒solid contact between solid electrolyte and electrode materials: they developed a liquid adhesive exhibiting good chemical/electrochemical stability and high wettability towards a series of electrodes and electrolytes (including Li metal and LLZTO), which could then be easily solidified into a polymer electrolyte layer via thermal curing, leading to a much smaller interface impedance and enhanced electrochemical performances of the SSLIB.

The use of 3D hosts is another promising strategy explored to promote the cycling stability of lithium metal anodes by solving the issues of dendrite growth and of infinite volume change of Li during stripping/plating processes [227]. These 3D hosts should exhibit high electric conductivities, good chemical stabilities, high porosities and lithiophilic properties [228]. Carbon materials can represent ideal 3D hosts, but they show poor wetting by lithium. Niu *et al.* [229] functionalized the surface of an electrospun carbon host with –NH functional groups: the strong interaction between –NH and Li enhanced the wettability of Li on the carbon surface, thus promoting the infiltration of molten Lithium within the porous structure. Moreover, the low contact angle also favours nucleation of Li during recharging, especially in pore channels or cavities, leading to self-filling of pores and to a self-smoothing electrode surface, in contrast with dendritic growth observed at untreated carbon surfaces.

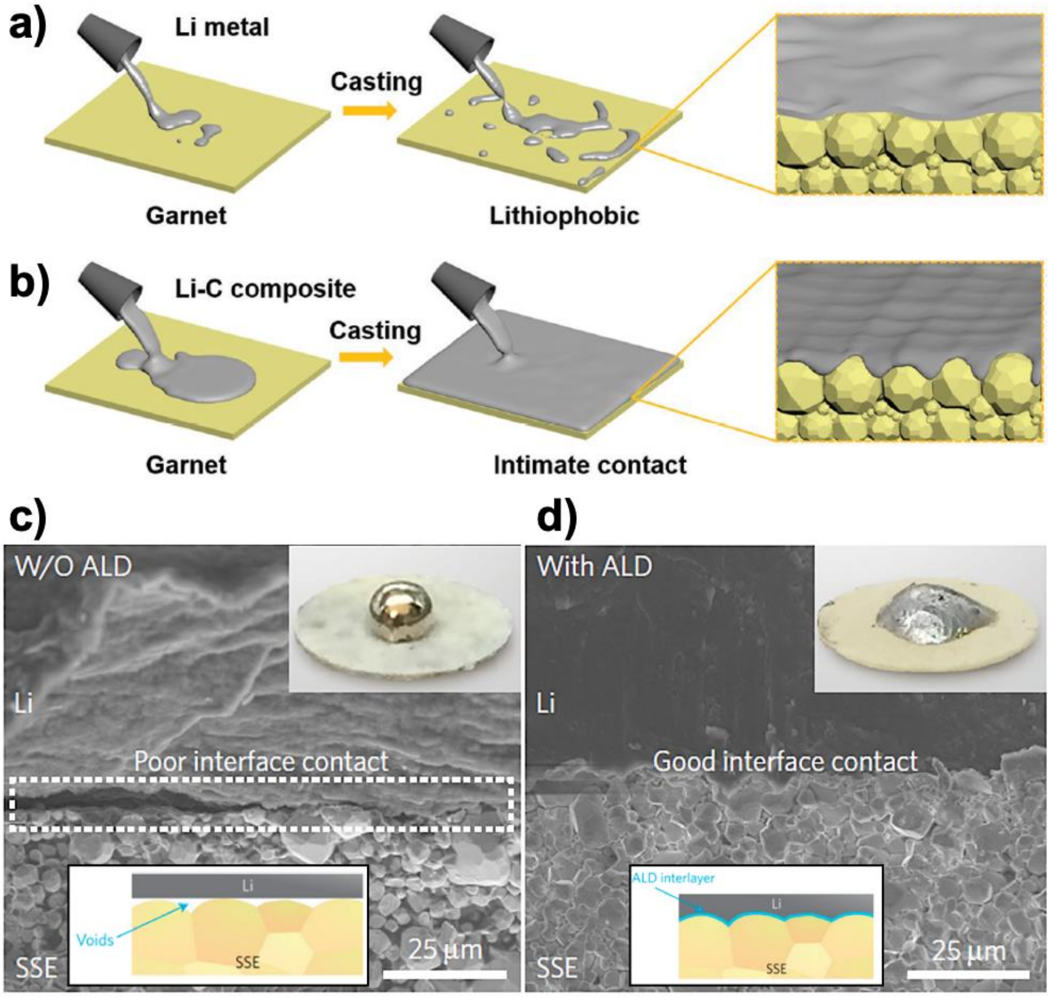

Figure 8. Schematic illustrations of casting (a) pure lithium (Li) and (b) lithium–graphite (Li–C) composite on garnet solid state electrolyte, showing poor and good contact respectively. Reproduced with permission [221]. SEM micrographs of the garnet solid-state electrolyte/Li metal interface (c) without and (d) with ALD-Al_2O_3 coating. Insets: schematic representation of melted Li metal on top of both pristine and treated garnet surface. Reproduced with permission [224].

6. Conclusions

In this review we aimed at demonstrating that the most recent scientific findings and technological advances in LIBs (likely including Li metal batteries) will allow for their survival in the near future. This will fully guarantee the use of the current infrastructures while improving the performances (mostly important, the specific capacitance), the cost and the safety of the final device. The intrinsic interdisciplinarity of this topic represents both its complexity and its key for success: only acting on the various sides of the battery one can reach the next target. However, these are strongly interdependent and designing smart interfaces should become as important as looking for smart materials.

On this basis, we here reviewed the main progressions made in some of the "weakest" part of LIBs: the electrolyte (solvent), the anode material and the issues related to the wettability of the separator. The importance of these topics is demonstrated by the impressive research efforts, that are no less than those focused on the so-called post-lithium ones (Na-ion, Li-air, Li-sulphur) as evident by any literature search.

Declaration of Competing Interest

The authors report no conflicts of interest

References

[1] M.S. Ziegler, J.E. Trancik, Re-examining rates of lithium-ion battery technology improvement and cost decline, Energy Environ. Sci. 14 (2021) 1635–1651. https://doi.org/10.1039/d0ee02681f.

[2] A. Battistel, M.S. Palagonia, D. Brogioli, F. La Mantia, R. Trócoli, Electrochemical Methods for Lithium Recovery: A Comprehensive and Critical Review, Adv. Mater. 32 (2020). https://doi.org/10.1002/adma.201905440.

[3] C.P. Grey, D.S. Hall, Prospects for lithium-ion batteries and beyond—a 2030 vision, Nat. Commun. 11 (2020) 2–5. https://doi.org/10.1038/s41467-020-19991-4.

[4] E. Pargoletti, A. Salvi, A. Giordana, G. Cerrato, M. Longhi, A. Minguzzi, G. Cappelletti, A. Vertova, Orr in non-aqueous solvent for li-air batteries: The influence of doped mno<inf>2</inf>-nanoelectrocatalyst, Nanomaterials. 10 (2020).

https://doi.org/10.3390/nano10091735.

[5] A. Minguzzi, G. Longoni, G. Cappelletti, E. Pargoletti, C. Di Bari, C. Locatelli, M. Marelli, S. Rondinini, A. Vertova, The influence of carbonaceous matrices and electrocatalytic MnO<inf>2</inf> nanopowders on lithium-air battery performances, Nanomaterials. 6 (2016). https://doi.org/10.3390/nano6010010.

[6] E. Pargoletti, G. Cappelletti, A. Minguzzi, S. Rondinini, M. Leoni, M. Marelli, A. Vertova, High-performance of bare and Ti-doped α-MnO2 nanoparticles in catalyzing the Oxygen Reduction Reaction, J. Power Sources. 325 (2016) 116–128. https://doi.org/10.1016/j.jpowsour.2016.06.020.

[7] F. Duffner, N. Kronemeyer, J. Tübke, J. Leker, M. Winter, R. Schmuch, Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure, Nat. Energy. 6 (2021) 123–134. https://doi.org/10.1038/s41560-020-00748-8.

[8] Y. Tian, G. Zeng, A. Rutt, T. Shi, H. Kim, J. Wang, J. Koettgen, Y. Sun, B. Ouyang, T. Chen, Z. Lun, Z. Rong, K. Persson, G. Ceder, Promises and Challenges of Next-Generation “beyond Li-ion” Batteries for Electric Vehicles and Grid Decarbonization, Chem. Rev. 121 (2021) 1623–1669. https://doi.org/10.1021/acs.chemrev.0c00767.

[9] M. Winter, B. Barnett, K. Xu, Before Li Ion Batteries, Chem. Rev. 118 (2018) 11433–11456. https://doi.org/10.1021/acs.chemrev.8b00422.

[10] A. Balducci, Ionic Liquids in Lithium-Ion Batteries, Top. Curr. Chem. 375 (2017) 20. https://doi.org/10.1007/s41061-017-0109-8.

[11] A. Eftekhari, Y. Liu, P. Chen, Different roles of ionic liquids in lithium batteries, J. Power Sources. 334 (2016) 221–239. https://doi.org/10.1016/j.jpowsour.2016.10.025.

[12] Q. Yang, Z. Zhang, X.-G. Sun, Y.-S. Hu, H. Xing, S. Dai, Ionic liquids and derived materials for lithium and sodium batteries, Chem. Soc. Rev. 47 (2018) 2020–2064. https://doi.org/10.1039/C7CS00464H.

[13] K. Liu, Z. Wang, L. Shi, S. Jungsuttiwong, S. Yuan, Ionic liquids for high performance lithium metal batteries, J. Energy Chem. 59 (2021) 320–333. https://doi.org/10.1016/j.jechem.2020.11.017.

[14] S. Chen, K. Wen, J. Fan, Y. Bando, D. Golberg, Progress and future prospects of high-voltage and high-safety electrolytes in advanced lithium batteries: from liquid to solid electrolytes, J. Mater. Chem. A. 6 (2018) 11631–11663. https://doi.org/10.1039/C8TA03358G.

[15] P. Jaumaux, Q. Liu, D. Zhou, X. Xu, T. Wang, Y. Wang, F. Kang, B. Li, G. Wang, Deep-Eutectic- Solvent- Based Self- Healing Polymer Electrolyte for Safe and Long- Life

Lithium- Metal Batteries, Angew. Chemie Int. Ed. 59 (2020) 9134–9142. https://doi.org/10.1002/anie.202001793.

[16] X.-B. Cheng, R. Zhang, C.-Z. Zhao, F. Wei, J.-G. Zhang, Q. Zhang, A Review of Solid Electrolyte Interphases on Lithium Metal Anode, Adv. Sci. 3 (2016) 1500213. https://doi.org/10.1002/advs.201500213.

[17] X. Cao, P. Gao, X. Ren, L. Zou, M.H. Engelhard, B.E. Matthews, J. Hu, C. Niu, D. Liu, B.W. Arey, C. Wang, J. Xiao, J. Liu, W. Xu, J.-G. Zhang, Effects of fluorinated solvents on electrolyte solvation structures and electrode/electrolyte interphases for lithium metal batteries, Proc. Natl. Acad. Sci. 118 (2021). https://doi.org/10.1073/pnas.2020357118.

[18] C.-C. Su, M. He, M. Cai, J. Shi, R. Amine, N.D. Rago, J. Guo, T. Rojas, A.T. Ngo, K. Amine, Solvation-protection-enabled high-voltage electrolyte for lithium metal batteries, Nano Energy. 92 (2022) 106720. https://doi.org/10.1016/j.nanoen.2021.106720.

[19] Y. Ugata, K. Shigenobu, R. Tatara, K. Ueno, M. Watanabe, K. Dokko, Solvate electrolytes for Li and Na batteries: structures, transport properties, and electrochemistry, Phys. Chem. Chem. Phys. 23 (2021) 21419–21436. https://doi.org/10.1039/D1CP02946K.

[20] X.-Q. Zhang, X. Chen, X.-B. Cheng, B.-Q. Li, X. Shen, C. Yan, J.-Q. Huang, Q. Zhang, Highly Stable Lithium Metal Batteries Enabled by Regulating the Solvation of Lithium Ions in Nonaqueous Electrolytes, Angew. Chemie Int. Ed. 57 (2018) 5301–5305. https://doi.org/10.1002/anie.201801513.

[21] S. YANASE, T. OI, Solvation of Lithium Ion in Organic Electrolyte Solutions and Its Isotopie Reduced Partition Function Ratios Studied by ab initio Molecular Orbital Method, J. Nucl. Sci. Technol. 39 (2002) 1060–1064. https://doi.org/10.1080/18811248.2002.9715294.

[22] A. von Wald Cresce, M. Gobet, O. Borodin, J. Peng, S.M. Russell, E. Wikner, A. Fu, L. Hu, H.-S. Lee, Z. Zhang, X.-Q. Yang, S. Greenbaum, K. Amine, K. Xu, Anion Solvation in Carbonate-Based Electrolytes, J. Phys. Chem. C. 119 (2015) 27255–27264. https://doi.org/10.1021/acs.jpcc.5b08895.

[23] S. Han, Structure and dynamics in the lithium solvation shell of nonaqueous electrolytes, Sci. Rep. 9 (2019) 5555. https://doi.org/10.1038/s41598-019-42050-y.

[24] J. Tong, S. Wu, N. von Solms, X. Liang, F. Huo, Q. Zhou, H. He, S. Zhang, The Effect of Concentration of Lithium Salt on the Structural and Transport Properties of Ionic Liquid-Based Electrolytes, Front. Chem. 7 (2020). https://doi.org/10.3389/fchem.2019.00945.

[25] T. Hou, K.D. Fong, J. Wang, K.A. Persson, The solvation structure, transport properties and reduction behavior of carbonate-based electrolytes of lithium-ion batteries, Chem. Sci. 12 (2021) 14740–14751. https://doi.org/10.1039/D1SC04265C.

[26] L. Meyer, D. Curran, R. Brow, S. Santhanagopalan, J. Porter, Operando Measurements of Electrolyte Li-ion Concentration during fast charging with FTIR/ATR, J. Electrochem. Soc. 168 (2021) 090502. https://doi.org/10.1149/1945-7111/ac1d7a.

[27] A. V. Karatrantos, M.S. Khan, C. Yan, R. Dieden, K. Urita, T. Ohba, Q. Cai, Ion Transport in Organic Electrolyte Solutions for Lithium-ion Batteries and Beyond, J. Energy Power Technol. 03 (2021) 1–1. https://doi.org/10.21926/jept.2103043.

[28] K. Matsumoto, R. Hagiwara, O. Tamada, Coordination environment around the lithium cation in solid Li2(EMIm)(N(SO2CF3)2)3 (EMIm=1-ethyl-3-methylimidazolium): Structural clue of ionic liquid electrolytes for lithium batteries, Solid State Sci. 8 (2006) 1103–1107. https://doi.org/10.1016/j.solidstatesciences.2005.12.017.

[29] Y. Saito, T. Umecky, J. Niwa, T. Sakai, S. Maeda, Existing Condition and Migration Property of Ions in Lithium Electrolytes with Ionic Liquid Solvent, J. Phys. Chem. B. 111 (2007) 11794–11802. https://doi.org/10.1021/jp072998r.

[30] J.-C. Lassègues, J. Grondin, C. Aupetit, P. Johansson, Spectroscopic Identification of the Lithium Ion Transporting Species in LiTFSI-Doped Ionic Liquids, J. Phys. Chem. A. 113 (2009) 305–314. https://doi.org/10.1021/jp806124w.

[31] J. Pitawala, J.-K. Kim, P. Jacobsson, V. Koch, F. Croce, A. Matic, Phase behaviour, transport properties, and interactions in Li-salt doped ionic liquids, Faraday Discuss. 154 (2012) 71–80. https://doi.org/10.1039/C1FD00056J.

[32] F. Castiglione, E. Ragg, A. Mele, G.B. Appetecchi, M. Montanino, S. Passerini, Molecular Environment and Enhanced Diffusivity of Li + Ions in Lithium-Salt-Doped Ionic Liquid Electrolytes, J. Phys. Chem. Lett. 2 (2011) 153–157. https://doi.org/10.1021/jz101516c.

[33] Z. Li, G.D. Smith, D. Bedrov, Li + Solvation and Transport Properties in Ionic Liquid/Lithium Salt Mixtures: A Molecular Dynamics Simulation Study, J. Phys. Chem. B. 116 (2012) 12801–12809. https://doi.org/10.1021/jp3052246.

[34] A. Deshpande, L. Kariyawasam, P. Dutta, S. Banerjee, Enhancement of Lithium Ion Mobility in Ionic Liquid Electrolytes in Presence of Additives, J. Phys. Chem. C. 117 (2013) 25343–25351. https://doi.org/10.1021/jp409498w.

[35] V. Lesch, S. Jeremias, A. Moretti, S. Passerini, A. Heuer, O. Borodin, A Combined Theoretical and Experimental Study of the Influence of Different Anion Ratios on Lithium Ion Dynamics in Ionic Liquids, J. Phys. Chem. B. 118 (2014) 7367–7375. https://doi.org/10.1021/jp501075g.

[36] F. Castiglione, A. Famulari, G. Raos, S. V. Meille, A. Mele, G.B. Appetecchi, S. Passerini, Pyrrolidinium-Based Ionic Liquids Doped with Lithium Salts: How Does Li + Coordination

Affect Its Diffusivity?, J. Phys. Chem. B. 118 (2014) 13679–13688. https://doi.org/10.1021/jp509387r.

[37] T. Méndez-Morales, J. Carrete, Ó. Cabeza, O. Russina, A. Triolo, L.J. Gallego, L.M. Varela, Solvation of Lithium Salts in Protic Ionic Liquids: A Molecular Dynamics Study, J. Phys. Chem. B. 118 (2014) 761–770. https://doi.org/10.1021/jp410090f.

[38] S. Menne, T. Vogl, A. Balducci, Lithium coordination in protic ionic liquids, Phys. Chem. Chem. Phys. 16 (2014) 5485. https://doi.org/10.1039/c3cp55183k.

[39] M. Ikeda, M. Aniya, Analysis of the ionic conductivity in lithium salt-containing ionic liquids based on the bond strength–coordination number fluctuation model, Solid State Ionics. 262 (2014) 476–481. https://doi.org/10.1016/j.ssi.2013.10.023.

[40] J. Pitawala, A. Martinelli, P. Johansson, P. Jacobsson, A. Matic, Coordination and interactions in a Li-salt doped ionic liquid, J. Non. Cryst. Solids. 407 (2015) 318–323. https://doi.org/10.1016/j.jnoncrysol.2014.08.043.

[41] Z. Li, O. Borodin, G.D. Smith, D. Bedrov, Effect of Organic Solvents on Li + Ion Solvation and Transport in Ionic Liquid Electrolytes: A Molecular Dynamics Simulation Study, J. Phys. Chem. B. 119 (2015) 3085–3096. https://doi.org/10.1021/jp510644k.

[42] K. Ueno, R. Tatara, S. Tsuzuki, S. Saito, H. Doi, K. Yoshida, T. Mandai, M. Matsugami, Y. Umebayashi, K. Dokko, M. Watanabe, Li + solvation in glyme–Li salt solvate ionic liquids, Phys. Chem. Chem. Phys. 17 (2015) 8248–8257. https://doi.org/10.1039/C4CP05943C.

[43] V. Lesch, Z. Li, D. Bedrov, O. Borodin, A. Heuer, The influence of cations on lithium ion coordination and transport in ionic liquid electrolytes: a MD simulation study, Phys. Chem. Chem. Phys. 18 (2016) 382–392. https://doi.org/10.1039/C5CP05111H.

[44] F. Wohde, R. Bhandary, J.M. Moldrickx, J. Sundermeyer, M. Schönhoff, B. Roling, Li+ ion transport in ionic liquid-based electrolytes and the influence of sulfonate-based zwitterion additives, Solid State Ionics. 284 (2016) 37–44. https://doi.org/10.1016/j.ssi.2015.11.017.

[45] J. Tong, X. Xiao, X. Liang, N. von Solms, F. Huo, H. He, S. Zhang, Insights into the solvation and dynamic behaviors of a lithium salt in organic- and ionic liquid-based electrolytes, Phys. Chem. Chem. Phys. 21 (2019) 19216–19225. https://doi.org/10.1039/C9CP01848D.

[46] W.J. Lin, Y. Xu, S. MacDonald, R. Gunckel, Z. Zhao, L.L. Dai, Tailoring intermolecular interactions to develop a low-temperature electrolyte system consisting of 1-butyl-3-methylimidazolium iodide and organic solvents, RSC Adv. 9 (2019) 36796–36807. https://doi.org/10.1039/C9RA07257H.

[47] S. Barik, M. Chakraborty, M. Sarkar, How Does Addition of Lithium Salt Influence the

Structure and Dynamics of Choline Chloride-Based Deep Eutectic Solvents?, J. Phys. Chem. B. 124 (2020) 2864–2878. https://doi.org/10.1021/acs.jpcb.9b11947.

[48] H. Srinivasan, V.K. Sharma, R. Mukhopadhyay, S. Mitra, Solvation and transport of lithium ions in deep eutectic solvents, J. Chem. Phys. 153 (2020) 104505. https://doi.org/10.1063/5.0018510.

[49] F. Schmidt, M. Schönhoff, Solvate Cation Migration and Ion Correlations in Solvate Ionic Liquids, J. Phys. Chem. B. 124 (2020) 1245–1252. https://doi.org/10.1021/acs.jpcb.9b11330.

[50] Y. Wang, W. Chen, Q. Zhao, G. Jin, Z. Xue, Y. Wang, T. Mu, Ionicity of deep eutectic solvents by Walden plot and pulsed field gradient nuclear magnetic resonance (PFG-NMR), Phys. Chem. Chem. Phys. 22 (2020) 25760–25768. https://doi.org/10.1039/D0CP01431A.

[51] N. Arai, H. Watanabe, E. Nozaki, S. Seki, S. Tsuzuki, K. Ueno, K. Dokko, M. Watanabe, Y. Kameda, Y. Umebayashi, Speciation Analysis and Thermodynamic Criteria of Solvated Ionic Liquids: Ionic Liquids or Superconcentrated Solutions?, J. Phys. Chem. Lett. 11 (2020) 4517–4523. https://doi.org/10.1021/acs.jpclett.0c00906.

[52] Y. Bao, M. Kitta, T. Ichii, T. Utsunomiya, H. Sugimura, Visualization of solvation structure on Li 4 Ti 5 O 12 (111)/ ionic liquid-based electrolyte interface by atomic force microscopy, Jpn. J. Appl. Phys. 60 (2021) SE1004. https://doi.org/10.35848/1347-4065/abf3a3.

[53] D. Tolmachev, N. Lukasheva, R. Ramazanov, V. Nazarychev, N. Borzdun, I. Volgin, M. Andreeva, A. Glova, S. Melnikova, A. Dobrovskiy, S.A. Silber, S. Larin, R.M. de Souza, M.C.C. Ribeiro, S. Lyulin, M. Karttunen, Computer Simulations of Deep Eutectic Solvents: Challenges, Solutions, and Perspectives, Int. J. Mol. Sci. 23 (2022) 645. https://doi.org/10.3390/ijms23020645.

[54] K. Shigenobu, T. Sudoh, M. Tabuchi, S. Tsuzuki, W. Shinoda, K. Dokko, M. Watanabe, K. Ueno, Effects of Li ion-solvent interaction on ionic transport and electrochemical properties in highly concentrated cyclic carbonate electrolytes, J. Non-Crystalline Solids X. 11–12 (2021) 100071. https://doi.org/10.1016/j.nocx.2021.100071.

[55] S. Fuladi, H. Gholivand, A. Ahmadiparidari, L.A. Curtiss, A. Salehi-Khojin, F. Khalili-Araghi, Multicomponent Phase Separation in Ternary Mixture Ionic Liquid Electrolytes, J. Phys. Chem. B. 125 (2021) 7024–7032. https://doi.org/10.1021/acs.jpcb.1c01327.

[56] A. Wettstein, D. Diddens, A. Heuer, Controlling Li + transport in ionic liquid electrolytes through salt content and anion asymmetry: a mechanistic understanding gained from molecular dynamics simulations, Phys. Chem. Chem. Phys. (2022). https://doi.org/10.1039/D1CP04830A.

[57] M.T. Zafarani-Moattar, H. Shekaari, A. Sadrmousavi-Dizaj, Some thermodynamic properties

and computational study of DESs (choline chloride/ethylene glycol and choline chloride/malonic acid) in lithium nitrate + propylene carbonate solutions at T = 298.15 K, J. Chem. Thermodyn. 165 (2022). https://doi.org/10.1016/j.jct.2021.106642.

[58] B. Guchhait, S. Das, S. Daschakraborty, R. Biswas, Interaction and dynamics of (alkylamide + electrolyte) deep eutectics: Dependence on alkyl chain-length, temperature, and anion identity, J. Chem. Phys. 140 (2014) 104514. https://doi.org/10.1063/1.4866178.

[59] S. Das, R. Biswas, B. Mukherjee, Orientational Jumps in (Acetamide + Electrolyte) Deep Eutectics: Anion Dependence, J. Phys. Chem. B. 119 (2015) 11157–11168. https://doi.org/10.1021/acs.jpcb.5b03022.

[60] A.D. Pauric, I.C. Halalay, G.R. Goward, Combined NMR and molecular dynamics modeling study of transport properties in sulfonamide based deep eutectic lithium electrolytes: LiTFSI based binary systems, Phys. Chem. Chem. Phys. 18 (2016) 6657–6667. https://doi.org/10.1039/C5CP05811B.

[61] H. Srinivasan, V.K. Sharma, S. Mitra, Water accelerates the hydrogen-bond dynamics and abates heterogeneity in deep eutectic solvent based on acetamide and lithium perchlorate, J. Chem. Phys. 155 (2021) 024505. https://doi.org/10.1063/5.0054942.

[62] V. Lesch, A. Heuer, B.R. Rad, M. Winter, J. Smiatek, Atomistic insights into deep eutectic electrolytes: the influence of urea on the electrolyte salt LiTFSI in view of electrochemical applications, Phys. Chem. Chem. Phys. 18 (2016) 28403–28408. https://doi.org/10.1039/C6CP04217A.

[63] A. Nandy, J. Smiatek, Mixtures of LiTFSI and urea: ideal thermodynamic behavior as key to the formation of deep eutectic solvents?, Phys. Chem. Chem. Phys. 21 (2019) 12279–12287. https://doi.org/10.1039/C9CP01440C.

[64] C.L. Berhaut, D. Lemordant, P. Porion, L. Timperman, G. Schmidt, M. Anouti, Ionic association analysis of LiTDI, LiFSI and LiPF 6 in EC/DMC for better Li-ion battery performances, RSC Adv. 9 (2019) 4599–4608. https://doi.org/10.1039/C8RA08430K.

[65] L.J. Hardwick, M. Holzapfel, A. Wokaun, P. Novák, Raman study of lithium coordination in EMI-TFSI additive systems as lithium-ion battery ionic liquid electrolytes, J. Raman Spectrosc. 38 (2007) 110–112. https://doi.org/10.1002/jrs.1632.

[66] K. Karuppasamy, J. Theerthagiri, D. Vikraman, C.-J. Yim, S. Hussain, R. Sharma, T. Maiyalagan, J. Qin, H.-S. Kim, Ionic Liquid-Based Electrolytes for Energy Storage Devices: A Brief Review on Their Limits and Applications, Polymers (Basel). 12 (2020) 918. https://doi.org/10.3390/polym12040918.

[67] T. Cui, A. Lahiri, T. Carstens, N. Borisenko, G. Pulletikurthi, C. Kuhl, F. Endres, Influence

of Water on the Electrified Ionic Liquid/Solid Interface: A Direct Observation of the Transition from a Multilayered Structure to a Double-Layer Structure, J. Phys. Chem. C. 120 (2016) 9341–9349. https://doi.org/10.1021/acs.jpcc.6b02549.

[68] H.G. Buss, S.Y. Chan, N.A. Lynd, B.D. McCloskey, Nonaqueous Polyelectrolyte Solutions as Liquid Electrolytes with High Lithium Ion Transference Number and Conductivity, ACS Energy Lett. 2 (2017) 481–487. https://doi.org/10.1021/acsenergylett.6b00724.

[69] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, Nat. Rev. Mater. 2 (2017) 16103. https://doi.org/10.1038/natrevmats.2016.103.

[70] S. Tang, W. Guo, Y. Fu, Advances in Composite Polymer Electrolytes for Lithium Batteries and Beyond, Adv. Energy Mater. 11 (2021) 2000802. https://doi.org/10.1002/aenm.202000802.

[71] S. Isikli, K.M. Ryan, Recent advances in solid-state polymer electrolytes and innovative ionic liquids based polymer electrolyte systems, Curr. Opin. Electrochem. 21 (2020) 188–191. https://doi.org/10.1016/j.coelec.2020.01.015.

[72] K. Ma, R. Jarosova, G.M. Swain, G.J. Blanchard, Charge-Induced Long-Range Order in a Room-Temperature Ionic Liquid, Langmuir. 32 (2016) 9507–9512. https://doi.org/10.1021/acs.langmuir.6b02639.

[73] H. Yildirim, J.B. Haskins, C.W. Bauschlicher, J.W. Lawson, Decomposition of Ionic Liquids at Lithium Interfaces. 1. Ab Initio Molecular Dynamics Simulations, J. Phys. Chem. C. 121 (2017) 28214–28234. https://doi.org/10.1021/acs.jpcc.7b09657.

[74] A. Basile, M. Hilder, F. Makhlooghiazad, C. Pozo- Gonzalo, D.R. MacFarlane, P.C. Howlett, M. Forsyth, Ionic Liquids and Organic Ionic Plastic Crystals: Advanced Electrolytes for Safer High Performance Sodium Energy Storage Technologies, Adv. Energy Mater. 8 (2018) 1703491. https://doi.org/10.1002/aenm.201703491.

[75] C. Xu, G. Yang, D. Wu, M. Yao, C. Xing, J. Zhang, H. Zhang, F. Li, Y. Feng, S. Qi, M. Zhuo, J. Ma, Roadmap on Ionic Liquid Electrolytes for Energy Storage Devices, Chem. – An Asian J. 16 (2021) 549–562. https://doi.org/10.1002/asia.202001414.

[76] D. Rochefort, Enabling new electrochemical methods with redox-active ionic liquids, Curr. Opin. Electrochem. 15 (2019) 125–132. https://doi.org/10.1016/j.coelec.2019.04.028.

[77] D.-Z. Zhang, Y. Ren, Y. Hu, L. Li, F. Yan, Ionic Liquid/Poly(ionic liquid)-based Semi-solid State Electrolytes for Lithium-ion Batteries, Chinese J. Polym. Sci. 38 (2020) 506–513. https://doi.org/10.1007/s10118-020-2390-1.

[78] A.K. Tripathi, Ionic liquid–based solid electrolytes (ionogels) for application in rechargeable lithium battery, Mater. Today Energy. 20 (2021) 100643.

https://doi.org/10.1016/j.mtener.2021.100643.

[79] S.S. Moganty, N. Jayaprakash, J.L. Nugent, J. Shen, L.A. Archer, Ionic-Liquid-Tethered Nanoparticles: Hybrid Electrolytes, Angew. Chemie Int. Ed. 49 (2010) 9158–9161. https://doi.org/10.1002/anie.201004551.

[80] Y. Lu, S.S. Moganty, J.L. Schaefer, L.A. Archer, Ionic liquid-nanoparticle hybrid electrolytes, J. Mater. Chem. 22 (2012) 4066. https://doi.org/10.1039/c2jm15345a.

[81] K.S. Korf, Y. Lu, Y. Kambe, L.A. Archer, Piperidinium tethered nanoparticle-hybrid electrolyte for lithium metal batteries, J. Mater. Chem. A. 2 (2014) 11866–11873. https://doi.org/10.1039/C4TA02219J.

[82] C.F.J. Francis, I.L. Kyratzis, A.S. Best, Lithium- Ion Battery Separators for Ionic- Liquid Electrolytes: A Review, Adv. Mater. 32 (2020) 1904205. https://doi.org/10.1002/adma.201904205.

[83] M.A.R. Martins, S.P. Pinho, J.A.P. Coutinho, Insights into the Nature of Eutectic and Deep Eutectic Mixtures, J. Solution Chem. 48 (2019) 962–982. https://doi.org/10.1007/s10953-018-0793-1.

[84] G. García, S. Aparicio, R. Ullah, M. Atilhan, Deep Eutectic Solvents: Physicochemical Properties and Gas Separation Applications, Energy & Fuels. 29 (2015) 2616–2644. https://doi.org/10.1021/ef5028873.

[85] K.H. Kim, A. Eudes, K. Jeong, C.G. Yoo, C.S. Kim, A. Ragauskas, Integration of renewable deep eutectic solvents with engineered biomass to achieve a closed-loop biorefinery, Proc. Natl. Acad. Sci. 116 (2019) 13816–13824. https://doi.org/10.1073/pnas.1904636116.

[86] M.C. Gutiérrez, M.L. Ferrer, L. Yuste, F. Rojo, F. del Monte, Bacteria Incorporation in Deep-eutectic Solvents through Freeze-Drying, Angew. Chemie Int. Ed. 49 (2010) 2158–2162. https://doi.org/10.1002/anie.200905212.

[87] J.T. Gorke, F. Srienc, R.J. Kazlauskas, Deep eutectic solvents for Candida antarctica lipase B-catalyzed reactions, ACS Symp. Ser. 1038 (2010) 169–180. https://doi.org/10.1021/bk-2010-1038.ch014.

[88] A.P. Abbott, G. Capper, K.J. McKenzie, K.S. Ryder, Electrodeposition of zinc–tin alloys from deep eutectic solvents based on choline chloride, J. Electroanal. Chem. 599 (2007) 288–294. https://doi.org/10.1016/j.jelechem.2006.04.024.

[89] A.P. Abbott, K.J. McKenzie, K.S. Ryder, Electropolishing and Electroplating of Metals Using Ionic Liquids Based on Choline Chloride, in: 2007: pp. 186–197. https://doi.org/10.1021/bk-2007-0975.ch013.

[90] S. Grecchi, S. Arnaboldi, S. Rizzo, P.R. Mussini, Advanced chiral molecular media for

enantioselective electrochemistry and electroanalysis, Curr. Opin. Electrochem. (2021) 100810. https://doi.org/10.1016/j.coelec.2021.100810.

[91] D. Dhingra, Bhawna, S. Pandey, Effect of lithium chloride on the density and dynamic viscosity of choline chloride/urea deep eutectic solvent in the temperature range (303.15–358.15) K, J. Chem. Thermodyn. 130 (2019) 166–172. https://doi.org/10.1016/j.jct.2018.10.003.

[92] H. Ogawa, H. Mori, Lithium salt/amide-based deep eutectic electrolytes for lithium-ion batteries: electrochemical, thermal and computational study, Phys. Chem. Chem. Phys. 22 (2020) 8853–8863. https://doi.org/10.1039/D0CP01255F.

[93] B. Joos, T. Vranken, W. Marchal, M. Safari, M.K. Van Bael, A.T. Hardy, Eutectogels: A New Class of Solid Composite Electrolytes for Li/Li-Ion Batteries, Chem. Mater. 30 (2018) 655–662. https://doi.org/10.1021/acs.chemmater.7b03736.

[94] B. Joos, J. Volders, R.R. da Cruz, E. Baeten, M. Safari, M.K. Van Bael, A.T. Hardy, Polymeric Backbone Eutectogels as a New Generation of Hybrid Solid-State Electrolytes, Chem. Mater. 32 (2020) 3783–3793. https://doi.org/10.1021/acs.chemmater.9b05090.

[95] M.W. Logan, S. Langevin, B. Tan, A.W. Freeman, C. Hoffman, D.B. Trigg, K. Gerasopoulos, UV-cured eutectic gel polymer electrolytes for safe and robust Li-ion batteries, J. Mater. Chem. A. 8 (2020) 8485–8495. https://doi.org/10.1039/D0TA01901A.

[96] C. Wang, H. Zhang, S. Dong, Z. Hu, R. Hu, Z. Guo, T. Wang, G. Cui, L. Chen, High Polymerization Conversion and Stable High-Voltage Chemistry Underpinning an In Situ Formed Solid Electrolyte, Chem. Mater. 32 (2020) 9167–9175. https://doi.org/10.1021/acs.chemmater.0c02481.

[97] Z. Wu, Y.F. Long, X. Lv, J. Su, Y. Wen, Microwave heating synthesis of spindle-like LiMnPO 4 /C in a deep eutectic solvent, Ceram. Int. 43 (2017) 6089–6095. https://doi.org/10.1016/j.ceramint.2017.02.001.

[98] Z. Wu, R.-R. Huang, H. Yu, Y.-C. Xie, X.-Y. Lv, J. Su, Y.-F. Long, Y.-X. Wen, Deep Eutectic Solvent Synthesis of LiMnPO4/C Nanorods as a Cathode Material for Lithium Ion Batteries, Materials (Basel). 10 (2017) 134. https://doi.org/10.3390/ma10020134.

[99] S. Rao, X. Zou, S. Wang, T. Shi, Y. Lu, L. Ji, H.-Y. Hsu, Q. Xu, X. Lu, Electrodeposition of Porous Sn-Ni-Cu Alloy Anode for Lithium-Ion Batteries from Nickel Matte in Deep Eutectic Solvents, J. Electrochem. Soc. 166 (2019) D427–D434. https://doi.org/10.1149/2.0881910jes.

[100] L. Chen, J. Deng, S. Hong, H. Lian, Rapid, tunable synthesis of porous carbon xerogels with expanded graphite and their application as anodes for Li-ion batteries, J. Colloid Interface

Sci. 565 (2020) 368–377. https://doi.org/10.1016/j.jcis.2020.01.048.

[101] A. Boisset, S. Menne, J. Jacquemin, A. Balducci, M. Anouti, Deep eutectic solvents based on N-methylacetamide and a lithium salt as suitable electrolytes for lithium-ion batteries, Phys. Chem. Chem. Phys. 15 (2013) 20054. https://doi.org/10.1039/c3cp53406e.

[102] Z. Wang, J. Ru, Y. Hua, D. Wang, J. Bu, Morphology-Controlled Preparation of Sn Powders by Electrodeposition in Deep Eutectic Solvent as Anodes for Lithium Ion Batteries, J. Electrochem. Soc. 167 (2020) 082504. https://doi.org/10.1149/1945-7111/ab8824.

[103] M. Wang, Q. Tan, L. Liu, J. Li, A low-toxicity and high-efficiency deep eutectic solvent for the separation of aluminum foil and cathode materials from spent lithium-ion batteries, J. Hazard. Mater. 380 (2019) 120846. https://doi.org/10.1016/j.jhazmat.2019.120846.

[104] M.K. Tran, M.-T.F. Rodrigues, K. Kato, G. Babu, P.M. Ajayan, Deep eutectic solvents for cathode recycling of Li-ion batteries, Nat. Energy. 4 (2019) 339–345. https://doi.org/10.1038/s41560-019-0368-4.

[105] M.J. Roldán-Ruiz, M.L. Ferrer, M.C. Gutiérrez, F. del Monte, Highly Efficient p-Toluenesulfonic Acid-Based Deep-Eutectic Solvents for Cathode Recycling of Li-Ion Batteries, ACS Sustain. Chem. Eng. 8 (2020) 5437–5445. https://doi.org/10.1021/acssuschemeng.0c00892.

[106] Y. Chen, Y. Lu, Z. Liu, L. Zhou, Z. Li, J. Jiang, L. Wei, P. Ren, T. Mu, Efficient Dissolution of Lithium-Ion Batteries Cathode LiCoO 2 by Polyethylene Glycol-Based Deep Eutectic Solvents at Mild Temperature, ACS Sustain. Chem. Eng. 8 (2020) 11713–11720. https://doi.org/10.1021/acssuschemeng.0c03624.

[107] S. Wang, Z. Zhang, Z. Lu, Z. Xu, A novel method for screening deep eutectic solvent to recycle the cathode of Li-ion batteries, Green Chem. 22 (2020) 4473–4482. https://doi.org/10.1039/D0GC00701C.

[108] N. Peeters, K. Binnemans, S. Riaño, Solvometallurgical recovery of cobalt from lithium-ion battery cathode materials using deep-eutectic solvents, Green Chem. 22 (2020) 4210–4221. https://doi.org/10.1039/D0GC00940G.

[109] G. Zante, A. Braun, A. Masmoudi, R. Barillon, D. Trébouet, M. Boltoeva, Solvent extraction fractionation of manganese, cobalt, nickel and lithium using ionic liquids and deep eutectic solvents, Miner. Eng. 156 (2020) 106512. https://doi.org/10.1016/j.mineng.2020.106512.

[110] H. Wang, M. Li, S. Garg, Y. Wu, M. Nazmi Idros, R. Hocking, H. Duan, S. Gao, A.J. Yago, L. Zhuang, T.E. Rufford, Cobalt Electrochemical Recovery from Lithium Cobalt Oxides in Deep Eutectic Choline Chloride+Urea Solvents, ChemSusChem. 14 (2021) 2972–2983. https://doi.org/10.1002/cssc.202100954.

[111] P.G. Schiavi, P. Altimari, M. Branchi, R. Zanoni, G. Simonetti, M.A. Navarra, F. Pagnanelli, Selective recovery of cobalt from mixed lithium ion battery wastes using deep eutectic solvent, Chem. Eng. J. 417 (2021) 129249. https://doi.org/10.1016/j.cej.2021.129249.

[112] X. Baokou, M. Anouti, Physical Properties of a New Deep Eutectic Solvent Based on a Sulfonium Ionic Liquid as a Suitable Electrolyte for Electric Double-Layer Capacitors, J. Phys. Chem. C. 119 (2015) 970–979. https://doi.org/10.1021/jp5110455.

[113] Y. Chen, D. Yu, L. Fu, M. Wang, D. Feng, Y. Yang, X. Xue, J. Wang, T. Mu, The dynamic evaporation process of the deep eutectic solvent LiTf 2 N: N -methylacetamide at ambient temperature, Phys. Chem. Chem. Phys. 21 (2019) 11810–11821. https://doi.org/10.1039/C9CP00148D.

[114] O.E. Geiculescu, D.D. DesMarteau, S.E. Creager, O. Haik, D. Hirshberg, Y. Shilina, E. Zinigrad, M.D. Levi, D. Aurbach, I.C. Halalay, Novel binary deep eutectic electrolytes for rechargeable Li-ion batteries based on mixtures of alkyl sulfonamides and lithium perfluoroalkylsulfonimide salts, J. Power Sources. 307 (2016) 519–525. https://doi.org/10.1016/j.jpowsour.2015.11.072.

[115] L. Millia, V. Dall'Asta, C. Ferrara, V. Berbenni, E. Quartarone, F.M. Perna, V. Capriati, P. Mustarelli, Bio-inspired choline chloride-based deep eutectic solvents as electrolytes for lithium-ion batteries, Solid State Ionics. 323 (2018) 44–48. https://doi.org/10.1016/j.ssi.2018.05.016.

[116] P. Jiang, L. Chen, H. Shao, S. Huang, Q. Wang, Y. Su, X. Yan, X. Liang, J. Zhang, J. Feng, Z. Liu, Methylsulfonylmethane-Based Deep Eutectic Solvent as a New Type of Green Electrolyte for a High-Energy-Density Aqueous Lithium-Ion Battery, ACS Energy Lett. 4 (2019) 1419–1426. https://doi.org/10.1021/acsenergylett.9b00968.

[117] Q. Cheng, W. Xu, S. Qin, S. Das, T. Jin, A. Li, A.C. Li, B. Qie, P. Yao, H. Zhai, C. Shi, X. Yong, Y. Yang, Full Dissolution of the Whole Lithium Sulfide Family (Li 2 S 8 to Li 2 S) in a Safe Eutectic Solvent for Rechargeable Lithium–Sulfur Batteries, Angew. Chemie Int. Ed. 58 (2019) 5557–5561. https://doi.org/10.1002/anie.201812611.

[118] T.T.A. Dinh, T.T.K. Huynh, L.T.M. Le, T.T.T. Truong, O.H. Nguyen, K.T.T. Tran, M. V. Tran, P.H. Tran, W. Kaveevivitchai, P.M.L. Le, Deep Eutectic Solvent Based on Lithium Bis[(trifluoromethyl)sulfonyl] Imide (LiTFSI) and 2,2,2-Trifluoroacetamide (TFA) as a Promising Electrolyte for a High Voltage Lithium-Ion Battery with a LiMn 2 O 4 Cathode, ACS Omega. 5 (2020) 23843–23853. https://doi.org/10.1021/acsomega.0c03099.

[119] M.F. Lagadec, R. Zahn, V. Wood, Characterization and performance evaluation of lithium-ion battery separators, Nat. Energy. 4 (2019) 16–25. https://doi.org/10.1038/s41560-018-

0295-9.

[120] P. Arora, Z. (John) Zhang, Battery Separators, Chem. Rev. 104 (2004) 4419–4462. https://doi.org/10.1021/cr020738u.

[121] D. Li, D. Shi, Y. Xia, L. Qiao, X. Li, H. Zhang, Superior Thermally Stable and Nonflammable Porous Polybenzimidazole Membrane with High Wettability for High-Power Lithium-Ion Batteries, ACS Appl. Mater. Interfaces. 9 (2017) 8742–8750. https://doi.org/10.1021/acsami.6b16316.

[122] C. Zhu, T. Nagaishi, J. Shi, H. Lee, P.Y. Wong, J. Sui, K. Hyodo, I.S. Kim, Enhanced Wettability and Thermal Stability of a Novel Polyethylene Terephthalate-Based Poly(Vinylidene Fluoride) Nanofiber Hybrid Membrane for the Separator of Lithium-Ion Batteries, ACS Appl. Mater. Interfaces. 9 (2017) 26400–26406. https://doi.org/10.1021/acsami.7b06303.

[123] H. Li, D. Wu, J. Wu, L.-Y. Dong, Y.-J. Zhu, X. Hu, Flexible, High-Wettability and Fire-Resistant Separators Based on Hydroxyapatite Nanowires for Advanced Lithium-Ion Batteries, Adv. Mater. 29 (2017) 1703548. https://doi.org/10.1002/adma.201703548.

[124] A. Davoodabadi, C. Jin, D.L. Wood III, T.J. Singler, J. Li, On electrolyte wetting through lithium-ion battery separators, Extrem. Mech. Lett. 40 (2020) 100960. https://doi.org/10.1016/j.eml.2020.100960.

[125] A. Davoodabadi, J. Li, Y. Liang, D.L. Wood, T.J. Singler, C. Jin, Analysis of electrolyte imbibition through lithium-ion battery electrodes, J. Power Sources. 424 (2019) 193–203. https://doi.org/10.1016/j.jpowsour.2019.03.115.

[126] S.S. Zhang, A review on the separators of liquid electrolyte Li-ion batteries, J. Power Sources. 164 (2007) 351–364. https://doi.org/10.1016/j.jpowsour.2006.10.065.

[127] J.B. Habedank, F.J. Günter, N. Billot, R. Gilles, T. Neuwirth, G. Reinhart, M.F. Zaeh, Rapid electrolyte wetting of lithium-ion batteries containing laser structured electrodes: in situ visualization by neutron radiography, Int. J. Adv. Manuf. Technol. 102 (2019) 2769–2778. https://doi.org/10.1007/s00170-019-03347-4.

[128] C. Sauter, R. Zahn, V. Wood, Understanding Electrolyte Infilling of Lithium Ion Batteries, J. Electrochem. Soc. 167 (2020) 100546. https://doi.org/10.1149/1945-7111/ab9bfd.

[129] G. Soliveri, V. Pifferi, R. Annunziata, L. Rimoldi, V. Aina, G. Cerrato, L. Falciola, G. Cappelletti, D. Meroni, Alkylsilane–SiO 2 Hybrids. A Concerted Picture of Temperature Effects in Vapor Phase Functionalization, J. Phys. Chem. C. 119 (2015) 15390–15400. https://doi.org/10.1021/acs.jpcc.5b04048.

[130] A. Davoodabadi, J. Li, Y. Liang, R. Wang, H. Zhou, D. Wood, T.J. Singler, C. Jin,

Characterization of Surface Free Energy of Composite Electrodes for Lithium-Ion Batteries, J. Electrochem. Soc. 165 (2018) A2493–A2501. https://doi.org/10.1149/2.0341811jes.

[131] G. Cappelletti, S. Ardizzone, D. Meroni, G. Soliveri, M. Ceotto, C. Biaggi, M. Benaglia, L. Raimondi, Wettability of bare and fluorinated silanes: A combined approach based on surface free energy evaluations and dipole moment calculations, J. Colloid Interface Sci. 389 (2013) 284–291. https://doi.org/10.1016/j.jcis.2012.09.008.

[132] R. l'Abee, F. DaRosa, M.J. Armstrong, M.M. Hantel, D. Mourzagh, High temperature stable Li-ion battery separators based on polyetherimides with improved electrolyte compatibility, J. Power Sources. 345 (2017) 202–211. https://doi.org/10.1016/j.jpowsour.2017.02.005.

[133] F.J. Günter, J.B. Habedank, D. Schreiner, T. Neuwirth, R. Gilles, G. Reinhart, Introduction to Electrochemical Impedance Spectroscopy as a Measurement Method for the Wetting Degree of Lithium-Ion Cells, J. Electrochem. Soc. 165 (2018) A3249–A3256. https://doi.org/10.1149/2.0081814jes.

[134] R.-S. Kühnel, S. Obeidi, M. Lübke, A. Lex-Balducci, A. Balducci, Evaluation of the wetting time of porous electrodes in electrolytic solutions containing ionic liquid, J. Appl. Electrochem. 43 (2013) 697–704. https://doi.org/10.1007/s10800-013-0558-x.

[135] A. Schilling, P. Gümbel, M. Möller, F. Kalkan, F. Dietrich, K. Dröder, X-ray Based Visualization of the Electrolyte Filling Process of Lithium Ion Batteries, J. Electrochem. Soc. 166 (2019) A5163–A5167. https://doi.org/10.1149/2.0251903jes.

[136] W.J. Weydanz, H. Reisenweber, A. Gottschalk, M. Schulz, T. Knoche, G. Reinhart, M. Masuch, J. Franke, R. Gilles, Visualization of electrolyte filling process and influence of vacuum during filling for hard case prismatic lithium ion cells by neutron imaging to optimize the production process, J. Power Sources. 380 (2018) 126–134. https://doi.org/10.1016/j.jpowsour.2018.01.081.

[137] S.K. Mohammadian, Y. Zhang, Improving wettability and preventing Li-ion batteries from thermal runaway using microchannels, Int. J. Heat Mass Transf. 118 (2018) 911–918. https://doi.org/10.1016/j.ijheatmasstransfer.2017.11.063.

[138] D.H. Jeon, Enhancing electrode wettability in lithium-ion battery via particle-size ratio control, Appl. Mater. Today. 22 (2021) 100976. https://doi.org/10.1016/j.apmt.2021.100976.

[139] A. Shodiev, E. Primo, O. Arcelus, M. Chouchane, M. Osenberg, A. Hilger, I. Manke, J. Li, A.A. Franco, Insight on electrolyte infiltration of lithium ion battery electrodes by means of a new three-dimensional-resolved lattice Boltzmann model, Energy Storage Mater. 38 (2021) 80–92. https://doi.org/10.1016/j.ensm.2021.02.029.

[140] H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, X. Zhang, A review of recent developments in

membrane separators for rechargeable lithium-ion batteries, Energy Environ. Sci. 7 (2014) 3857–3886. https://doi.org/10.1039/C4EE01432D.

[141] C.M. Costa, M.M. Silva, S. Lanceros-Méndez, Battery separators based on vinylidene fluoride (VDF) polymers and copolymers for lithium ion battery applications, RSC Adv. 3 (2013) 11404. https://doi.org/10.1039/c3ra40732b.

[142] J. Pröll, B. Schmitz, A. Niemöeller, B. Robertz, M. Schäfer, M. Torge, P. Smyrek, H.J. Seifert, W. Pfleging, Femtosecond laser patterning of lithium-ion battery separator materials: impact on liquid electrolyte wetting and cell performance, in: U. Klotzbach, K. Washio, C.B. Arnold (Eds.), Laser-Based Micro- Nanoprocessing IX, SPIE, 2015: p. 93511F. https://doi.org/10.1117/12.2079018.

[143] R. Xu, H. Huang, Z. Tian, J. Xie, C. Lei, Effects of Coated Separator Surface Morphology on Electrolyte Interfacial Wettability and Corresponding Li–Ion Battery Performance, Polymers (Basel). 12 (2020) 117. https://doi.org/10.3390/polym12010117.

[144] T. Knoche, F. Surek, G. Reinhart, A Process Model for the Electrolyte Filling of Lithium-ion Batteries, Procedia CIRP. 41 (2016) 405–410. https://doi.org/10.1016/j.procir.2015.12.044.

[145] R. Zahn, M.F. Lagadec, M. Hess, V. Wood, Improving Ionic Conductivity and Lithium-Ion Transference Number in Lithium-Ion Battery Separators, ACS Appl. Mater. Interfaces. 8 (2016) 32637–32642. https://doi.org/10.1021/acsami.6b12085.

[146] Y. Zhang, J.-J. Yuan, Y.-Z. Song, X. Yin, C.-C. Sun, L.-P. Zhu, B.-K. Zhu, Tannic acid/polyethyleneimine-decorated polypropylene separators for Li-Ion batteries and the role of the interfaces between separator and electrolyte, Electrochim. Acta. 275 (2018) 25–31. https://doi.org/10.1016/j.electacta.2018.03.099.

[147] J. Xie, Y.-C. Lu, A retrospective on lithium-ion batteries, Nat. Commun. 11 (2020) 2499. https://doi.org/10.1038/s41467-020-16259-9.

[148] M.-S. Wu, T.-L. Liao, Y.-Y. Wang, C.-C. Wan, Assessment of the Wettability of Porous Electrodes for Lithium-Ion Batteries, J. Appl. Electrochem. 34 (2004) 797–805. https://doi.org/10.1023/B:JACH.0000035599.56679.15.

[149] L. Kong, Y. Wang, H. Yu, B. Liu, S. Qi, D. Wu, W.-H. Zhong, G. Tian, J. Wang, In Situ Armoring: A Robust, High-Wettability, and Fire-Resistant Hybrid Separator for Advanced and Safe Batteries, ACS Appl. Mater. Interfaces. 11 (2019) 2978–2988. https://doi.org/10.1021/acsami.8b17521.

[150] M. Wang, X. Chen, H. Wang, H. Wu, X. Jin, C. Huang, Improved performances of lithium-ion batteries with a separator based on inorganic fibers, J. Mater. Chem. A. 5 (2017) 311–318. https://doi.org/10.1039/C6TA08404D.

[151] H. Jeon, D. Yeon, T. Lee, J. Park, M.-H. Ryou, Y.M. Lee, A water-based Al2O3 ceramic coating for polyethylene-based microporous separators for lithium-ion batteries, J. Power Sources. 315 (2016) 161–168. https://doi.org/10.1016/j.jpowsour.2016.03.037.

[152] W. Chen, Y. Liu, Y. Ma, W. Yang, Improved performance of lithium ion battery separator enabled by co-electrospinnig polyimide/poly(vinylidene fluoride-co-hexafluoropropylene) and the incorporation of TiO2-(2-hydroxyethyl methacrylate), J. Power Sources. 273 (2015) 1127–1135. https://doi.org/10.1016/j.jpowsour.2014.10.026.

[153] M. Li, Y. Liao, Q. Liu, J. Xu, P. Sun, H. Shi, W. Li, Application of the imidazolium ionic liquid based nano-particle decorated gel polymer electrolyte for high safety lithium ion battery, Electrochim. Acta. 284 (2018) 188–201. https://doi.org/10.1016/j.electacta.2018.07.140.

[154] C.L. Yang, H.Y. Liu, Q.L. Xia, Z.H. Li, Q.Z. Xiao, G.T. Lei, Effects of SiO2 Nanoparticles and Diethyl Carbonate on the Electrochemical Properties of a Fibrous Nanocomposite Polymer Electrolyte for Rechargeable Lithium Batteries, Arab. J. Sci. Eng. 39 (2014) 6711–6720. https://doi.org/10.1007/s13369-014-1192-6.

[155] Z. Xue, D. He, X. Xie, Poly(ethylene oxide)-based electrolytes for lithium-ion batteries, J. Mater. Chem. A. 3 (2015) 19218–19253. https://doi.org/10.1039/C5TA03471J.

[156] X. Ma, P. Kolla, R. Yang, Z. Wang, Y. Zhao, A.L. Smirnova, H. Fong, Electrospun polyacrylonitrile nanofibrous membranes with varied fiber diameters and different membrane porosities as lithium-ion battery separators, Electrochim. Acta. 236 (2017) 417–423. https://doi.org/10.1016/j.electacta.2017.03.205.

[157] S.J. Cho, H. Choi, J.H. Youk, Evaluation of PBI Nanofiber Membranes as a High-temperature Resistance Separator for Lithium-ion Batteries, Fibers Polym. 21 (2020) 993–998. https://doi.org/10.1007/s12221-020-9955-z.

[158] P. Sun, Y. Liao, X. Luo, Z. Li, T. Chen, L. Xing, W. Li, The improved effect of co-doping with nano-SiO 2 and nano-Al 2 O 3 on the performance of poly(methyl methacrylate-acrylonitrile-ethyl acrylate) based gel polymer electrolyte for lithium ion batteries, RSC Adv. 5 (2015) 64368–64377. https://doi.org/10.1039/C5RA10409B.

[159] S. Goriparti, E. Miele, F. De Angelis, E. Di Fabrizio, R. Proietti Zaccaria, C. Capiglia, Review on recent progress of nanostructured anode materials for Li-ion batteries, J. Power Sources. 257 (2014) 421–443. https://doi.org/10.1016/j.jpowsour.2013.11.103.

[160] P. Raghavan, X. Zhao, J. Manuel, G.S. Chauhan, J.-H. Ahn, H.-S. Ryu, H.-J. Ahn, K.-W. Kim, C. Nah, Electrochemical performance of electrospun poly(vinylidene fluoride-co-hexafluoropropylene)-based nanocomposite polymer electrolytes incorporating ceramic

fillers and room temperature ionic liquid, Electrochim. Acta. 55 (2010) 1347–1354. https://doi.org/10.1016/j.electacta.2009.05.025.

[161] E. Lizundia, C.M. Costa, R. Alves, S. Lanceros-Méndez, Cellulose and its derivatives for lithium ion battery separators: A review on the processing methods and properties, Carbohydr. Polym. Technol. Appl. 1 (2020) 100001. https://doi.org/10.1016/j.carpta.2020.100001.

[162] M. Li, X. Wang, Y. Wang, B. Chen, Y. Wu, R. Holze, A gel polymer electrolyte based on composite of nonwoven fabric and methyl cellulose with good performance for lithium ion batteries, RSC Adv. 5 (2015) 52382–52387. https://doi.org/10.1039/C5RA07182H.

[163] H. Zhang, J. Liu, M. Guan, Z. Shang, Y. Sun, Z. Lu, H. Li, X. An, H. Liu, Nanofibrillated Cellulose (NFC) as a Pore Size Mediator in the Preparation of Thermally Resistant Separators for Lithium Ion Batteries, ACS Sustain. Chem. Eng. 6 (2018) 4838–4844. https://doi.org/10.1021/acssuschemeng.7b04203.

[164] B.S. Lalia, Y.A. Samad, R. Hashaikeh, Nanocrystalline cellulose-reinforced composite mats for lithium-ion batteries: electrochemical and thermomechanical performance, J. Solid State Electrochem. 17 (2013) 575–581. https://doi.org/10.1007/s10008-012-1894-1.

[165] H. Cheng, J.G. Shapter, Y. Li, G. Gao, Recent progress of advanced anode materials of lithium-ion batteries, J. Energy Chem. 57 (2021) 451–468. https://doi.org/10.1016/j.jechem.2020.08.056.

[166] Y. Cao, M. Li, J. Lu, J. Liu, K. Amine, Bridging the academic and industrial metrics for next-generation practical batteries, Nat. Nanotechnol. 14 (2019) 200–207. https://doi.org/10.1038/s41565-019-0371-8.

[167] M. Zhao, Y. Xia, L. Mei, Diffusion and condensation of lithium atoms in single-walled carbon nanotubes, Phys. Rev. B. 71 (2005) 165413. https://doi.org/10.1103/PhysRevB.71.165413.

[168] G. Qi, T. Rabczuk, Ab-initio investigation of lithium adsorption on short carbon nanotubes considering effects of the tube length, Carbon N. Y. 155 (2019) 727–733. https://doi.org/10.1016/j.carbon.2019.08.027.

[169] D.W. Kim, S.M. Jung, C. Senthil, S.-S. Kim, B.-K. Ju, H.Y. Jung, Understanding Excess Li Storage beyond LiC 6 in Reduced Dimensional Scale Graphene, ACS Nano. 15 (2021) 797–808. https://doi.org/10.1021/acsnano.0c07173.

[170] Y. Zhang, Q. Wan, N. Yang, Recent Advances of Porous Graphene: Synthesis, Functionalization, and Electrochemical Applications, Small. 15 (2019) 1903780. https://doi.org/10.1002/smll.201903780.

[171] S.M. Jung, D.W. Kim, H.Y. Jung, Which is the most effective pristine graphene electrode for energy storage devices: aerogel or xerogel?, Nanoscale. 11 (2019) 17563–17570. https://doi.org/10.1039/C9NR06898H.

[172] R. Ikram, B. Mohamed Jan, S. Atif Pervez, V.M. Papadakis, W. Ahmad, R. Bushra, G. Kenanakis, M. Rana, Recent Advancements of N-Doped Graphene for Rechargeable Batteries: A Review, Crystals. 10 (2020) 1080. https://doi.org/10.3390/cryst10121080.

[173] A. Rajkamal, R. Thapa, Carbon Allotropes as Anode Material for Lithium- Ion Batteries, Adv. Mater. Technol. 4 (2019) 1900307. https://doi.org/10.1002/admt.201900307.

[174] R. Fang, K. Chen, L. Yin, Z. Sun, F. Li, H.-M. Cheng, The Regulating Role of Carbon Nanotubes and Graphene in Lithium-Ion and Lithium-Sulfur Batteries, Adv. Mater. 31 (2019) 1800863. https://doi.org/10.1002/adma.201800863.

[175] Q. Cheng, Porous Graphene Sponge Additives for Lithium Ion Batteries with Excellent Rate Capability, Sci. Rep. 7 (2017) 925. https://doi.org/10.1038/s41598-017-01025-7.

[176] D. Sun, Z. Tan, X. Tian, F. Ke, Y. Wu, J. Zhang, Graphene: A promising candidate for charge regulation in high-performance lithium-ion batteries, Nano Res. (2021). https://doi.org/10.1007/s12274-021-3405-0.

[177] Y. Lu, L. Yu, X.W. (David) Lou, Nanostructured Conversion-type Anode Materials for Advanced Lithium-Ion Batteries, Chem. 4 (2018) 972–996. https://doi.org/10.1016/j.chempr.2018.01.003.

[178] Y. Miao, P. Hynan, A. von Jouanne, A. Yokochi, Current Li-Ion Battery Technologies in Electric Vehicles and Opportunities for Advancements, Energies. 12 (2019) 1074. https://doi.org/10.3390/en12061074.

[179] S. Sharma, A.K. Panwar, M.M. Tripathi, Storage technologies for electric vehicles, J. Traffic Transp. Eng. (English Ed. 7 (2020) 340–361. https://doi.org/10.1016/j.jtte.2020.04.004.

[180] G. Song, H. Bin Son, D.-Y. Han, M. Je, S. Nam, S. Park, A renewable future: a comprehensive perspective from materials to systems for next-generation batteries, Mater. Chem. Front. 5 (2021) 3344–3377. https://doi.org/10.1039/D1QM00071C.

[181] V. Augustyn, J. Come, M.A. Lowe, J.W. Kim, P.L. Taberna, S.H. Tolbert, H.D. Abruña, P. Simon, B. Dunn, High-rate electrochemical energy storage through Li + intercalation pseudocapacitance, Nat. Mater. 12 (2013) 518–522. https://doi.org/10.1038/nmat3601.

[182] Z. Liu, W. Dong, J. Wang, C. Dong, Y. Lin, I.W. Chen, F. Huang, Orthorhombic Nb2O5-x for Durable High-Rate Anode of Li-Ion Batteries, IScience. 23 (2020) 100767. https://doi.org/10.1016/j.isci.2019.100767.

[183] R.X. Sun, Y. Yue, X.F. Cheng, K. Zhang, S.Y. Jin, G.Y. Liu, Y.X. Fan, Y. Bao, X. Di Liu,

Ionic liquid-induced ultrathin and uniform N-doped carbon-wrapped T-Nb2O5 microsphere anode for high-performance lithium-ion battery, Rare Met. 40 (2021) 3205–3214. https://doi.org/10.1007/s12598-020-01681-1.

[184] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.-M. Tarascon, Nano-sized transition-metal oxides as negative-electrode materials for lithium-ion batteries, Nature. 407 (2000) 496–499. https://doi.org/10.1038/35035045.

[185] J. Cabana, L. Monconduit, D. Larcher, M.R. Palacín, Beyond Intercalation-Based Li-Ion Batteries: The State of the Art and Challenges of Electrode Materials Reacting Through Conversion Reactions, Adv. Mater. 22 (2010) E170–E192. https://doi.org/10.1002/adma.201000717.

[186] M. Dewan, T. Majumder, S.B. Majumder, Electrophoretically deposited bismuth iron oxide as dual role anode material for both lithium and sodium-ion batteries, Mater. Today Commun. 27 (2021) 102358. https://doi.org/10.1016/j.mtcomm.2021.102358.

[187] W. Sun, X. Rui, J. Zhu, L. Yu, Y. Zhang, Z. Xu, S. Madhavi, Q. Yan, Ultrathin nickel oxide nanosheets for enhanced sodium and lithium storage, J. Power Sources. 274 (2015) 755–761. https://doi.org/10.1016/j.jpowsour.2014.10.105.

[188] S. Hariharan, K. Saravanan, P. Balaya, α-MoO3: A high performance anode material for sodium-ion batteries, Electrochem. Commun. 31 (2013) 5–9. https://doi.org/10.1016/j.elecom.2013.02.020.

[189] Y. Jiang, M. Hu, D. Zhang, T. Yuan, W. Sun, B. Xu, M. Yan, Transition metal oxides for high performance sodium ion battery anodes, Nano Energy. 5 (2014) 60–66. https://doi.org/10.1016/j.nanoen.2014.02.002.

[190] S. Komaba, T. Mikumo, N. Yabuuchi, A. Ogata, H. Yoshida, Y. Yamada, Electrochemical Insertion of Li and Na Ions into Nanocrystalline Fe[sub 3]O[sub 4] and α-Fe[sub 2]O[sub 3] for Rechargeable Batteries, J. Electrochem. Soc. 157 (2010) A60. https://doi.org/10.1149/1.3254160.

[191] X. Zhou, X. Liu, Y. Xu, Y. Liu, Z. Dai, J. Bao, An SbO x /Reduced Graphene Oxide Composite as a High-Rate Anode Material for Sodium-Ion Batteries, J. Phys. Chem. C. 118 (2014) 23527–23534. https://doi.org/10.1021/jp507116t.

[192] Z. Wang, Z. Sun, J. Li, Y. Shi, C. Sun, B. An, H.-M. Cheng, F. Li, Insights into the deposition chemistry of Li ions in nonaqueous electrolyte for stable Li anodes, Chem. Soc. Rev. 50 (2021) 3178–3210. https://doi.org/10.1039/D0CS01017K.

[193] F. Wang, B. Wang, J. Li, B. Wang, Y. Zhou, D. Wang, H. Liu, S. Dou, Prelithiation: A Crucial Strategy for Boosting the Practical Application of Next-Generation Lithium Ion

Battery, ACS Nano. 15 (2021) 2197–2218. https://doi.org/10.1021/acsnano.0c10664.

[194] S. Guo, Y. Feng, L. Wang, Y. Jiang, Y. Yu, X. Hu, Architectural Engineering Achieves High- Performance Alloying Anodes for Lithium and Sodium Ion Batteries, Small. 17 (2021) 2005248. https://doi.org/10.1002/smll.202005248.

[195] C.-M. Park, J.-H. Kim, H. Kim, H.-J. Sohn, Li-alloy based anode materials for Li secondary batteries, Chem. Soc. Rev. 39 (2010) 3115. https://doi.org/10.1039/b919877f.

[196] Z. Lin, X. Lan, X. Xiong, R. Hu, Recent development of Sn–Fe-based materials as a substitute for Sn–Co–C anodes in Li-ion batteries: a review, Mater. Chem. Front. 5 (2021) 1185–1204. https://doi.org/10.1039/D0QM00582G.

[197] L. Xu, W. Liu, Y. Hu, L. Luo, Stress-resilient electrode materials for lithium-ion batteries: strategies and mechanisms, Chem. Commun. 56 (2020) 13301–13312. https://doi.org/10.1039/D0CC05359G.

[198] F. Wu, J. Maier, Y. Yu, Guidelines and trends for next-generation rechargeable lithium and lithium-ion batteries, Chem. Soc. Rev. 49 (2020) 1569–1614. https://doi.org/10.1039/C7CS00863E.

[199] S. Jin, Y. Ye, Y. Niu, Y. Xu, H. Jin, J. Wang, Z. Sun, A. Cao, X. Wu, Y. Luo, H. Ji, L.-J. Wan, Solid–Solution-Based Metal Alloy Phase for Highly Reversible Lithium Metal Anode, J. Am. Chem. Soc. 142 (2020) 8818–8826. https://doi.org/10.1021/jacs.0c01811.

[200] X. Liang, Q. Pang, I.R. Kochetkov, M.S. Sempere, H. Huang, X. Sun, L.F. Nazar, A facile surface chemistry route to a stabilized lithium metal anode, Nat. Energy. 2 (2017) 17119. https://doi.org/10.1038/nenergy.2017.119.

[201] K. Feng, M. Li, W. Liu, A.G. Kashkooli, X. Xiao, M. Cai, Z. Chen, Silicon-Based Anodes for Lithium-Ion Batteries: From Fundamentals to Practical Applications, Small. 14 (2018). https://doi.org/10.1002/smll.201702737.

[202] M. Ge, C. Cao, G.M. Biesold, C.D. Sewell, S.M. Hao, J. Huang, W. Zhang, Y. Lai, Z. Lin, Recent Advances in Silicon-Based Electrodes: From Fundamental Research toward Practical Applications, Adv. Mater. 33 (2021) 1–42. https://doi.org/10.1002/adma.202004577.

[203] J. Zhuang, X. Xu, G. Peleckis, W. Hao, S.X. Dou, Y. Du, Silicene: A Promising Anode for Lithium-Ion Batteries, Adv. Mater. 29 (2017) 1–8. https://doi.org/10.1002/adma.201606716.

[204] G. Veerappan, SunyoungYoo, K. Zhang, M. Ma, B. Kang, J.H. Park, High-reversible capacity of Perovskite BaSnO3/rGO composite for Lithium-Ion Battery Anodes, Electrochim. Acta. 214 (2016) 31–37. https://doi.org/10.1016/j.electacta.2016.07.076.

[205] P. Nithyadharseni, M.V. Reddy, B. Nalini, M. Kalpana, B.V.R. Chowdari, Sn-based Intermetallic Alloy Anode Materials for the Application of Lithium Ion Batteries,

Electrochim. Acta. 161 (2015) 261–268. https://doi.org/10.1016/j.electacta.2015.02.057.

[206] H. Chang, Y.-R. Wu, X. Han, T.-F. Yi, Recent developments in advanced anode materials for lithium-ion batteries, Energy Mater. (2021). https://doi.org/10.20517/energymater.2021.02.

[207] L. Chen, J.G. Connell, A. Nie, Z. Huang, K.R. Zavadil, K.C. Klavetter, Y. Yuan, S. Sharifi-Asl, R. Shahbazian-Yassar, J.A. Libera, A.U. Mane, J.W. Elam, Lithium metal protected by atomic layer deposition metal oxide for high performance anodes, J. Mater. Chem. A. 5 (2017) 12297–12309. https://doi.org/10.1039/C7TA03116E.

[208] K. Park, J.B. Goodenough, Dendrite-Suppressed Lithium Plating from a Liquid Electrolyte via Wetting of Li 3 N, Adv. Energy Mater. 7 (2017) 1700732. https://doi.org/10.1002/aenm.201700732.

[209] L. Ye, X. Li, A dynamic stability design strategy for lithium metal solid state batteries, Nature. 593 (2021) 218–222. https://doi.org/10.1038/s41586-021-03486-3.

[210] X. Ji, S. Hou, P. Wang, X. He, N. Piao, J. Chen, X. Fan, C. Wang, Solid- State Electrolyte Design for Lithium Dendrite Suppression, Adv. Mater. 32 (2020) 2002741. https://doi.org/10.1002/adma.202002741.

[211] J. Kasemchainan, S. Zekoll, D. Spencer Jolly, Z. Ning, G.O. Hartley, J. Marrow, P.G. Bruce, Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells, Nat. Mater. 18 (2019) 1105–1111. https://doi.org/10.1038/s41563-019-0438-9.

[212] F. Shen, M.B. Dixit, X. Xiao, K.B. Hatzell, Effect of Pore Connectivity on Li Dendrite Propagation within LLZO Electrolytes Observed with Synchrotron X-ray Tomography, ACS Energy Lett. 3 (2018) 1056–1061. https://doi.org/10.1021/acsenergylett.8b00249.

[213] C. Wang, Y. Gong, B. Liu, K. Fu, Y. Yao, E. Hitz, Y. Li, J. Dai, S. Xu, W. Luo, E.D. Wachsman, L. Hu, Conformal, Nanoscale ZnO Surface Modification of Garnet-Based Solid-State Electrolyte for Lithium Metal Anodes, Nano Lett. 17 (2017) 565–571. https://doi.org/10.1021/acs.nanolett.6b04695.

[214] X.-B. Cheng, C.-Z. Zhao, Y.-X. Yao, H. Liu, Q. Zhang, Recent Advances in Energy Chemistry between Solid-State Electrolyte and Safe Lithium-Metal Anodes, Chem. 5 (2019) 74–96. https://doi.org/10.1016/j.chempr.2018.12.002.

[215] L. Zhang, T. Yang, C. Du, Q. Liu, Y. Tang, J. Zhao, B. Wang, T. Chen, Y. Sun, P. Jia, H. Li, L. Geng, J. Chen, H. Ye, Z. Wang, Y. Li, H. Sun, X. Li, Q. Dai, Y. Tang, Q. Peng, T. Shen, S. Zhang, T. Zhu, J. Huang, Lithium whisker growth and stress generation in an in situ atomic force microscope–environmental transmission electron microscope set-up, Nat. Nanotechnol. 15 (2020) 94–98. https://doi.org/10.1038/s41565-019-0604-x.

[216] X. Chen, W. He, L.-X. Ding, S. Wang, H. Wang, Enhancing interfacial contact in all solid state batteries with a cathode-supported solid electrolyte membrane framework, Energy Environ. Sci. 12 (2019) 938–944. https://doi.org/10.1039/C8EE02617C.

[217] K.K. Fu, Y. Gong, B. Liu, Y. Zhu, S. Xu, Y. Yao, W. Luo, C. Wang, S.D. Lacey, J. Dai, Y. Chen, Y. Mo, E. Wachsman, L. Hu, Toward garnet electrolyte–based Li metal batteries: An ultrathin, highly effective, artificial solid-state electrolyte/metallic Li interface, Sci. Adv. 3 (2017) e1601659. https://doi.org/10.1126/sciadv.1601659.

[218] H. Xu, Y. Li, A. Zhou, N. Wu, S. Xin, Z. Li, J.B. Goodenough, Li 3 N-Modified Garnet Electrolyte for All-Solid-State Lithium Metal Batteries Operated at 40 °C, Nano Lett. 18 (2018) 7414–7418. https://doi.org/10.1021/acs.nanolett.8b03902.

[219] H. Huo, N. Zhao, J. Sun, F. Du, Y. Li, X. Guo, Composite electrolytes of polyethylene oxides/garnets interfacially wetted by ionic liquid for room-temperature solid-state lithium battery, J. Power Sources. 372 (2017) 1–7. https://doi.org/10.1016/j.jpowsour.2017.10.059.

[220] D. Dong, B. Zhou, Y. Sun, H. Zhang, G. Zhong, Q. Dong, F. Fu, H. Qian, Z. Lin, D. Lu, Y. Shen, J. Wu, L. Chen, H. Chen, Polymer Electrolyte Glue: A Universal Interfacial Modification Strategy for All-Solid-State Li Batteries, Nano Lett. 19 (2019) 2343–2349. https://doi.org/10.1021/acs.nanolett.8b05019.

[221] J. Duan, W. Wu, A.M. Nolan, T. Wang, J. Wen, C. Hu, Y. Mo, W. Luo, Y. Huang, Lithium-Graphite Paste: An Interface Compatible Anode for Solid-State Batteries, Adv. Mater. 31 (2019) 1807243. https://doi.org/10.1002/adma.201807243.

[222] W. Luo, Y. Gong, Y. Zhu, Y. Li, Y. Yao, Y. Zhang, K.K. Fu, G. Pastel, C.-F. Lin, Y. Mo, E.D. Wachsman, L. Hu, Reducing Interfacial Resistance between Garnet-Structured Solid-State Electrolyte and Li-Metal Anode by a Germanium Layer, Adv. Mater. 29 (2017) 1606042. https://doi.org/10.1002/adma.201606042.

[223] Y. Li, X. Chen, A. Dolocan, Z. Cui, S. Xin, L. Xue, H. Xu, K. Park, J.B. Goodenough, Garnet Electrolyte with an Ultralow Interfacial Resistance for Li-Metal Batteries, J. Am. Chem. Soc. 140 (2018) 6448–6455. https://doi.org/10.1021/jacs.8b03106.

[224] X. Han, Y. Gong, K. (Kelvin) Fu, X. He, G.T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E.D. Wachsman, L. Hu, Negating interfacial impedance in garnet-based solid-state Li metal batteries, Nat. Mater. 16 (2017) 572–579. https://doi.org/10.1038/nmat4821.

[225] Y. Li, B. Xu, H. Xu, H. Duan, X. Lü, S. Xin, W. Zhou, L. Xue, G. Fu, A. Manthiram, J.B. Goodenough, Hybrid Polymer/Garnet Electrolyte with a Small Interfacial Resistance for Lithium- Ion Batteries, Angew. Chemie Int. Ed. 56 (2017) 753–756.

https://doi.org/10.1002/anie.201608924.

[226] R. Chen, Q. Li, X. Yu, L. Chen, H. Li, Approaching Practically Accessible Solid-State Batteries: Stability Issues Related to Solid Electrolytes and Interfaces, Chem. Rev. 120 (2020) 6820–6877. https://doi.org/10.1021/acs.chemrev.9b00268.

[227] X.-B. Cheng, R. Zhang, C.-Z. Zhao, Q. Zhang, Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review, Chem. Rev. 117 (2017) 10403–10473. https://doi.org/10.1021/acs.chemrev.7b00115.

[228] M. Zhu, B. Li, S. Li, Z. Du, Y. Gong, S. Yang, Dendrite-Free Metallic Lithium in Lithiophilic Carbonized Metal-Organic Frameworks, Adv. Energy Mater. 8 (2018) 1703505. https://doi.org/10.1002/aenm.201703505.

[229] C. Niu, H. Pan, W. Xu, J. Xiao, J.-G. Zhang, L. Luo, C. Wang, D. Mei, J. Meng, X. Wang, Z. Liu, L. Mai, J. Liu, Self-smoothing anode for achieving high-energy lithium metal batteries under realistic conditions, Nat. Nanotechnol. 14 (2019) 594–601. https://doi.org/10.1038/s41565-019-0427-9.