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Synthesis and Processing of Battery Materials: Giving it the Plasma Touch

Vijay Shankar Rangasamy^{*[a, b]} and Annick Vanhulse^[a, b]



Li-ion batteries (LIBs) are currently the most preferred energy storage devices in portable applications. Recent surge in the production of electric vehicles in the wake of the current global warming scenario has strongly increased the demand for LIBs, thereby reinforcing the need for new battery chemistries as well as making the existing production chain more efficient and sustainable. Several new technologies are explored to achieve these goals. Among them, plasma technology has the potential to simplify the synthesis and modification of battery materials, enable 'dry' and 'green' processing that eliminate the need for solvents that are often toxic, expensive, flammable, and energy-intensive. In this review, we have attempted to provide an overview of state-of-the-art (scientific) research and development with respect to the application of plasma-based processes in the synthesis and modification of materials for battery components. We have explored various applications wherein plasma-based processes have been demonstrated in the processing of electrode materials, electrolytes, and separators in addition to the recent developments in the context of solid-state and flexible batteries. Our analysis shows that plasma-

based technologies are slowly but steadily gaining attention in these areas. Several technical and conventional issues remain, which require innovations at the conceptual as well as engineering levels. Technical issues include the selection of appropriate plasma type and precursors, plasma density, selectivity, and a preferable shift from vacuum to atmospheric conditions. The conventional issues include the practical difficulties in converting or adapting the assembly lines to plasma-based technology. From a business perspective, all that matters is the cost per mAh g^{-1} of energy produced, for which, unfortunately, we do not have sufficient quantitative data yet with regard to the materials processed by plasma-based technologies. However, the battery manufacturing sector is now open for innovations like never before. Therefore, it remains to be seen how plasma technologies embrace this opportunity and penetrate the battery production sector, where the key parameters are efficiency and cost-effectiveness. Would 'giving it the plasma touch' bring added value to the battery manufacturing processes? That is the question we try to address in this review.

1. Introduction

Lithium-ion batteries (LIBs) have emerged as the most dominant and preferred storage devices in the portable electronics market, revolutionizing the way we communicate and share information. The advent of electric vehicles and the ambitious push to integrate energy storage systems in smart grids have only increased the demand for batteries with high energy and power densities.^[1–5] On the other end of the scale, the emergence of the Internet of Things (IoT) has also put the versatility of LIBs into perspective.^[6,7] This enormous scale that pervades several applications and devices implies severe compromises in the performance parameters such as the energy and power density, cost, safety, and environmental impact.^[8–10] As Larcher and Tarascon point out, today's market economy prioritizes the cost associated with the production of energy conversion and storage devices.^[11] As shown in Figure 1, the production of the battery materials is by far the most energy-intensive step in the life cycle of a battery.

For instance, implementing more efficient synthesis methods, re-designing the particle morphology and size distribution, and applying a protective or functionalized layer are some of the methods to improve the performance of the components of a battery. Among the several methods explored to accomplish these material improvements, plasma-based meth-

ods are a promising approach because of their scalability, controllability, and reproducibility.

Plasma technology has been gaining attention in several areas that value quality, efficiency, and flexibility.^[12] Its versatile application potential enables plasma technology to offer innovative solutions in diverse industrial applications ranging from high-quality tools and plasma displays to surface modification of plastics, textiles and glass. In the field of microelectronics, plasma-based processes are used in several production steps such as plasma cleaning, etching, and coating deposition.^[13] These are but a few examples that showcase the potential of plasma technology, which is still far

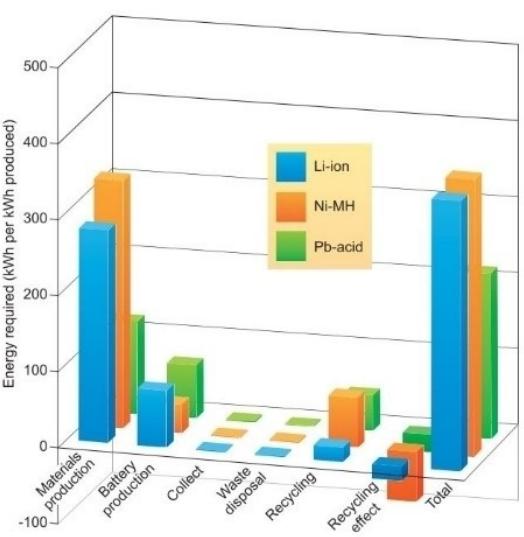


Figure 1. Energy required for the production of a 1 kWh electrochemical energy storage system. Reproduced with permission from Ref. [11]. Copyright (2014) Springer Nature.

[a] Dr. V. S. Rangasamy, Dr. A. Vanhulsel
 VITO, Sustainable Materials Unit
 Boeretang 200, 2400 Mol, Belgium
 E-mail: vijay.rangasamy@vito.be

[b] Dr. V. S. Rangasamy, Dr. A. Vanhulsel
 EnergyVille
 Thor Park, 3600 Genk, Belgium

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from being realized completely. Most industrial plasmas are generated by applying electric and/or magnetic fields in a gas volume. Consequently, the atoms and molecules of the gas particles gain kinetic energy and acquire higher rotational and vibrational energies. The increased collisions between the atoms and molecules make the electrons and the positively charged ions free from their parent atoms and molecules, resulting in a partially ionized gas, also referred to as the fourth state of matter.

Plasmas can be broadly classified into two groups – high-temperature or fusion plasmas and the relatively low-temperature plasmas (gas discharges). A further sub-classification of plasmas can be made based on whether the temperature of all species, namely electrons, ions, and neutral species is the same (thermal or equilibrium plasmas) or different (non-thermal or non-equilibrium plasmas). Among the different types of plasma, some operate at low gas pressures (vacuum plasmas), while others can operate at atmospheric pressure. The plasmas of interest for technological applications, namely the glow discharge and thermal plasmas, are highlighted in orange color in Figure 2, which shows the various types of plasma classified based on their electron density and temperature.^[14] For a detailed description of the classification of plasmas and the applications of gas discharge plasmas, the reader is referred to the review by Bogaerts et al.^[15] The energy of the electrons is an important factor for initiating chemical reactions. This energy can be systematically matched by factors such as the choice of the gases and the reactor geometry. Plasmas can be excited by direct or alternating current, or by applying high-frequency electromagnetic fields. Atmospheric pressure plasmas are preferred for continuous processes as they offer energy efficiency in plasma chemical reactions.^[16–18] Atmospheric pressure plasmas can be classified into four main types – corona, dielectric barrier, gliding arc, and spark discharge. In these plasmas, much of the electrical energy is utilized to increase the electron energy, rather than heating the entire gas stream.^[18] The resultant free radicals and excited ions oxidize, reduce or modify the surface exposed to the plasma. In addition, the low maintenance requirements of these plasma sources are relatively cost-effective.



Vijay Shankar Rangasamy received his Ph.D. in Physics in 2014 from KU Leuven. He has been a post-doctoral fellow at KU Leuven, and he is currently a researcher at the Flemish Institute of Technological Research (VITO). His research interests include Li-ion, Na-ion and Li-S batteries, fuel cells, plasma processing of energy storage materials, and the study of surface and bulk phenomena in energy storage and conversion systems.

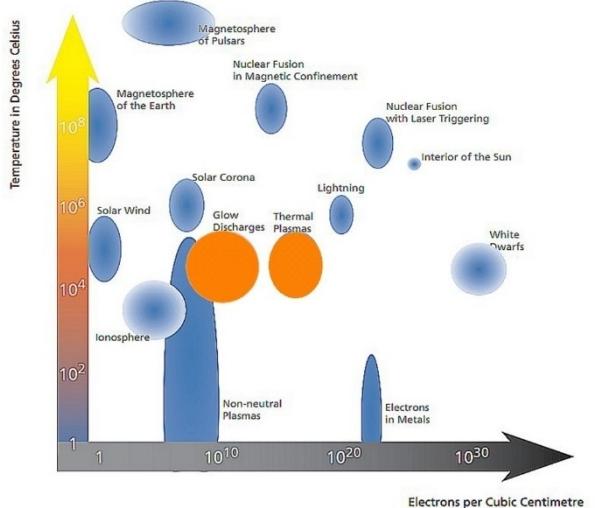


Figure 2. Various types of plasma in terms of electron density and temperature. Reproduced from Ref. [14] with permission. Copyright (2005) Wiley-VCH.

Figure 3 shows a schematic of the different types of non-thermal plasmas.^[19] Perhaps the major advantage of using plasma technology to process battery components is the range of processing scales possible in the different plasma-based techniques. The processing scale can vary from a few milligrams per hour (mg/h) in non-thermal plasmas to kilograms per hour (kg/h) in thermal plasmas.^[20] Once the chemical processes are well understood and the precursors and control parameters are optimized, the plasma-based process can be easily upgraded to the industrial scale. Plasma technologies provide better control and tunability of parameters compared to other conventional methods used in the synthesis or processing of materials. As the control parameters are the voltage, frequency, gas composition and pressure, the reactions under plasma can be performed without using any toxic solvents or contaminants.

The reaction mechanisms taking place in thermal vs. non-thermal (equilibrium vs non-equilibrium) plasmas are very different from each other. Therefore, the outcome, for instance



Dr. Ir. Annick Vanhulsel is M.Sc. in Materials Engineering and holds a PhD degree in Surface Technology (University of Leuven, 2002). She is project leader at VITO (Belgium) in the field of sustainable materials. Her main area of expertise is the development of coatings and innovative (plasma) technologies for surface engineering and she is (co-)author of 40 publications in this field. Her current R&D interests include sustainable processing of materials and future generation batteries, in collaboration with both national and international networks and industry.

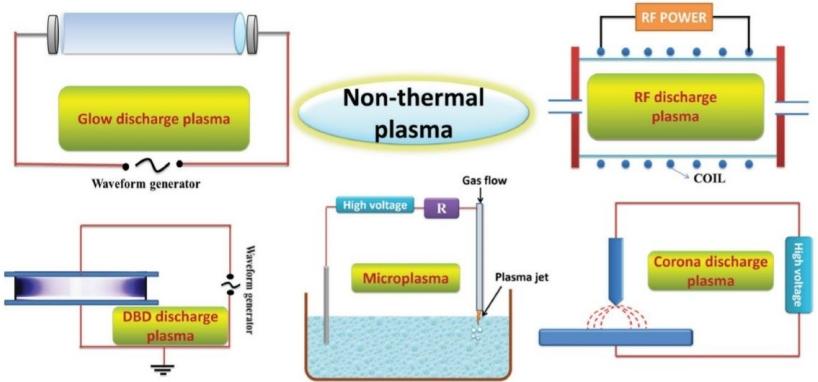


Figure 3. Non-thermal plasma types. Reproduced from Ref. [19] with permission. Copyright (2018) Wiley-VCH.

the type of coating and the processing rate, are also very different in most cases. This is illustrated in Figure 4, which shows the variation of silicon nanoparticle processing rate when different plasma synthesis tools are used.

The electron temperature of typical LIB materials during synthesis and modification is in the 1–20 eV range.^[20] Such temperatures can be achieved by plasma technology, whereas it is not possible by most of the conventional chemical processes such as solid-state reaction and wet chemical methods. This is apparent from the fact that nanoparticles synthesized in low-temperature plasmas are often obtained with crystalline structure. This is an interesting phenomenon because the gas temperature in these plasmas is often close to room temperature, and particles are exposed to the plasma only for a short duration. A numerical study by Mangolini and Kortshagen revealed that the particle temperatures can exceed the gas temperature by hundreds of Kelvin during the synthesis by plasma technique.^[22] With optimized control parameters and precursors, plasma-based methods result in highly reproducible processing capability. In addition, most of the plasma processes enable the treatment of materials and components in a 'dry'

condition without the need for toxic and expensive chemical solvents, thus leading to a 'green technology'. This is one area where plasma technology scores over most conventional processes. The number of steps and time required to synthesize and modify materials can be significantly reduced by using plasma technologies, thereby reducing the cost to produce LIBs in the long run, to offset the relatively high initial investment.^[23]

Plasma technologies are slowly but steadily finding their way into the various processes involved in the synthesis and modification of materials for batteries. At research level, this can be seen by the steady increase in the publication of research articles dealing with the application of plasma in battery research. Figure 5 illustrates the emergence of plasma technologies in state-of-the-art battery materials research. Although the adaption of these technologies has not yet been dramatic, the current trend is promising. Most of these studies focus on the synthesis and coating of cathode materials, followed by anode materials and then by the modification of separators. In this review, we attempt to provide an overview of state-of-the-art scientific research and development with

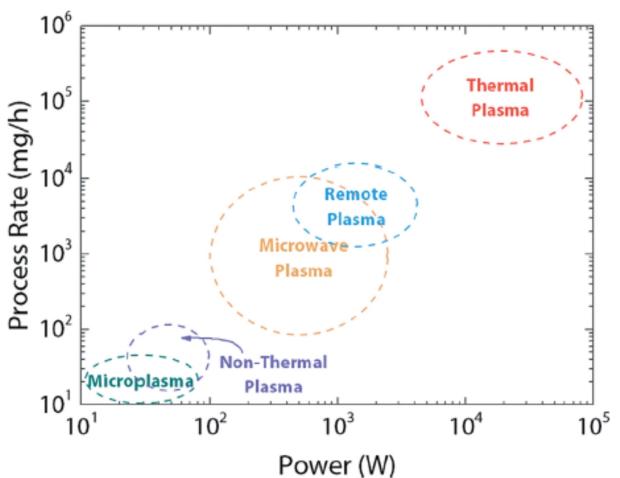


Figure 4. Processing rate for Si nanoparticle synthesis as a function of source power. Reproduced from Ref. [21] with permission. Copyright (2016) Wiley-VCH.

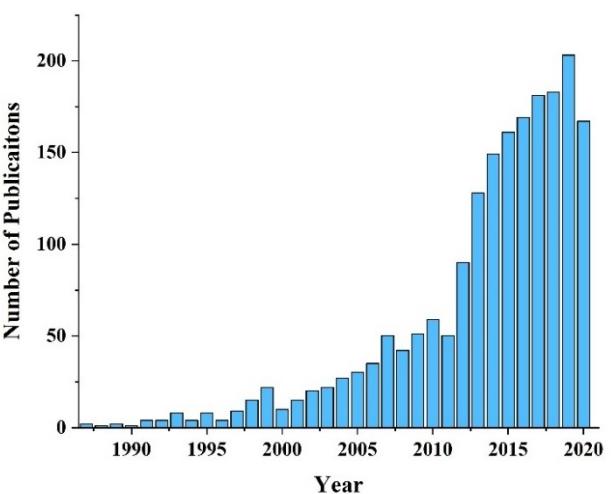


Figure 5. Number of publications as shown in the ISI Web of Science with the keywords "Battery" AND "Plasma" as on the 3rd of December 2020.

respect to the application of plasma-based processes in the synthesis and modification of materials for battery components. We have explored various applications wherein plasma-based processes and setups have been demonstrated in the processing of electrode materials, electrolytes, and separators in addition to the recent developments in the context of solid-state and flexible batteries, as well as lithium metal batteries.

2. Plasmas in the Context of Current and Next-Generation LIBs

A state-of-the-art rechargeable lithium-ion battery is composed of individual electrochemical cells each of which consists of a positive and a negative electrode connected to an external circuit. A schematic of a typical LIB is shown in Figure 6. A separator, which is an electronic insulator but an ionic conductor, and prevents physical contact between the electrodes. The cells also contain an electrolyte that conducts ions to and from the electrodes. Most of such cells contain **intercalation** compounds whose 2D or 3D crystal lattice acts as the host for the Li^+ ions. These ions can be inserted into or extracted from the host structure during cycling of the cell. One of the problems arising in this mechanism is the structural changes in the intercalation compounds due to the stress created on their lattice structure by the insertion and extraction of ions. Another serious problem is the safety issue when using lithium metal as the anode. The reaction between lithium and the electrolyte forms a resistive film on the metal layer. After multiple charge/discharge cycles, this resistive film grows in thickness, eventually leading to the formation of dendrites that penetrate the separator and short the battery. Such problems offer research challenges that could be mitigated by several innovative methods. After being abandoned due to safety issues and the successful commercialization of Li-ion batteries with graphite anode, lithium metal anode is finding its way back as we are in desperate need to get the maximum capacity and cycle life from batteries in modern applications such as electric vehicles. This is particularly evident in the case of solid-state

batteries.^[24,25] Unfortunately, there is no panacea to entirely solve all these problems by a single strategy.

Several material optimizations and innovations are needed to improve the performance of future/next generation LIBs. For instance, the lattice volume expansion can be reduced by tailoring the particle morphology, size distribution and the crystal structure of the electrode to form an efficient ion diffusion path. In compounds with excellent structural stability but poor electronic conductivity, a conductive layer could be coated to improve the inter-particle electron transport. Separators can be modified for better resistance against dendrites, for efficient uptake of electrolyte, or for higher Li^+ mobility by anchoring metal oxides or other suitable functional groups to the surface.

Besides material synthesis and functionalization of the base materials, the processing of the electrodes contains several steps and hence more room for improvement. Electrodes are conventionally prepared by applying a slurry of the active material with carbon and a polymeric binder on a current collector. This method results in two problems – the solvent used is often toxic – and the binder does not participate in the electrochemical reactions, thereby adding an inert weight to the electrode.^[27] These problems could be overcome if the active material is directly deposited on the current collector. Such binder-free electrode will have a higher energy density, as there is less inert material in the electrode composition. Plasma technology has the potential to solve some of these issues better than conventional methods. This is summarized in the concept map illustrated in Figure 7.

The choice of the plasma technology for these modifications depends on various factors such as the production or processing scale, chemical purity or selectivity required, and the chemistry of the materials to be processed. For instance, considering the processing rates for the production of Si-based nanoparticles by using various plasma tools given in Figure 4, it is apparent that the materials synthesis throughput of non-thermal plasmas is not compatible with electric vehicle (EV) requirements, because the electrode active materials account for about 40% of the weight of an LIB and a typical EV battery pack weighs more than 450 kg.^[27] Therefore, thermal plasmas are mostly used to synthesize nano-sized powders on a large scale and to deposit thick coatings on battery materials.^[28–30] Techniques such as plasma spraying of suspensions enables precise control of the material chemistry, thus enabling partial substitution of electrode materials. Meanwhile, non-thermal plasmas are more suitable for applications requiring chemical selectivity and high purity with controlled size distribution, such as nanoparticle synthesis on small to medium scales, and surface modification. As most non-thermal plasmas operate in vacuum conditions, the operating costs are rather high. Consequently, atmospheric pressure plasma processes have gained much interest, especially for the synthesis of nanomaterials.^[31] Besides, specific types of plasma-assisted mechanochemical processes have also been applied to process energy storage materials. For instance, the application of dielectric barrier discharge (DBD) plasma-assisted milling has been discussed by Ouyang et al.^[32]

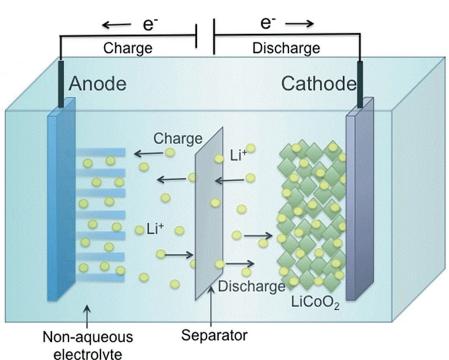


Figure 6. Schematic representation of a lithium-ion battery. Reproduced from Ref. [26] with permission. Copyright (2015) The Royal Society of Chemistry.

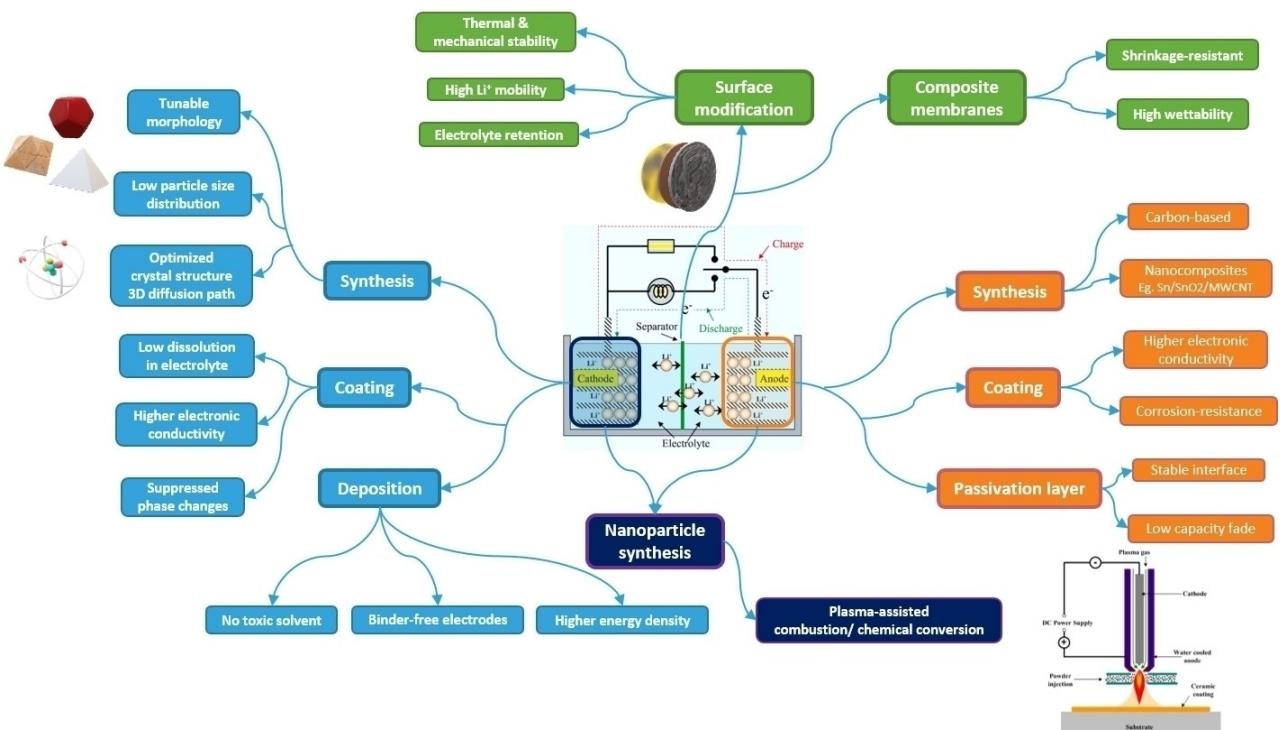


Figure 7. A concept map showing the possibilities to improve synthesis and modification of battery components by using plasma technologies.

3. Plasma Processing of Cathode Materials

3.1. Synthesis of Cathode Materials

The positive electrode, generally referred to as the cathode in battery literature, is arguably the key component in a rechargeable Li-ion battery, as its properties directly affect the battery performance. Therefore, a significant bulk of battery research activities focus on the synthesis processes and modification methods of cathodes. As state-of-the-art Li-ion batteries do not use lithium metal anode, the positive electrode must act as the source of lithium.^[3] Among the several approaches to enhance the electrode capacity, tuning the morphology of the electrode material to obtain a porous structure with high surface area is the most promising. Highly porous materials with a robust network of nanometer-sized domains are highly desirable in this context.

Thermal plasmas are ideal for the synthesis of nanoparticles as they possess high enthalpy to support the reaction kinetics in addition to rapid quenching rate (10^{3-6} K/s).^[33] Materials with very high melting and boiling points that are not achievable by conventional methods can be processed by thermal plasmas. Lithium-based intercalation powders have been prepared by plasma reaction of lithium and metal precursors mixed with alcohol in O₂ atmosphere.^[34] The feed solution is atomized by the O₂ gas into fine reactant droplets which form an intercalation powder on exposure to the plasma. Watanabe et al. have demonstrated a one-step synthesis of lithium metal oxide nanoparticles by using induction thermal plasma and studied the formation mechanism of the nanoparticles.^[33] For example, by injecting powdered precursors (Li₂CO₃ and metal

oxides) into the plasma using a mixture of Ar and O₂ as the plasma forming gas, they obtained LiCoO₂ particles with a size distribution of 50–80 nm with pentagonal and hexagonal morphologies. The conceptual diagram of formation mechanism of Li–Me oxide nanoparticles is shown in Figure 8. The authors hypothesize that above the melting point, the metal oxide particles in a liquid-like state react with condensed lithium oxide, and their co-condensation eventually results in the formation of lithium-metal oxide.

The chemical bonding state between a LiCoO₂ (LCO) cathode and ZrO₂ has been recently studied by Hata et al. by applying pulsed arc plasma deposition technique.^[35] The modified cathode was tested in CR2032 coin cell configuration with Li anode and an electrolyte formulation of 1 M LiPF₆ in a

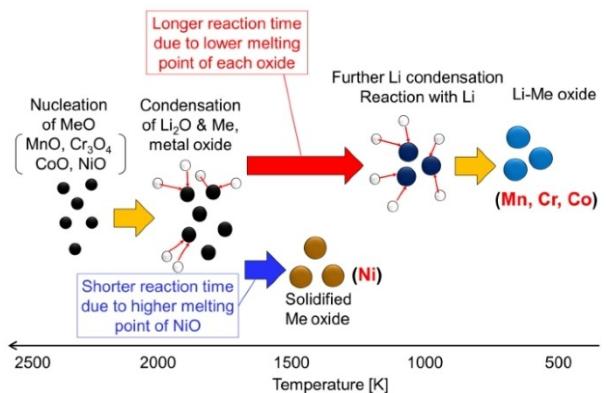


Figure 8. Formation mechanism of Li–Me oxide nanoparticles in a thermal plasma. Reproduced from Ref. [33]. Copyright (2016) The Authors.

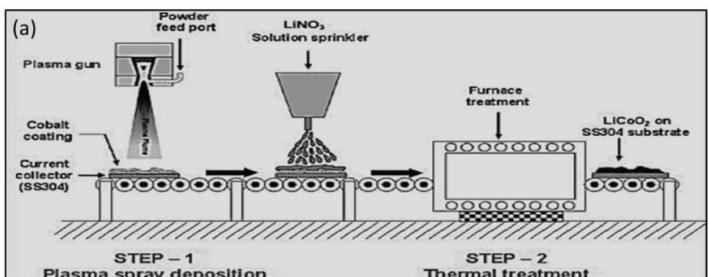


Figure 9. Schematic of the process to deposit binder free LiCoO_2 by plasma spraying technique. Reproduced from Ref. [36] with permission. Copyright (2011) Elsevier.

3:7 (vol.) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). It was observed that the oxygen pressure has a strong impact on the chemical bonding states between LCO and ZrO_2 , the reactivity of the modified cathode with the electrolyte, resulting in difference in the quality of the cathode-electrolyte interphase (CEI) layer formed, and consequently the capacity retention. At an oxygen pressure of 1 Pa, $\text{Zr}-\text{O}-\text{Co}$ bonding was observed on the surface. The bulk structure of LCO remained unaffected. An inorganic-rich CEI layer was formed, which slowed down the capacity decay observed in the unmodified electrode. When the oxygen pressure was increased to 30 Pa, a weaker $\text{Zr}-\text{O}-\text{Zr}$ bonding was observed on the surface, which could not retain the CEI layer on prolonged cycling, resulting in only smaller improvements in capacity retention.

A rapid, scalable manufacturing process of porous, nanostructured LiCoO_2 directly deposited on a current collector by plasma-spraying has been demonstrated by Pentyala et al.^[36] The schematic of this process is shown in Figure 9. Direct deposition of the active material on the current collector enables binder-free electrode processing. An efficient method to accomplish this is plasma spraying, which is a line-of-sight process of injecting a substance into a high temperature plasma jet stream. The injected substance is deposited on a substrate placed in the line-of-sight of the nozzle of the plasma torch.^[37]

Lithium iron phosphate (LiFePO_4 or LFP) with olivine structure is one of the most studied and commercialized cathode material next only to LCO, primarily due to the

abundance and low cost of iron compared to cobalt. Simulations have shown that the minimum migration energy for the lithium ions is along the [010] direction and that their diffusion coefficient in the bulk is significantly lower than at the nanoscale, as illustrated in Figure 10.^[38] Therefore, synthesizing LFP nanoparticles has been one of the top priorities of battery researchers, for which several approaches, including plasma techniques, have been applied.

Liu et al. used electric discharge assisted mechanical milling (EDAMM) to prepare LFP by feeding the mixed precursors into a reaction vessel adapted with two curved stainless-steel electrodes.^[39] The discharge caused by applying an AC power accelerates the sintering process, and the olivine material was synthesized after only one minute of reaction. Interestingly, LFP of high purity could be obtained within 10 minutes in this process. It is to be noted that multiple steps of intermittent grinding and calcination spanning several hours must be performed to achieve similar result in a typical solid-state method, whereas wet-chemical methods require toxic solvents and it is rather difficult to preserve the Fe (II) oxidation state along the process. Nevertheless, when electrochemical tests were performed on the cathodes prepared from the LFP obtained in the EDAMM method, only about 60% of the capacity of conventionally prepared LFP was observed. This could be possibly improved by further optimizing the precursor material selection, energy of the electrical discharge, and suitable additives to improve the electronic conductivity of the LFP powder, given the advantages of the method in terms of cost and processing time.

LiFePO_4 nanospheres of 50–100 nm diameter by inductively coupled thermal plasma (ICP) torch synthesis has been reported by Veilleux et al. In this method, the sol-gel precursors of LFP were fed to a reactor at 200 torr pressure with a mixture of Ar and H_2 as the plasma gas to maintain the Fe^{2+} oxidation state.^[40] The obtained particles were coated with carbon originating from the oxalic acid used in the precursors. This method is advantageous compared to conventional carbon coatings which are usually applied in a post-synthesis procedure, such as the pyrolysis of organic precursors or chemical/physical vapor deposition. As a further step, the authors have also demonstrated the direct deposition of the LFP material on nickel substrate by modifying the reactor setup. They used a supersonic nozzle to increase the plasma jet velocity and a water-cooled robotized arm to manipulate the Ni substrate

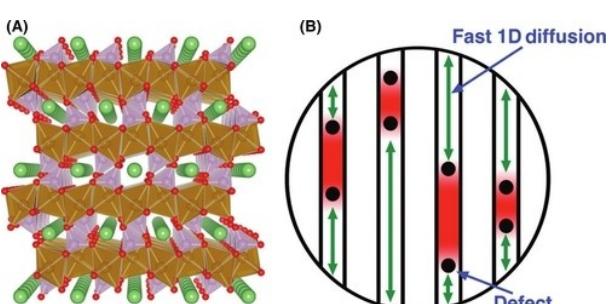


Figure 10. A) Crystal structure of LFP illustrating the diffusion channels along the [010] direction; B) Point defects in the channels restrict the mobility of the lithium ions. Reproduced from Ref. [38] with permission. Copyright (2010) American Chemical Society.

under the plasma jet. A post-process annealing was required to obtain crystalline LFP coating. Comparison of cyclic voltammetry curves showed that the Li-ion diffusion coefficient of the plasma-deposited LFP coating was one order of magnitude higher than that of the plasma-synthesized powder.

Recently, processes such as energy enhanced atomic layer deposition (ALD) have been applied to synthesize battery materials. For instance, plasma-assisted ALD has been used to build nanostructured Li-ion batteries. As these methods enable deposition of ultrathin films (1–100 nm) with precise growth control (Å-level resolution), they could be relevant for surface modification of particle-based electrodes and for the deposition of conformal nanostructured components in 3D-structured electrodes and microbatteries.^[41,42]

Dobbelaere et al. have demonstrated the synthesis of LiFePO₄ by plasma-enhanced atomic layer deposition on planar platinum-coated silicon substrates.^[43] The substrate was sequentially exposed to trimethyl phosphate (TMP) plasma, O₂ plasma, and tert-butylferrocene (TBF) plasma. An amorphous film of FePO₄ was formed at a growth rate of 1.1 nm/cycle, which was activated by electrochemical lithiation. Cells were assembled with FePO₄ as the working electrode coated on planar or 3D structured Si substrates. 1 M LiClO₄ in propylene carbonate was used as the electrolyte. Li metal acted as the counter and reference electrode. In the cells with FePO₄ coated on planar substrates, only 8% of the theoretical capacity of LFP could be obtained. The capacity of the material could be increased to about 60% of the theoretical capacity by conformally depositing it on a 3D-microstructured substrate consisting of platinum-coated silicon micropillars (Figure 11). The authors attributed the higher capacity of the 3D electrode compared to the planar electrode to the increased surface area of the micropillar electrodes and the possible difference in the morphology and stoichiometry of the material when deposited on substrates with the two different structures.

Jiang et al. synthesized nanosized LiMn₂O₄ (LMO) with polyhedral morphology using a plasma-enhanced low temperature solid-state strategy (PE-LTSS).^[44] They ball milled MnO₂ and LiOH before injecting the mixture into a PECVD tube furnace set at 500 °C with an RF power of 200 W in oxygen atmosphere. The resultant LMO spinel material yielded an initial discharge capacity of 130 mAh⁻¹, 95% of which it retained compared to only 75% in the case of the reference sample prepared by solid-state reaction. The authors attribute the

improved electrochemical performance to the finer particle size (400–450 nm) and controlled morphology achieved through this method.

Binder-free LMO thin films were directly deposited on a current collector by Chen et al. in a two-step process.^[45] First, the LMO thin film was obtained by a low-temperature sol-gel synthesis. The thin film was then treated with pulsed-DC plasma under pure O₂ atmosphere to form a dense nanocrystalline surface layer. This layer increases the stability and the ionic conductivity of the active material. The electrodes were plasma-treated for various durations, and were electrochemically tested up to a rate of 45 C in CR2032 coin cells with 1 M LiPF₆ in EC/EMC (1:2 volume ratio) as the electrolyte. The samples treated for 5 and 30 minutes showed a 65% capacity retention at 10 C and 32% at 35 C, while the reference sample showed a capacity retention of only 50% and 12%, respectively. The charge-transfer resistance of the plasma-treated electrodes were observed to be decreased by about 65% due to the uniform distribution of current on the denser and smoother surface as a result of the plasma treatment.

Researchers at the Korean Advanced Institute of Science and Technology (KAIST) have devised a post-treatment process to enhance the degree of crystallinity of lithium transition metal (LiMeO) thin films by plasma treatment.^[46] They deposited the LiMeO thin film on a Pt/Ti/SiO₂/Si substrate using an RF power of 100 W at a vapor deposition pressure of 3 mTorr and a substrate temperature of 350 °C with Ar and O₂ gases flowing at a rate of 8 sccm. While platinum acts as the current collector, the titanium layer blocks platinum diffusion at high temperature. They treated the vapor-deposited LiMeO thin film in oxygen or inert gas plasma to enhance the degree of crystallinity, surface flatness and electrochemical stability. The XRD patterns of the plasma-treated thin films of LCO (Figure 12) show sharper peaks compared to the film treated in a conventional furnace at 800 °C. The XRD pattern of the untreated thin film is also shown as a reference.

It is interesting that the crystallization process which requires 800 °C and a treatment time of at least 2 hours by conventional methods can be accomplished by this microwave plasma treatment method within 5 to 20 minutes at a relatively lower temperature of 390 °C.

A method for in-situ deposition of active materials by plasma spraying was patented by Applied Materials, Inc. in 2013.^[47] As represented by the flow diagram in Figure 13, this

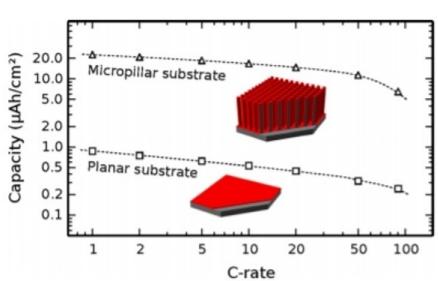
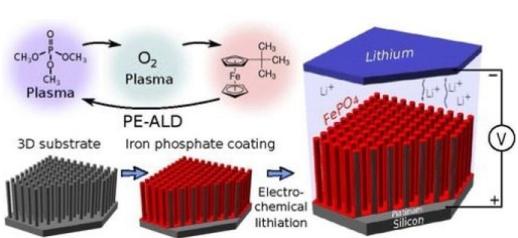


Figure 11. (Left) LFP deposition sequence. (Right) Capacity of LFP as a function of C-rate on a 3D micropillar substrate compared to a planar substrate. Reproduced from Ref. [43] with permission. Copyright (2016) American Chemical Society.

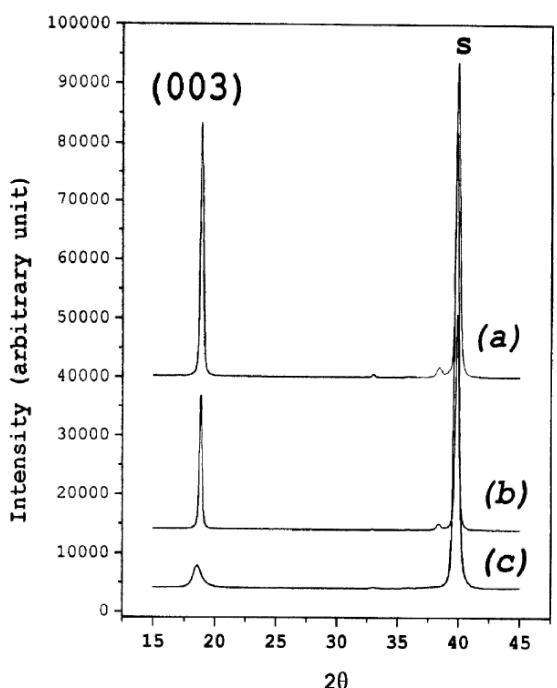


Figure 12. XRD patterns of LiCoO_2 a) treated with microwave plasma, b) prepared at 800°C , c) and without any heat treatment. The peak marked 'S' denotes the X-ray diffraction peak of the substrate. Reproduced from Ref. [46].

method involves the activation of precursor particles dispersed in a carrying medium by an electric field and then mixing the activated precursor particles with a combustible gas to convert them into nanocrystals, which are eventually deposited on a substrate.

It is also possible to blend a secondary precursor with the nanocrystals during deposition to enhance the adhesion and conductivity. In this method, copper or aluminum current collectors were used as the substrate. The first precursor could be a solution, suspension, or slurry of the active materials of diameters up to 100 nm. The energy applied by the plasma excites thermal motion of the atoms in the particles, causing them to move to lower energy crystal lattice positions. A carbon-containing gas such as acetylene is used since carbon can act as a binder as well as conductive layer. The precursor mixture is then fed into the processing chamber in which DC energy is applied to form a plasma. The precursor mixture is atomized with a carrier gas such as N_2 , H_2 , He or Ar.

Varadarajan et al. demonstrated the synthesis of vanadium pentoxide (V_2O_5) nanoparticles and nanorods using a high throughput solution plasma spray deposition technique, the schematic of which is shown in Figure 14. In this method, the vanadium solution precursors were injected into the plasma plume to achieve in-flight atomization. V_2O_5 of pure nanocrystalline phase in the size range of 20–50 nm produced by this process was directly deposited on aluminum or stainless steel sheets.^[48] These sheets were then soaked in a solution containing PVDF binder and conductive carbon black additive to prepare the electrodes. Cells with 1 M LiPF_6 in EC/DMC (1:1) electrolyte were assembled to compare the electrochemical properties. The electrodes based on these V_2O_5 films showed reversible insertion and extraction of Li^+ ions, resulting in discharge capacity of more than 200–240 mAh g^{-1} . The authors highlight the scope for further improvement in the capacity retention which could be accomplished by in situ carbon coating of the films by using suitable carbonizing precursors such as acetylene.

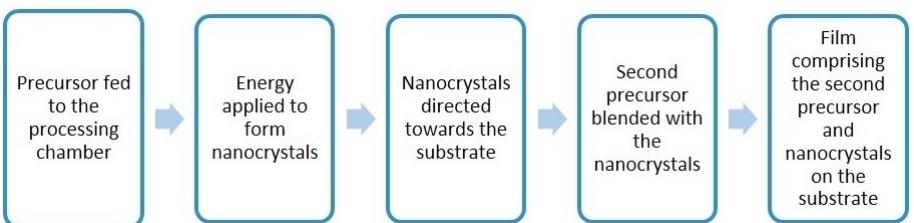


Figure 13. Flow diagram summarizing the deposition of active material nanocrystals by plasma spraying method.^[47]

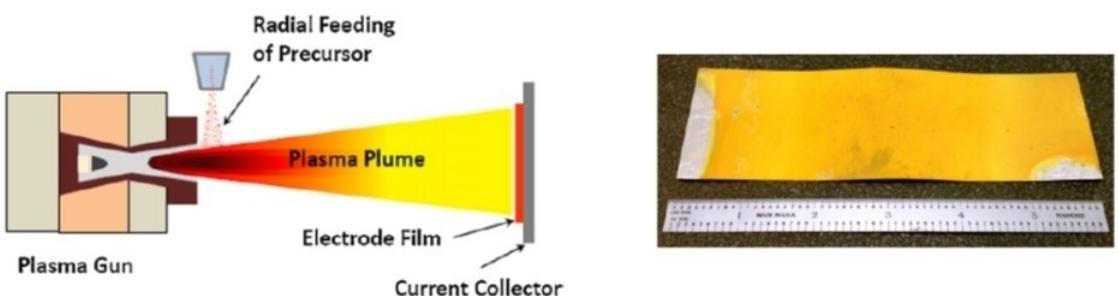


Figure 14. (Left) Schematic of the solution plasma spray deposition setup and (Right) Photograph of the as-sprayed V_2O_5 film. Reproduced from Ref. [48] with permission. Copyright (2011) Elsevier.

3.2. Coating of Cathode Materials

One of the key challenges in state-of-the-art batteries is the instability of the cathode-electrolyte interface at voltages higher than 4.3 V. Although solid electrolytes with wide electrochemical stability window are being explored, the large charge-transfer resistance at the solid-solid interface is a more serious bottleneck.^[8] A common approach to improve the cathode properties is to coat the surface of the electrode material by specific functional groups. The purpose of the coating varies according to the requirement. For instance, carbon-coating the surface of the particles is expected to improve electrical transport in the material, whereas a metal oxide layer such as Al_2O_3 or ZrO_2 could be explored to improve the structural stability of the electrode material by suppressing undesired phase transitions during charge/discharge cycles. Other goals of surface coating include reduction of cationic defects in the crystal lattice, inhibition of transition metal dissolution (especially Mg), HF scavenging to reduce electrolyte acidity, and enhancement of the solid electrolyte interphase (SEI) layer on the surface. Thus, surface coating is an important aspect in improving the electrochemical performance of the battery.

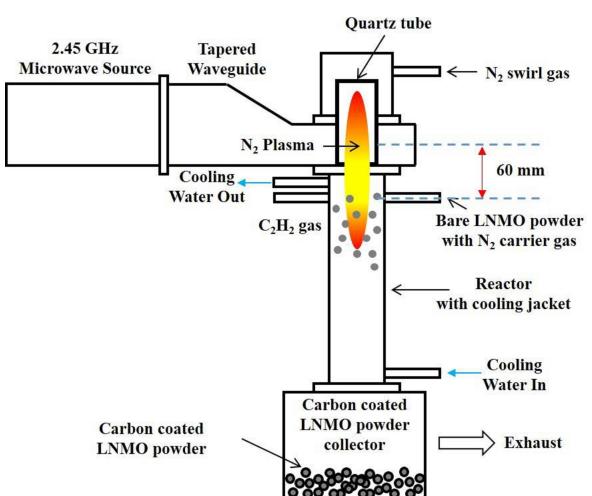


Figure 15. Schematic diagram of one-step carbon coating method for LNMO using the atmospheric microwave plasma torch system. Reproduced from Ref. [51] with permission from Elsevier.

Among these, carbon coating is the most explored strategy which increases the electronic conductivity of the electrode material.^[49] Plasma treatment of powders has been shown to improve their dispersibility, introduce desirable oxygen vacancies or interstitials, and enhance the processability in general.^[50]

Ku et al. used an atmospheric microwave plasma torch system (Figure 15) with acetylene gas as carbon precursor to carbon-coat the spinel-structured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode powder in a single-step process.^[51] The carbon coating on LNMO enhanced the rate capability and cycle performance especially at 50 °C compared to bare LNMO. At 10 C rate with increased temperature, the LNMO/C showed a discharge capacity of 104 mAh g^{-1} compared to 0.15 mAh g^{-1} for bare LNMO at 50 °C. The effective carbon coating of the LNMO was attributed to the microwave plasma torch which is capable of creating a highly reactive chemical environment abundant in radicals that act as catalyst for the coating of the carbon layer on the LNMO particles. High degrees of ionization and dissociation are possible at relatively lower gas flow and lower power conditions with microwave plasma torches compared to other electrical excitation methods. The high temperature and plasma density obtained in these systems enhance the kinetics of the chemical reaction, enabling uniform coating of the electrode material in a single-step process. Thus, the atmospheric microwave plasma torch system appears to be a promising tool that could facilitate direct carbon-coating of materials in significantly shorter treatment time at lower cost, whereas conventional carbon-coating methods involve longer thermal treatment time and multiple processing steps, and consequently higher cost. It might be interesting to apply this technique to carbon-coat other electrode materials for LIBs and compare the cost, processability and performance.

A facile plasma-enhanced method to synthesize alumina-coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (LNCM) has been reported by Jiang et al.^[52] The LNCM powder was mixed with an aluminum-based precursor and transferred to a plasma-enhanced tube furnace with pressure controls. Al_2O_3 -coated LNCM powder with a coating thickness of 5 nm was obtained after a plasma treatment time of 20 minutes at 350 °C and an oxygen partial pressure of 50 Pa. Figure 16 shows the TEM images of the untreated and plasma-treated LNCM powder. On cycling at 55 °C, the Al_2O_3 -coated LNCM obtained by plasma treatment

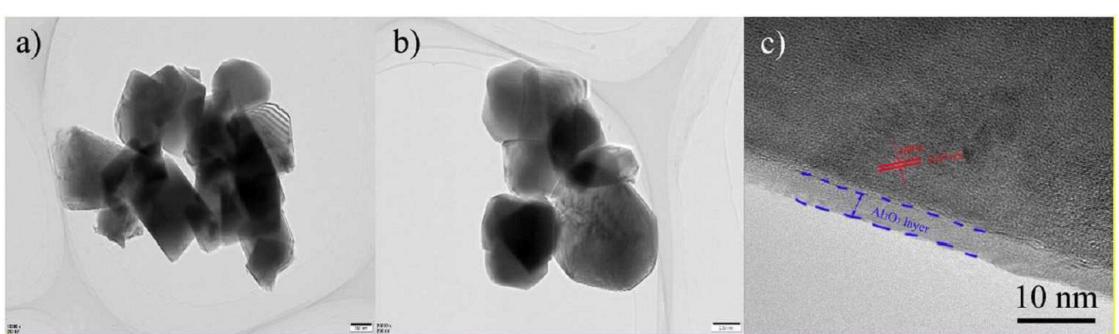


Figure 16. TEM image of a) LNCM and b) $\text{Al}_2\text{O}_3@\text{LNCM}$, c) HR-TEM image $\text{Al}_2\text{O}_3@\text{LNCM}$. Reproduced from Ref. [52] under the terms of the CC BY license. Copyright (2020) The Authors.

showed 85% capacity retention after 100 cycles, compared to 52% in the case of bare LNCM. This improvement is attributed to the Al_2O_3 coating formed by the plasma-enhanced method which prevents the dissolution of metal ions in the electrolyte and also reduces the decomposition of the electrolyte normally occurring due to the cathode-electrolyte reactions.

As the energy density and capacity of lithium-ion technology are levelling off, there has been tremendous interest on a number of post-lithium ion technologies such as lithium-sulfur ($\text{Li}-\text{S}$) and lithium- O_2 batteries. Perhaps the holy grail of this quest is to use conversion cathodes with high volumetric capacities such as sulfur or oxygen in combination with a pure metal anode. As an active cathode material, elemental sulfur has a charge storage capacity an order of magnitude higher than the capacity of state-of-the-art materials.^[53] However, the poor conductivity and low electrode stability of sulfur results in its inefficient electrochemical reduction and solubility in the electrolyte, respectively. Although these problems can be partially solved by confining sulfur into conductive hosts such as mesoporous carbon or metal organic frameworks, the higher capacity is retained only for a few cycles.^[54] The capacity fading is too high to use the cell in practical applications. In one of the promising strategies to overcome this problem, researchers at Toyota Motor have proposed encapsulating the active sulfur within polyelectrolyte membranes which would restrict the diffusion of polysulfides while allowing the Li^+ ions to diffuse.^[55] To accomplish this, they have applied the polyelectrolyte multilayer (PEML) assembly technique which involves sequential absorption of oppositely charged polyions from a dilute solution onto a substrate.^[56] With a wide range of polyion building blocks available for the PEML capsule, this methodology is analogous to a "Lego" set of membrane structures offering unlimited possibilities to explore and apply in order to improve the cycle life of $\text{Li}-\text{S}$ batteries. This method involves forming a primer or foundation layer such as branched polyethyleneimine (bPEI) to the carbon-sulfur composite core. The coated carbon-sulfur core is subsequently exposed to lithium chloride aqueous solutions of polyelectrolytes with alternating positive and negative charge.

Recently, a method to reduce inkjet-printed flexible graphene oxide surfaces by using hydrogen plasma has been demonstrated by Homola et al. This process uses an atmospheric DBD plasma source (Figure 17) the treatment by which only the surface of the graphene oxide layer is reduced, decreasing the sheet resistance of the reduced graphene oxide by about six orders of magnitude.^[57] The large-area atmospheric post-processing by dry plasma reduction of the films could be a sustainable method to produce electrodes for flexible low-cost devices from reduced graphene oxide, for instance, supercapacitors and solar cells. Such processes, if adapted for roll-to-roll manufacturing, could be of immense use in the manufacture of flexible batteries as well.

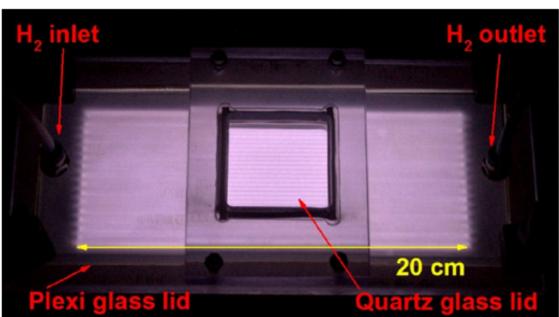


Figure 17. Atmospheric DBD plasma treatment of reduced graphene oxide in pure hydrogen. Reproduced from Ref. [57] with permission. Copyright (2018) Wiley-VCH.

4. Plasma Processing of Anode Materials

There have been several reports on the application of plasma technologies to produce, modify and protect anode materials. The materials synthesized using plasmas are usually those with theoretical capacity higher than that of graphite. In this regard, Si ($> 3500 \text{ mAh g}^{-1}$) and Sn (994 mAh g^{-1}) are the most researched anode materials. In addition, plasma technology has been extensively used to synthesize carbon-based materials such as carbon nanotubes, graphene nanosheets and other nanostructures.^[58–61] Besides synthesis, plasma-assisted methods have been explored in the protection of metal anodes such as lithium by coating a protective layer, and pre-processing the anode by depositing a passivation layer to reduce the irreversible capacity loss during the first charge/discharge cycle.

4.1. Synthesis of Anode Materials

State-of-the-art LIB anodes are based on graphite which has a capacity of 375 mAh g^{-1} . This is rather insufficient given the high energy density, power density and cycle life required for modern applications. The most fascinating material as far as theoretical capacity is concerned is silicon, which could enhance the anode capacity by an order of magnitude to 4000 mAh g^{-1} .^[62] However, the volumetric energy density of the silicon anode is just about the same as other materials, considering the low tap density of Si nanomaterials.^[63] Furthermore, this capacity could not be retained beyond a few tens of cycles, due to the dramatic volume expansion (300%) of silicon during lithiation. While the first problem could be addressed by alloying Si with suitable materials, the second problem has been mitigated to some extent by using nanostructured silicon. Due to their larger aspect ratio, silicon nanostructures can withstand the volume expansion caused by successive lithiation and delithiation much better compared to bulk Si. The increased energy barrier for crack propagation (also known as Griffith's criterion) of the nanostructures result in lower volume expansion than bulk silicon. It has been observed that the smaller the size of the silicon nanostructure, the larger the charge storage capacity.^[64] In spite of this, an unstable solid electrolyte interphase (SEI) layer forms on the surface of the Si

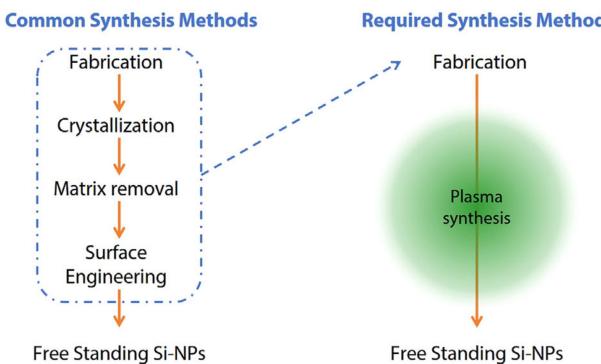


Figure 18. The difference between common synthesis routes and plasma synthesis of silicon nanoparticles. Reproduced Ref. [21] with permission. Copyright (2015) Wiley-VCH.

nanoparticles due to the reaction with the electrolyte salt, and this results in drastic capacity loss from 4000 mAh g^{-1} to 500 mAh g^{-1} within 50 cycles.^[65] Therefore, different means to synthesize Si nanoparticles (Si-NPs) with improved properties are being explored, of which plasma technologies have gained much interest.

Again, thermal plasmas are suitable for the synthesis of Si-NPs and their composites with high throughput. In conventional techniques, Si-NP synthesis involves multiple steps such as annealing, matrix removal by etching, and surface functionalization. On the other hand, plasma-based processes facilitate high throughput in a single step, as illustrated in Figure 18.^[21]

Kambara et al. synthesized silicon-based nanocomposites of core-shell structure from raw silicon powder using thermal plasma at a throughput of 6 g/minute.^[66] The crystalline Si nanoparticles were surrounded by an amorphous carbon shell. The authors show that the plasma treatment reduced the capacity decay, although the presence of SiC nanoparticles reduced the overall capacity. In order to inhibit such inevitable formation of SiC while coating the silicon nanoparticles with carbon, Chang et al. applied a tandem plasma reactor (TPR) which integrates two plasma sources in one reactor, as shown in Figure 19, and used graphite as the carbon precursor.^[67] They report a homogeneous Si/C nanocomposite formation in a single-step process. The Si/C nanocomposite could be directly deposited on copper foils at a mass loading of 50–100 $\mu\text{g/cm}^2$. When tested in coin cells with 1 M LiPF₆ in EC/DMC (1:1

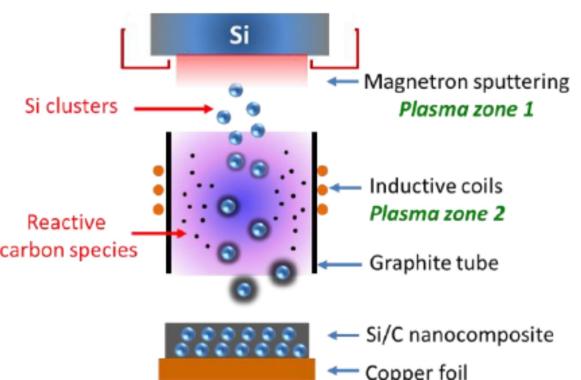


Figure 19. Schematic of the tandem plasma reactor used to produce Si/C nanocomposite in a single-step process. Reproduced from Ref. [67] with permission. Copyright (2014) The Royal Society of Chemistry.

volume) as the electrolyte, the Si/C nanocomposite electrodes retained 1760 and 1460 mAh g^{-1} after more than 400 cycles at current densities of 2.0 and 4.0 A g^{-1} , respectively. The authors suggest that SiC formation during the nanocomposite synthesis could be inhibited by using graphite as the carbon source, which reduces the density of reactive carbon species in the plasma. This result indicates that the key to inhibit the SiC formation is to use a precursor with lower reactivity.

Si-NPs can also be combined with other types of carbon-based nanomaterials. For instance, carbon nanotubes (CNTs) are particularly interesting composite materials for Si-NP based anodes because of their higher specific capacity of 600 mAh g^{-1} with respect to graphite. Their large aspect ratio buffers the expansion of Si-NPs during lithiation without pulverizing the electrode. Na et al. synthesized a composite material of commercially available multi-walled carbon nanotubes (MWCNTs) and Si-NPs in a thermal DC arc plasma jet.^[68] They controlled the density ratio of MWCNTs and Si-NPs by tuning the plasma power and varying the injection location of Si particles to obtain a nanocomposite with the structure of Si-NPs attached to the columns of the carbon nanotubes, as shown in the SEM micrographs of Figure 20.

In another approach, Jung et al. have demonstrated that P-doping the silicon nanoparticles could improve the anode capacity.^[69] They doped the Si nanoparticles with phosphorous using an ICP with double tube reactor in a PH₃/Ar and SiH₄/Ar gas mixture. The phosphorous atoms separately undergo a

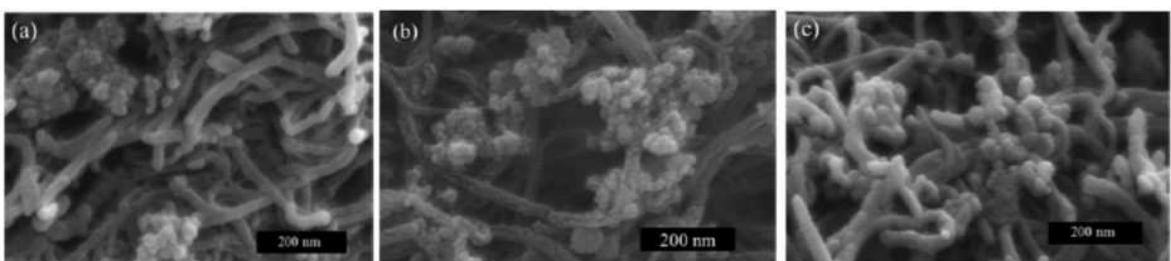


Figure 20. SEM images of MWCNT/Si-NP composites synthesized at plasma powers of a) 10.2, b) 11.3 and c) 12.6 kW. Reproduced from Ref. [68] with permission. Copyright (2014) Wiley-VCH.

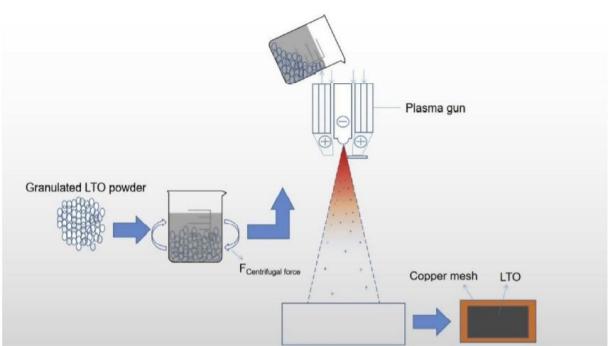


Figure 21. LTO electrode preparation process by atmospheric plasma spray method. Reproduced from Ref. [70] with permission. Copyright (2019) Elsevier.

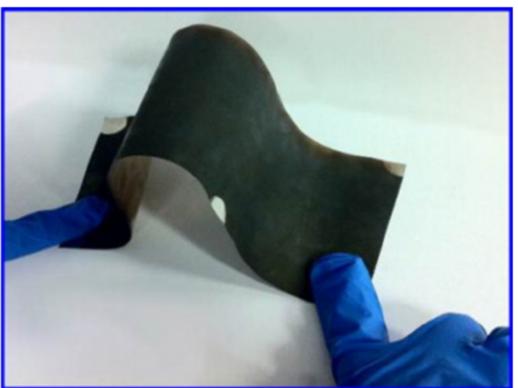


Figure 22. Flexible Co_3O_4 electrode deposited on stainless steel sheet by solution precursor plasma. Reproduced from Ref. [73] with permission. Copyright (2019) Elsevier.

reversible lithiation to form Li_3P , resulting in an initial capacity of 2113 mAh g^{-1} , of which 1000 mAh g^{-1} was retained after 100 cycles. Although the electrical conductivity is not enhanced by the P-doping, the formation of the reversible Li_3P phase enhanced the anode capacity. Thus, anodes based on silicon nanoparticles often outperform the carbon anodes albeit up to a few hundreds of charge/discharge cycles. Further studies aiming at improving the cycle life by in-depth analysis of the lithiation mechanism, volume expansion and SEI formation are likely to make more progress in the quest for better anode materials.

Recently, Liang et al. demonstrated a simplified procedure to synthesize $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes by employing the atmospheric plasma spray (APS) technique.^[70] Granulated LTO powders were sprayed on a copper mesh using a plasma gun with argon as the plasma gas, as illustrated in Figure 21. It was shown that spray granulation reduced the average particle size and improved the crystallinity of LTO, while preserving the molecular structure.

Donders et al. deposited Co_3O_4 thin films by using remote O_2 plasma atomic layer deposition (ALD) at a growth rate of $0.05 \text{ nm per ALD-cycle}$.^[71] Electrochemical analysis of the cobalt oxide electrode was performed in a three-electrode cell with lithium counter and reference electrode. The charge/discharge

capacity was observed to stabilize at 1000 mAh g^{-1} after 70 cycles.

Koshtyal et al. have used plasma-assisted ALD to deposit NiO films of thickness 28–30 nm on stainless steel.^[72] The deposited films showed a specific capacity of 1300 mAh g^{-1} , which is higher than the theoretical capacity of bulk NiO (718 mAh g^{-1}). The authors attribute this to the pseudo-capacity of the gel-like solid electrolyte interface (SEI) layer composed of LiF , Li_2CO_3 and other species formed on the NiO active layer.

A binder-free direct coating of anode material on the current collector by using a single-step, solution precursor plasma technique has been demonstrated by Tummala et al. They radially injected cobalt acetate tetrahydrate solution into the plasma plume and sprayed the resultant Co_3O_4 particles onto a stainless steel sheet substrate, forming a flexible electrode as shown in Figure 22. This electrode was tested in lithium half-cells with 1.5 M LiPF_6 dissolved in EC:DMC (1:2) solution as the electrolyte. At C/10 rate, the half-cell delivered capacity closer to the theoretical value of 890 mAh g^{-1} . However, the capacity fading was severe at higher C-rates, probably due to volume expansion, poor electronic conductivity and material fatigue, as no carbon additive was used in the electrode.^[73] More importantly, this rapid process eliminates the need for longer, multi-step processing and the use of binders, solvents and other additives. In addition, post-coating treatments such as calendaring are not required, which could significantly bring down the cost of electrode preparation.

4.2. Protection of Anode Materials

Among the currently known electrode materials, lithium metal has the most negative potential. This leads to the highest discharge voltage, and owing to the light weight of lithium, the highest energy density possible. However, the high reactivity of the lithium metal with the electrolyte results in the formation of a resistive film on the anode surface. In addition, the accumulation of electrochemically inactive lithium resulting from continued cycling eventually forms dendrites that could short the battery. Therefore, lithium metal electrodes are not used in rechargeable Li battery systems.^[74] In addition to this safety issue, lithium dendrites drastically reduce the Coulombic efficiency and shorten the cycling lifespan of the battery.^[75] This is summarized in Figure 23.^[76]

In one of the efforts to understand the formation and the evolution of the lithium dendrites, Harry et al. used hard X-ray microtomography on symmetric lithium-polymer-lithium cells. As shown in Figure 24, they observed the protrusion of the dendrites into the electrolyte on cycling until a short circuit was caused.^[77]

Several techniques and strategies have been applied to prevent this potentially dangerous reaction and realize rechargeable batteries with lithium metal anode. One of the best strategies is to coat a layer of a lithium-conducting material over the lithium metal anode to separate the anode from the electrolyte. This has been shown to extend the life of the battery and to enhance the electrochemical performance. For

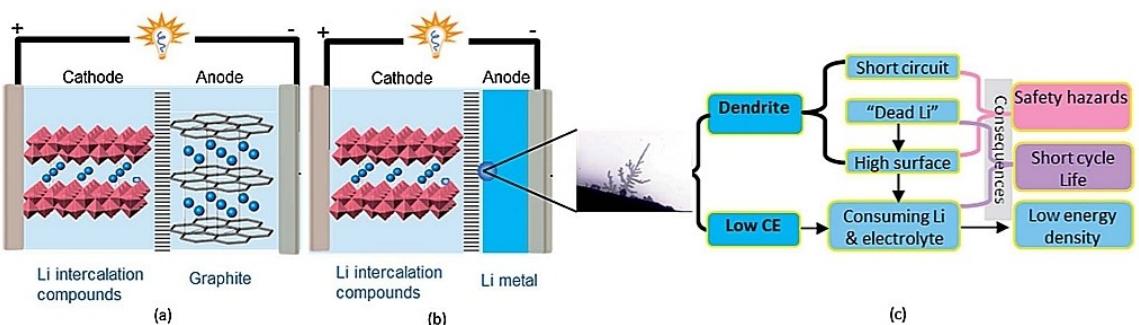


Figure 23. Schematic diagram of (a) Li-ion batteries; (b) Li metal batteries; (c) typical morphology of Li dendrites and the problems related to dendrites. Reproduced from Ref. [76] with permission. Copyright (2013) The Royal Society of Chemistry.

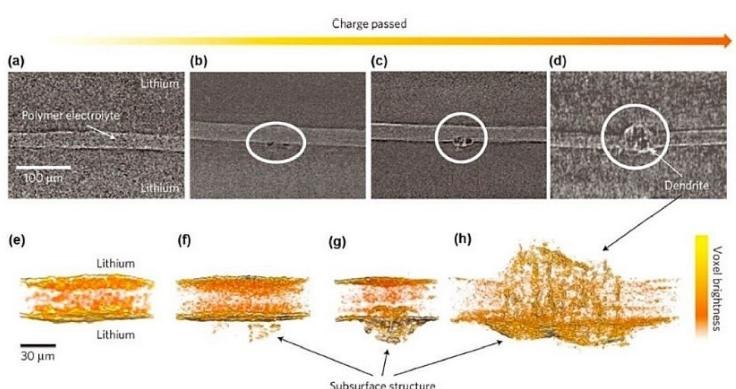


Figure 24. Evolution of Li dendrites observed by X-ray tomography. Reproduced from Ref. [77]. Copyright (2013) Springer Nature.

instance, a layer of Li_3N is coated on the lithium metal by a controlled exposure of the bare lithium to a nitrogen plasma.^[78] The grain boundaries between individual crystallites of Li_3N layers allow the liquid electrolyte to find its way to the bulk lithium electrode.^[79] Nevertheless, attempts to form stable Li_3N protective layers have been going on with some promising results. Yi Cui et al. demonstrated a method to treat molten lithium metal foil directly with nitrogen gas to generate pinhole-free Li_3N films directly bonded onto the lithium metal surface.^[79]

More recently, Chen et al. have reported their application of low-pressure N_2 plasma to passivate lithium metal with a multifunctional protective layer.^[80] They obtained a highly [001] oriented and flower-shaped Li_3N layer (Figure 25) on the surface of the lithium metal with a plasma activation time less than 5 minutes.

Zhu et al. reported a method to form lithiophilic nitride layer on nickel foam by a plasma process.^[81] Shown in Figure 26, these nitride decorated nickel foams (PNNF) of high specific surface area exhibited uniform lithium deposition by the formation of Li_3N . A full-cell assembled with the modified anode and LFP cathode displayed a high reversible capacity of 167 mAh g^{-1} at the end of 300 cycles at 1 C rate.

Another pre-formed lithium protective layer is lithium phosphorus oxynitride, popularly known as LiPON, the classical single-ion (Li^+ in this case) conducting material used to coat

lithium metal. The thickness of the film is typically between 0.1 and 0.5 μm . Such a protective layer prevents the undesirable oxidation of the lithium metal, in addition to preventing the metal from direct contact with the electrolyte. This in turn significantly reduces the possibility of lithium dendrite formation, thereby providing better safety as well as prolonging the battery cycle life. This method was first patented by John Bates in 1994, and then adapted by several others by applying various techniques, one of which is represented in Figure 27.^[82,83]

For instance, plasma-assisted deposition techniques have been explored to overcome porosity and columnar structures in the LiPON layer. It has been shown that the protective layer formed by such methods could enable the handling of the anode in ambient conditions.^[84] The plasma-deposited protective layer typically has surface roughness no greater than 500 \AA r.m.s. deviation, which is relatively smoother than protective layers deposited by other methods such as sputtering where the layer consists of columnar growths. This technique could also be adapted to Li–S batteries wherein the protective layer does not conduct anions such as S_8^- generated during the discharge of the sulfur electrode. This has been recently demonstrated by Wang et al. via a nitrogen plasma-assisted deposition method that is suitable for large-scale roll-to-roll production.^[85] The schematic of the deposition system is shown in Figure 28. Using an 8 kW E-beam evaporator and an

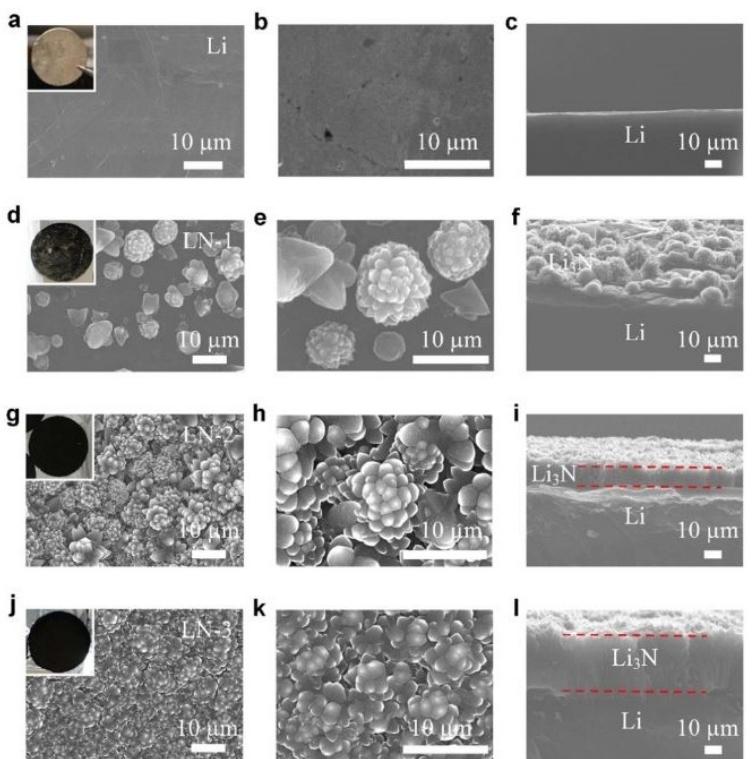


Figure 25. SEM images of bare Li and Li_3N film obtained at different durations of plasma treatment. Reproduced from Ref. [80] with permission from Elsevier.

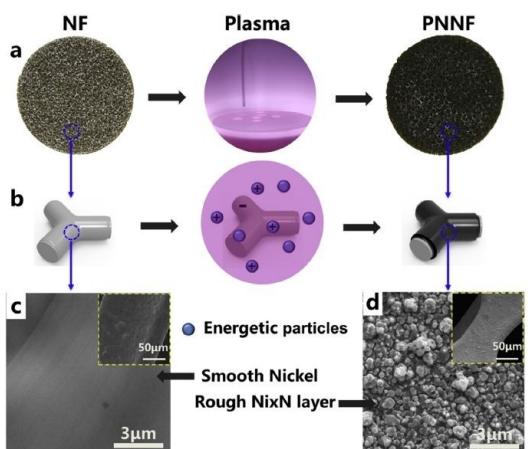


Figure 26. Schematic of the plasma nitridation process of PNNF. Reproduced from Ref. [81] with permission. Copyright (2019) Elsevier.

inductively coupled plasma reactor, the authors showed that the thickness of the LiPON coating could be controlled by the deposition time.

A modified approach is to stabilize the lithium metal electrode with an alloy layer that is comprised of lithium and aluminum, as first disclosed by PolyPlus Battery Co Inc.^[86] The lithium core is coated with a relatively thinner Al surface layer by plasma deposition. The Al–Li alloy layer is gradually formed by the diffusion of lithium into the Al layer. The surface coating increases the cycle life of the cell. A Li–S cell with a lithium anode coated with 0.8 micron Al–Li alloy layer was shown to

exhibit 3.5 times larger capacity than a Li–S cell without an Al–Li alloy layer.

Sion Power Corporation have developed a method to deposit a multi-layer structure on lithium metal. The multi-layer structure allows the diffusion of lithium ions while acting as a barrier to other cell components more effectively than single or dual layer interfacial films.^[87] This method overcomes the problem of undesirable by-products formed by the reaction between the precursors of the protective layer and the lithium metal. By depositing a buffer layer on the lithium surface prior to depositing the interfacial layer, side reactions at the lithium surface may be eliminated or significantly reduced. The outer layer which is in contact with the electrolyte or separator is ideally conductive to lithium ions and prevents electrolyte diffusion towards the metal anode, while accommodating the volume changes occurring during charge/discharge cycles. In this method, the amount of material deposited with the lithium metal is typically between 0.2% and 5% by weight of the lithium metal.

PolyPlus Battery Company have demonstrated a method to prepare ion-conducting membranes comprised of discrete layers of materials with different chemical functionalities.^[88] First, an ion-conducting layer such as Li_3N , Li_2P , LiF or LiPON is formed on the surface of lithium. This is followed by a second layer typically consisting of phosphorous-based or oxide-based glassy or amorphous metal ion conductors. By applying appropriate methods such as plasma spray deposition, it is possible to form a gradual transition from one functionality to another along the different layers of the film. The process

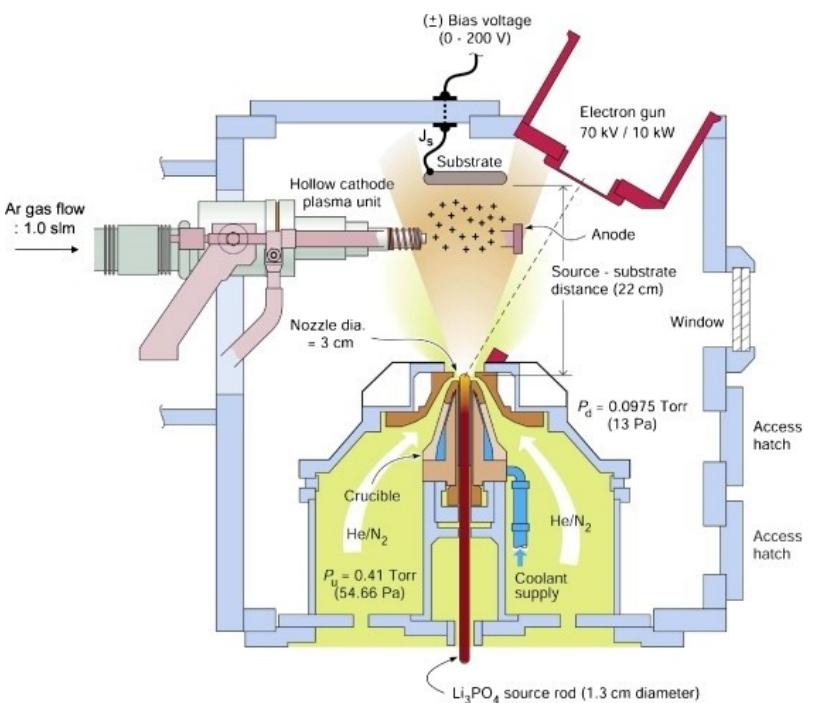


Figure 27. Schematic of the plasma-assisted directed vapor deposition (PA-DVD) process. Reproduced from Ref. [83] with permission. Copyright (2008) Elsevier.

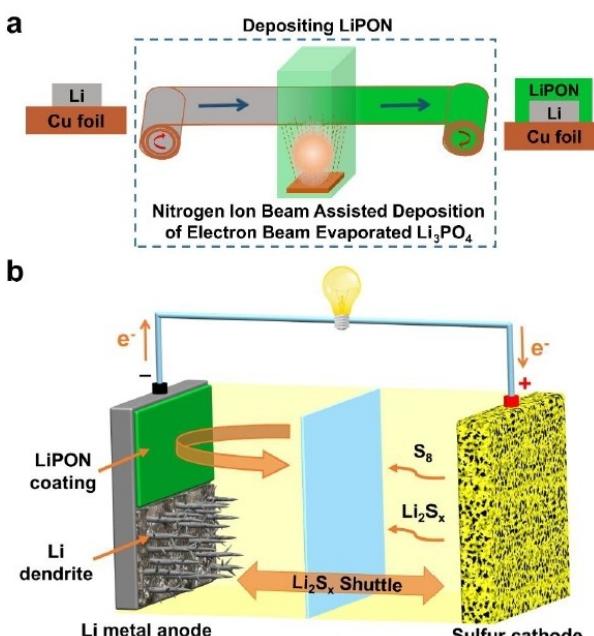


Figure 28. a) schematic of the mass production of LiPON-coated Li metal foils by a roll-to-roll system and b) the performance of a LiPON-coated Li metal anode in Li-S battery configuration. Reproduced from Ref. [85] with permission. Copyright (2018) Elsevier.

developed by PolyPlus is illustrated in Figure 29. In this case, lithium is evaporated in a nitrogen plasma to form Li_3N layer on the surface of a glassy ceramic material. Lithium is again evaporated onto this Li_3N layer, forming a stack of layers in which the lithium metal electrode is separated from the glassy

material layer by Li_3N , which allows Li ions to pass from the Li anode through the glass.

Besides lithium metal protection, plasma technology has also been applied to modify other anode materials to enhance lithium-ion diffusion. Zhu et al. used a plasma process to introduce oxygen vacancies in $\text{Li}_4\text{Ti}_5\text{O}_{12}$, an anode material for high-power Li-ion batteries.^[89] For this, they treated the LTO precursor in a H_2/N_2 plasma atmosphere at a pressure of 5 Pa and a temperature of 150°C. Lan et al. used a one-step atmospheric-pressure Ar/N_2 binary plasma jet irradiation to simultaneously nitrogen-dope and reduce the particle size of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material, which resulted in improved lithium ion diffusion and reduced charge-transfer resistance.^[90]

5. Plasma Processes for Solid-State Electrolytes

The current Li-ion chemistry is approaching its limits in terms of electrochemical performance. The demand for higher energy density, power density and safety does not appear to fade in the near future. Therefore, attention of the battery researchers has inevitably turned to solid-state batteries (SSB). The new challenges are more time-consuming and high-risk compared to those in LIBs. Although ceramic and polymer electrolytes with reasonable ionic conductivity have been developed, the major challenges are related to the electrode-electrolyte interface, ion transport, and scalability. For instance, dendrites remain a problem in the anode-electrolyte interface of SSBs. The problems at the cathode-electrolyte interface include lattice mismatch between the particles of the cathode and the electrolyte, delamination and loss of contact. In the case of

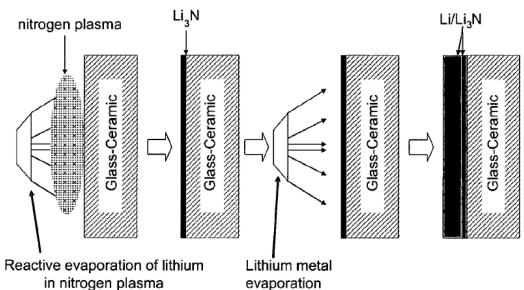


Figure 29. A plasma-assisted method to form a protective membrane composite. Reproduced from Ref. [88].

microbatteries, scalability becomes an issue as the packaging methods for liquid electrolytes cannot be scaled down as such.

The ceramic electrolytes are generally based on oxides, oxy-nitrides, nitrides, phosphates and sulfides. Figure 30 illustrates the evolution of solid electrolytes and their ionic conductivity over time.^[91] Among these, LiPON is one of the most studied solid electrolyte. In the context of plasma processes, plasma-assisted ALD technique has been demonstrated to deposit thin films of battery components. Here the challenge is to control the thickness of the solid-state electrolyte typically within the range of 500–2000 nm so that it is neither too thick to block the Li^+ ions nor too thin to create a short circuit.^[92] In this technique, the precursors are introduced in a predetermined sequence onto a substrate. The vapors of the precursors are fed to the reaction chamber, followed by the introduction of the reactant (plasma in this case) and allowed to react until the surface is saturated, thereby making the deposition self-limiting. The modified surface is then reacted with the next precursor and so forth. Thus, the deposition process is controlled at the atomic level and can be applied to assemble intricate 3D geometries.

Kozen et al. have demonstrated N_2 plasma-assisted atomic layer deposition (ALD) of LiPON as a solid electrolyte, and studied the effect of nitrogen content on the morphology and the ionic conductivity of the deposited LiPON thin film.^[93] They observed about two orders of magnitude increase in the ionic conductivity when the nitrogen content was increased from 1.8% to 16.3%.

Recently, Put et al. reported the deposition of LiPON by plasma-assisted ALD.^[94] A solid-state battery with the LiPON electrolyte, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) cathode and metallic lithium anode (Figure 31) could be cycled at 5 C rate, delivering a capacity of 0.3 Ah/cm^3 . A constant voltage plateau at 1.5 V typical of the Li-ion insertion/extraction in LTO was observed.

Within the solid electrolyte, the grain-grain interface directly affects the ionic conductivity whereas the electrode-electrolyte interface must retain good contact during the charge/discharge cycles. These two interfaces are sensitive to the sintering conditions. Spark plasma sintering (SPS) has been applied in the sintering of a variety of electrolytes and electrode materials for LIBs. In the SPS technique, the material is subjected to a uniaxial force and a pulsed direct current in low pressure conditions. The combined effect of current, pressure and heat enable high heating/cooling rates that result in high densification of the powders without any grain coarsening, consequently leading to better solid-solid interfacial contacts. The relatively shorter processing time (2–10 minutes) and the retention of the intrinsic properties of the powders make SPS a viable technique for the synthesis and processing of battery materials.^[95]

Lithium titanium phosphate (LTP), which crystallizes in the sodium superionic conductor (NASICON) structure, is an interesting solid electrolyte with stability in ambient conditions. The room-temperature ionic conductivity of LTP is in the order of 10^{-7} S/cm . A general approach to improve the conductivity is the partial substitution of the Ti^{4+} ions in $\text{LiTi}_2(\text{PO}_4)_3$ with

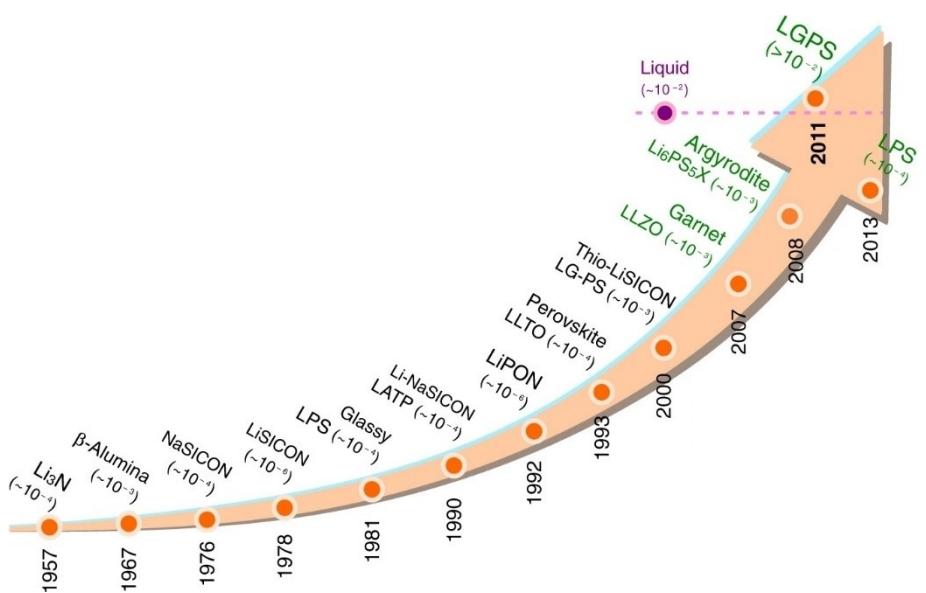


Figure 30. Evolution of solid electrolytes and their ionic conductivity. Reproduced from Ref. [91] with permission. Copyright (2020) The Authors.

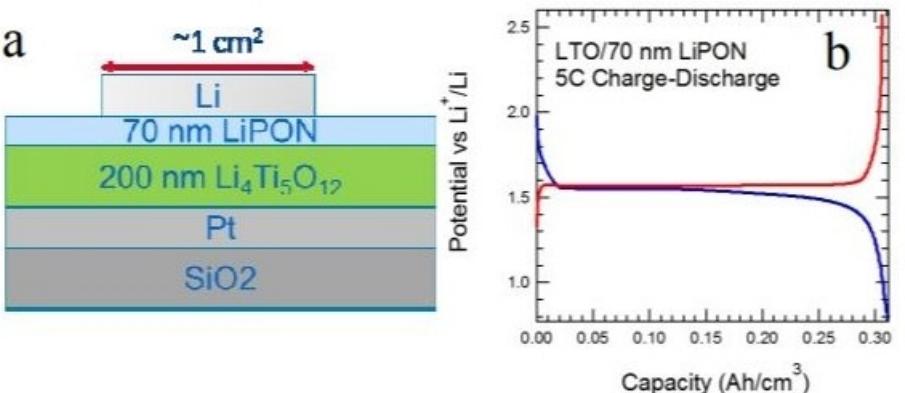


Figure 31. a) Schematic of the solid-state cell with ALD-deposited LiPON electrolyte; b) Charge/discharge curve of the solid-state battery. Reproduced from Ref. [94] with permission. Copyright (2019) The Electrochemical Society.

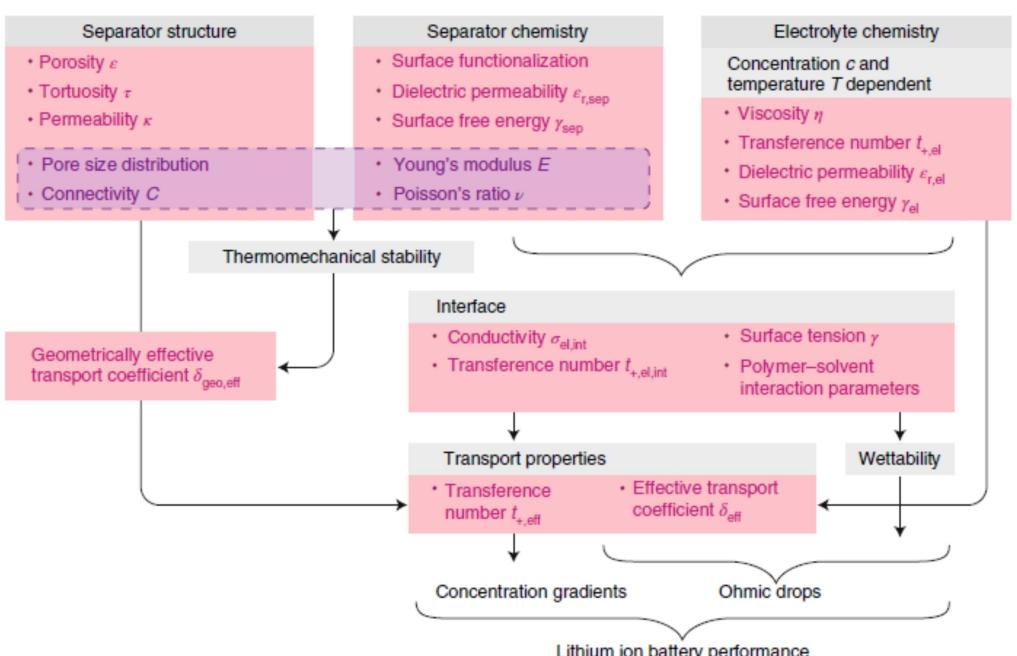


Figure 32. Impact of the separator and electrolyte properties on the overall LIB performance. Reproduced from Ref. [104] with permission. Copyright (2018) Springer Nature.

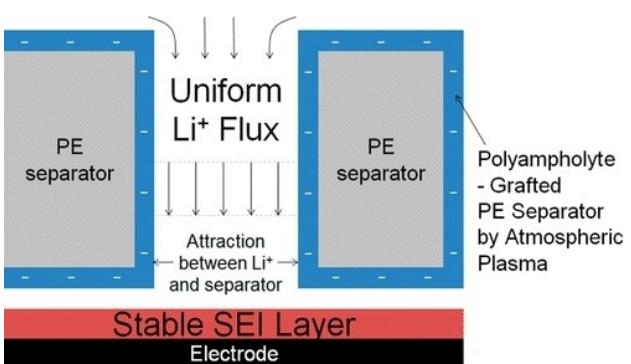


Figure 33. Graphical representation of polyampholyte-grafted PE separator in an LIB configuration. Reproduced from Ref. [107] with permission. Copyright (2016) American Chemical Society.

trivalent ions, preferably Al³⁺ to form lithium aluminum titanium phosphate (LATP). It has been shown that it is possible to enhance the conductivity of pure phase LTP by using spark plasma sintering (SPS). Compared to conventional sintering, the conductivity of pure LTP can be improved by about two orders of magnitude by applying spark plasma sintering due to the higher densification possible (81% of theoretical density compared to 53% by conventional sintering).^[96] Similar improvements by the densification and nanosizing facilitated by the SPS technique have been reported for a wide array of ceramic electrolyte families such as perovskites, garnets, NASICON and others are elaborated in the reviews by Kali et al. and Zhu et al.^[95,97]

Recently, Westover et al. have demonstrated the plasma synthesis of nanocrystalline $\text{Li}_{3.5}\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4$ and amorphous

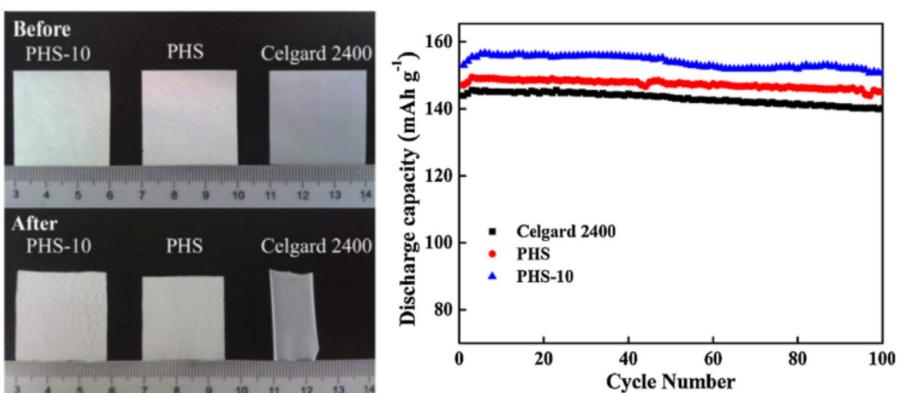


Figure 34. Thermal shrinkage of plasma-treated and commercial separators (Left) and the corresponding cycle performance in LFP/Li cells at 0.2 C. Reproduced from Ref. [108] with permission. Copyright (2015) Elsevier.

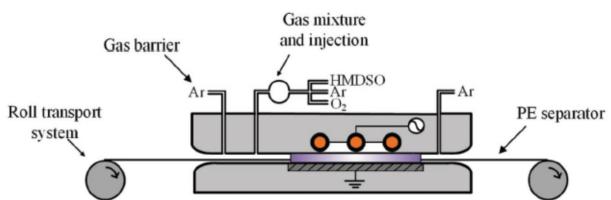


Figure 35. Schematic of the roll-to-roll plasma coating system. Reproduced from Ref. [110]. Copyright (2018) Wiley-VCH.

$\text{Li}_{2.7}\text{Si}_{0.7}\text{P}_{0.3}\text{O}_{3.17}\text{N}_{0.22}$ nanopowders by injecting the precursors directly into a plasma torch.^[98] The rapid quench reactor enables the condensation of the vapor containing the plasma-treated particles into spherical nanopowders.

Solid polymer electrolytes (SPEs) are considered a strong competitor for ceramic electrolytes, mainly owing to their flexibility and relatively higher ionic conductivity. SPEs are typically prepared by dissolving alkali metal salts in ion-conducting polymer matrices. The most common example is the poly(ethylene oxide)(PEO)-LiX (X = ClO_4^- , PF_6^- , TFSI etc.) system. However, the room temperature ionic conductivity of such systems are lower than that of liquid electrolytes. One way to address this problem is to reduce the electrolyte

resistance by decreasing the thickness of the polymer film. The feasibility of using SPEs for electric vehicles and other ambient temperature applications has been studied since the 1980s.^[99] Back in 1988, Ogumi et al. demonstrated the preparation of ultra-thin SPEs by a plasma polymerization process.^[100] They polymerized octamethylcyclotetrasiloxane (OMCTS) with poly(propylene oxide) (PPO) and LiClO_4 by using RF plasma and studied the electrolyte properties in an all-solid-state battery comprising a TiS_2 thin film cathode and lithium anode. A reasonable rechargeability was observed at an applied current density of $16 \mu\text{A}/\text{cm}^2$. Typical of SPEs, a Vogel-Tamman-Fulcher (VTF) type temperature dependence of ionic conductivity was observed, as the ionic conductivity is a combination of ion hopping and the segmental motion of the polymer chains.

In addition to the deposition of polymerized films on suitable substrates, plasma treatment of polymers could result in several benefits such as removal of organic impurities from the surfaces, etching of the surface to increase the surface roughness and area, crosslinking and grafting of desired functional groups, and so on.^[101] As both the cation and the anion are mobile in a typical polymer-lithium salt system, it is desirable to confine the mobility of the bulky anion so that only the Li^+ ions are mobile. The transference number of the

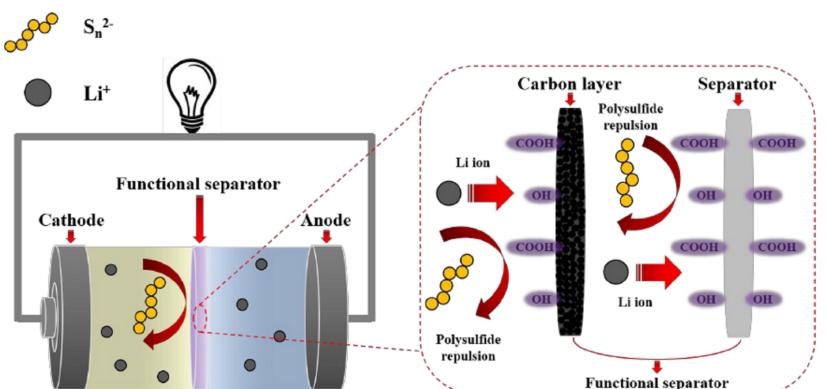


Figure 36. Schematic of a Li–S cell employing a carbon-coated separator modified by a plasma. Reproduced from Ref. [116] with permission. Copyright (2019) The Royal Society of Chemistry.

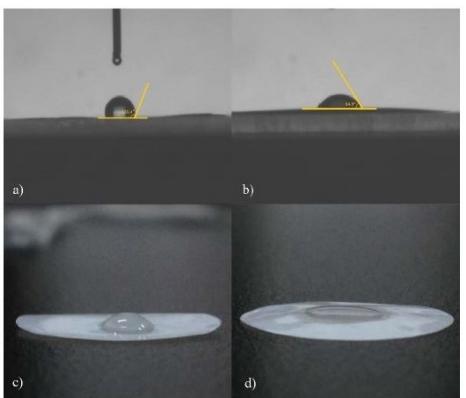


Figure 37. Contact angle measurement of water on a) untreated separator and b) O₂ plasma-treated separator; wetting behavior of electrolyte on c) untreated and d) O₂ plasma-treated separator. Reproduced from Ref. [117] with permission. Copyright (2015) The Royal Society of Chemistry.

Li⁺ ion in this case is closer to unity. To achieve this condition, Kwak et al. used a plasma polymerization method to synthesize an organic-inorganic thin film based on C₂H₄ and Li₃PO₄.^[102] They used RF plasma to polymerize ethylene, simultaneously sputtering the inorganic Li₃PO₄. As a result, the Li⁺ ions are distributed in the polymer backbone as well as the dispersed inorganic phase.

Recently, plasma polymerization has been used to prepare all-solid-state, free-standing polymer electrolytes with ionic liquids as building blocks and ethylene oxide-based surfactants as crosslinking agents by Tran et al.^[103] The electrolytes were prepared by using RF plasma under atmospheric pressure to polymerize a thin ionic liquid film coated on a glass plate. The plasma treatment time was 10 minutes. The ionic conductivity of these polymer electrolytes at room temperature was 2.28 × 10⁻³ S/cm. The authors attribute such high ionic conductivity to the interaction between the ionic liquid and the crosslinking agent facilitated by the plasma polymerization process, which promotes ion diffusion across the electrolyte.

It could be noted that not many such materials deposited or processed by plasma-assisted techniques have been tested in battery configurations. Nevertheless, new reports of using these techniques to deposit materials, especially for all-solid-

state batteries have been emerging in the recent years. This is a positive sign for the future of battery research.

6. Plasma Processes for Separators

Although the separator is not an electrochemically active component, it is still a critical component of a battery as it ensures both the safety of the cell and the efficient ion transport between the electrodes.^[104] Separators will be inseparable from the battery architecture until a complete shift away from liquid electrolytes towards all solid-state batteries – which by even the most optimistic predictions – is many years away.^[105] Ionic conductivity and transference number of ions are two important parameters in the performance of the Li-ion battery. In a typical cell, these parameters do not entirely depend on the properties of the electrolyte but are also influenced by the porosity and surface properties of the separator, as highlighted in Figure 32. It has been shown that the standard separator structure reduces the ionic conductivity of electrolyte in the pore space by about 5–20% of the value of bulk liquid electrolyte.^[106]

Conventional separators are polymeric membranes or non-woven fabrics. Their desirable properties include high wettability, excellent thermal, mechanical and chemical stability, high porosity and electrolyte retention. Polypropylene (PP) and polyethylene oxide (PEO) are the most commonly used polymers for separators. There have been several attempts to improve these separators by plasma-based surface modification. The goal of such treatments is to increase the hydrophilic character of the surface, which results in increased wettability and electrolyte retention. Another strategy to improve separator performance is to use plasma sources to graft specific functional groups to increase the lithium ion mobility. For instance, Han et al. demonstrate a simple method of atmospheric plasma-induced grafting of polyampholyte over a polyethylene membrane (Figure 33).^[107] Besides hydrophilicity, the charges of the grafted polymers also improved the capacity retention and the uniformity of the SEI layer, as observed in the full cell tests.

Composite membranes in which oxides such as SiO₂ were deposited by plasma-assisted methods have also been reported. For instance, plasma treatment of a PP nonwoven fabric

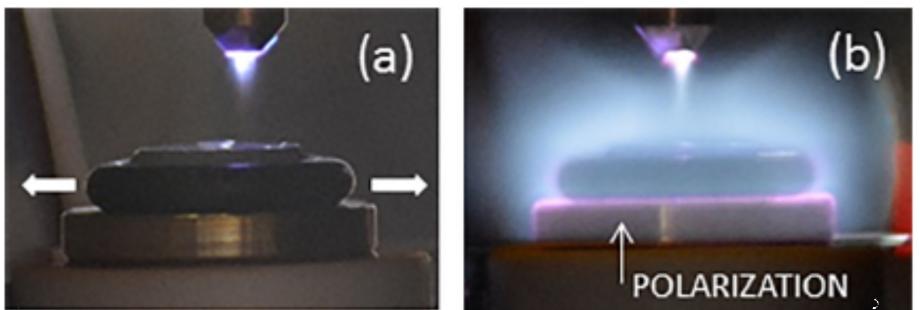


Figure 38. Microtorch reactor in a) scanning mode and b) static mode pulsed discharge. Reproduced from Ref. [120] with the permission. Copyright (2019) AIP Publishing.

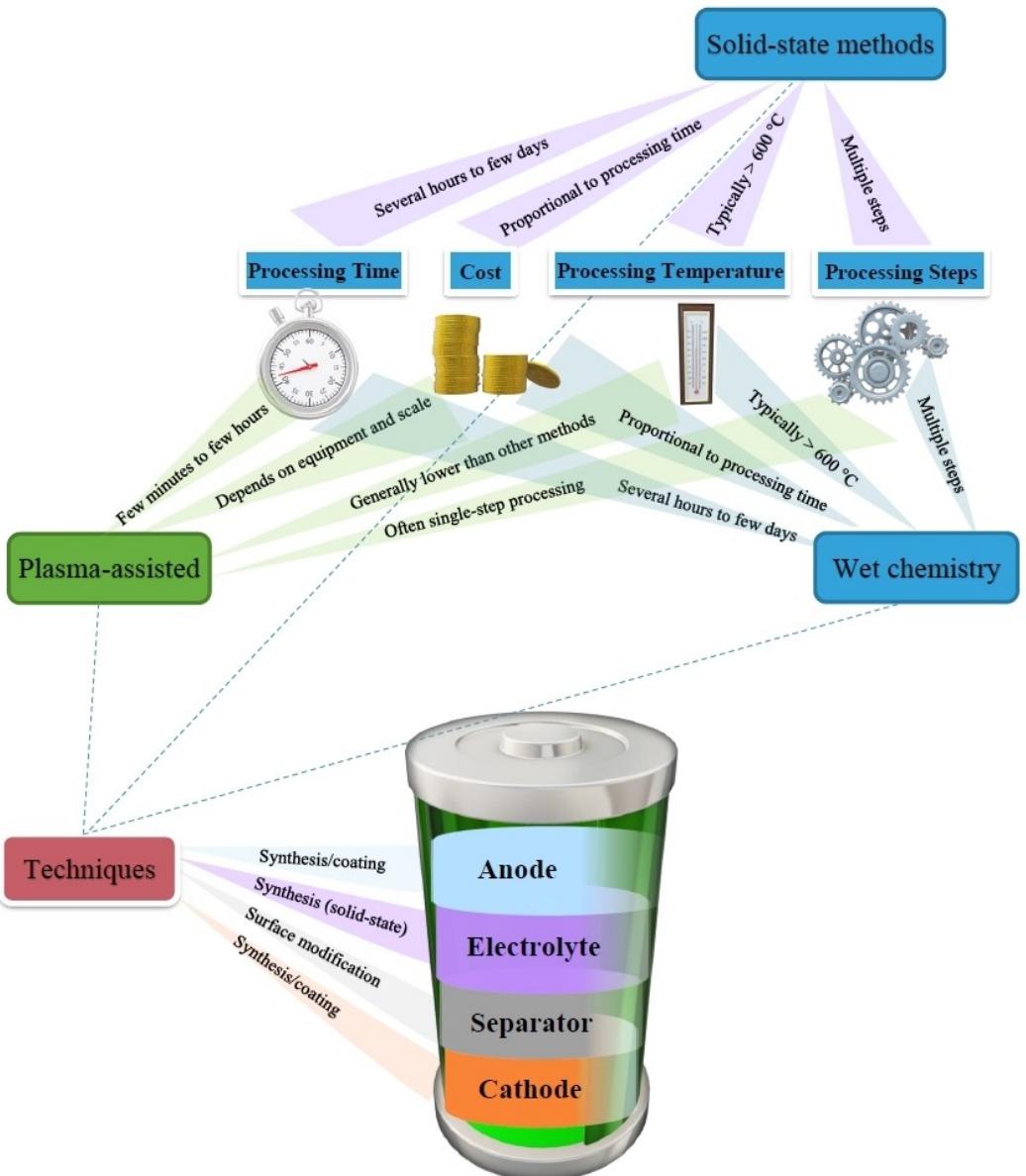


Figure 39. Comparison of plasma-assisted techniques with conventional techniques in the synthesis and modification of battery materials.

coated with a slurry of PVdF, hexafluoropropylene (HFP) and SiO₂ has been shown to improve the mechanical strength and thermal stability, showing only 3% shrinkage at 100°C for 30 minutes, compared to 43% shrinkage in the commercial Celgard 2400 separator under similar conditions, as shown in Figure 34.^[108] When tested in coin cells with LFP cathode, the cells with the plasma-treated separators retained 98% of their initial capacity after 100 cycles, and showed better rate capability compared to the cells with untreated separators.

In a demonstration of the advantages of atmospheric-pressure plasma, Tseng et al. have shown that the hydrophilicity of the separator can be tailored by controlling the plasma power input during the surface activation.^[109] Qin et al. used a reactive atmospheric pressure plasma in a binder-free, roll-to-roll configuration to coat PE separators with a SiO_xC_yH_z

nanostructured film.^[110] The schematic is shown in Figure 35. The electrochemical performance of the cells as a function of plasma treatment of the separator was carried out by testing the separators in LTO/Li half-cells with 1 M LiPF₆ in EC:DEC (50:50 w/w) electrolyte. The coated PE separators were shown to retain significantly higher discharge capacity at C-rates higher than 2 C compared to uncoated separators (for example, 37% capacity retention of coated separator at 10 C rate compared to only 7% capacity retention by the uncoated separator).

As far as surface treatment of polymers is concerned, dielectric barrier discharges (DBDs) are the preferred choice, as they combine the advantages of non-equilibrium plasma while enabling easy operation at atmospheric pressure. Another interesting aspect of DBDs is their scalability from small

laboratory reactors to large industrial installations.^[111,112] Jeon et al. have demonstrated the advantage of a pre-treatment in atmospheric plasma to modify the hydrophobic surface of commercial PE separators to hydrophilic type. The pre-treatment of a water-based, ceramic (Al_2O_3)-coated separator resulted in improved rate capability and cycle life compared to the cells with unmodified separators.^[113] The plasma-treated separators maintained 94.7% of the initial discharge capacity up to the 1000th cycle at 0.5 C rate, whereas the capacity of cells with the bare PE separators significantly faded after only 300 cycles. Suzhen et al. have made a comparative study of surface modification of polypropylene membranes by remote and direct argon plasma.^[114] They grafted acrylic acid monomer onto the surface of the PP membrane and compared the hydrophilicity and graft yield of the plasma-treated membranes. Their results suggest that the remote plasma treatment leads to a membrane surface with the least damage and more permanent hydrophilicity than the direct plasma treatment.

Laurita et al. have reported a ten-fold increase in the electrolyte uptake in their atmospheric plasma-treated poly(vinylidene fluoride) (PVdF)-based electrospun separators compared to the uptake of commercial separators. They attribute this improvement to the increase in the viscosity of the plasma-treated PVdF solution and the crosslinking of the chains to obtain defect-free nanofibers.^[115]

In the case of Li–S batteries, one of the core areas of research is to mitigate the so-called ‘shuttling effect’ by which the highly soluble polysulfides (Li_2S_x ; $x=4\text{--}8$) migrate from the cathode through the porous polymeric separator to the anode.^[53] This shuttling of the polysulfides results in the loss of active material as well as the degradation of the lithium metal anode. Eventually, the Coulombic efficiency of the battery is significantly lowered on successive charge-discharge cycles. In this context, modification of the separator surface with specific functional groups is considered an effective method to overcome the shuttling effect.

Ahn et al. applied a low-pressure RF plasma to carbon-coat the cathode side of a polyethylene separator used in Li–S batteries by using different plasma gases (CO_2 , N_2 , and O_2) and treatment time (Figure 36) and found the CO_2 plasma to be the most effective in improving the electrochemical properties of the separator. They report that the polysulfide permeation rate through the CO_2 -plasma-modified functional separator is reduced by about 70 times. When the modified separator was used in a Li–S battery, an initial capacity of 1204 mAh g^{-1} was obtained, of which 802 mAh g^{-1} was retained after 100 cycles at 0.2 C rate, an enhancement by 57% and 61%, respectively, compared to the capacity of the cell using a pristine separator.^[116]

Wang et al. have applied oxygen plasma to crosslink electronegative functional groups such as -COOH and -OH on commercial polypropylene separator.^[117] They observed an improved wettability (Figure 37) and reduced electronic conductivity of the separator after surface modification. The shuttling effect of the polysulfides was limited by their electrostatic repulsion of the oxygenic functional groups introduced

onto the surface of the separator, resulting in enhanced cycling stability.

Huang et al. reported similar results in the case of Li-ion batteries. They used cyclonic atmospheric-pressure plasma to modify the separator surface with higher concentrations of oxygen functional groups.^[118] Yin et al. have reported the modification of a commercial PP membrane with acrylic acid (AA) monomer by using atmospheric pressure glow discharge plasma jet.^[119] The resultant PAA-coated separators, with polar groups grafted on their surface, showed a three-fold increase in the electrolyte uptake.

Rogez et al. have reported an enhanced wettability of commercial poly(ethylene) separator after cold micro-plasma treatments at low-pressure conditions with liquid and gas ammonia precursors.^[120] The plasma kinetics involve the interaction of the OH radicals with the ammonia groups to form amine groups according to the reaction [Eq. (1)]



Scanning as well as static mode of plasma treatment were explored, and the scanning mode with liquid precursor (Figure 38) yielded the best results. The plasma-treated separators were tested in lithium half-cells with LTO anodes and LiPF_6 in EC:DMC (50:50 in volume) as the electrolyte and showed a capacity retention three times higher (113 mAh g^{-1}) than that of the cells with untreated separators (38 mAh g^{-1}) after 100 cycles at 2 C rate. In this study, the authors highlight the important role of water to form hydroxyl radicals during the reaction of the polymer surface with the ammonia precursors in order to improve the effectiveness of the plasma treatment.

Pan et al. applied a paper-making process to directly laminate each side of a plasma-treated PE separator with a thin, flexible and hydrophilic cellulose nanofiber layer.^[121] The mesoporous cellulose nanofiber layer was observed to stabilize the Li metal anode by generating a uniform Li^+ flux toward the electrode through its homogenous nanochannels. The tri-layer separator retained its mechanical dimensions at 200 °C even as the internal PE layer is melted – and blocks the ion transport through the separator – thereby facilitating an effective thermal shutdown function.

7. Gaps in Available Research

The examples presented in this review show the versatility of plasma technologies in the synthesis and modification of battery components. They also demonstrate the fact that the choice of the most appropriate type of plasma is not always straightforward.

Most of the studies reported are at the level of ‘proof-of-concept’. There have been fascinating reports on the synthesis, coating and surface treatment of several battery materials by using plasma technology. Perhaps the next step should be to focus more on the electrochemical characterization. For instance, studies such as electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) should be emphasized

to evaluate the various components of the internal cell resistance and the reversibility of the redox processes, respectively. The charge/discharge cycling profiles must stand the test of time, quite literally, as only long-term capacity trends over hundreds of cycles and high C-rates would be meaningful in an “apples-to-apples” comparison with the battery materials synthesized by conventional methods. Based on this foundation, the technology readiness level (TRL) of plasma-based processes for battery materials needs to be further increased by doing more R&D. Currently, almost all the electrochemical performance of the plasma-synthesized/modifed materials have been evaluated in coin cell configuration. More data is required at pouch cell level and higher levels. However, it has to be acknowledged that a large number of variables are involved in arriving at figures of merit in both the fields. In the case of battery performance, these variables include electrode active material loading, coating and drying conditions, electrolyte formulation, binder material, electrode porosity and tap density, charging/discharging rates etc. In the case of plasma technologies, the type of plasma (thermal or non-thermal, low-pressure or atmospheric pressure), reactor geometry, production or deposition rate, scalability etc. are some of the critical variables. The accumulation of all these variables make it practically difficult to arrive at standard figures of merit.

Considering these factors, it is obvious that producing a substitute (or improved) material is more efficient than changing the whole assembly line. At industrial level, electrode synthesis/modification processes that are not compatible with roll-to-roll manufacturing might find it difficult to make it to the assembly lines.

A large number of the plasma-based processes for battery materials are in their early stages. Therefore, further optimizations are required to obtain the best results from plasma technologies. Figure 39 illustrates the comparison of plasma-assisted techniques with other methods in terms of processing time, temperature, cost, and number of processing steps. A generalized evaluation of the different techniques based on these parameters is not practically possible. This is because the same technique which could be used to efficiently and economically synthesize or process one material might be inefficient and expensive for another material. The quality of the product and the efficiency of the process when using the different techniques vary for different materials and purposes. It is with this in mind that we have highlighted the typical range for each parameter when using different techniques, as reported in literature, to provide an unbiased overview. For instance, the processing time with plasma-assisted techniques could be relatively shorter and often involve a single-step process as in the case of direct deposition of the electrode material, whereas conventional methods require several hours or more for the processing and involve multiple steps.

Similarly, while atmospheric plasma methods could be relatively economical, low-pressure plasma methods require higher investments and operational cost for the reaction chambers, transfer lines and vacuum pumps. Currently, there is no benchmark for the cost of the materials synthesized by

plasma technology per mAh g^{-1} of the energy produced. This is because most of the research use equipment and expertise developed in-house, making the comparison with other techniques rather difficult. Another aspect of plasma-based techniques is that the scalability varies with the type of plasma technique used, as mentioned in Section 1. As far as the processing temperature is concerned, most of the plasma-assisted methods operate at temperatures well below 500°C , whereas solid-state reaction methods require higher temperature steps with intermediate grinding to achieve similar results. On a similar note, although some wet chemistry methods such as the hydrothermal method enable material synthesis at relatively lower temperatures, they often require multiple steps including filtration, washing, and drying of solvents in addition to a further post-treatment at higher temperature to remove the remnant impurities and to improve the crystallinity of the material. Hence, it is important to use a cautious approach when comparing plasma-based techniques with other techniques.

8. Summary and Outlook

Clearly, plasma-based technologies are increasingly being explored for synthesis and modification of battery components. The actual application of plasma technologies in current battery materials production on industrial scale is still limited. Replacement of conventional processes by plasma-based alternatives in state-of-the-art assembly lines will require further development steps both at conceptual and engineering levels. For the production of next-generation batteries, new enabling technologies need to be developed that contribute to a more sustainable production.

Some key lessons learned from the literature review are:

- Considerable knowledge of the reaction and collision kinetics of carbon and silicon anode materials and some metal oxide cathode materials in plasmas has been gained. This knowledge must be replicated for other materials too, especially for polyanionic materials.
- Driven by the advantages of simpler and solvent-free synthesis possibilities, the choice of appropriate plasma technology depends on several factors such as the scale, selectivity, and the quality required.
- Most importantly, the cost per mAh g^{-1} of the energy produced from materials synthesized or modified by using plasma technology will be the deciding factor to use plasma-based technologies to process battery materials.
- As most non-thermal plasmas involve vacuum conditions and consequently higher operating cost and other complications, atmospheric pressure plasmas might be more practical to enter the assembly lines.
- Another area where plasma processing can be quickly adapted is the surface modification of separators by using non-thermal plasmas. Electrolyte retention, wettability and selectivity of the separator are of primary concern, especially in Li–S batteries to achieve maximum cycling performance.

Although the scientific literature occasionally reports superior performance in lab conditions, the practical translation of these results to commercialization requires a rendezvous of academic and industrial metrics. Thus, it remains to be seen how plasma technologies will enter the battery assembly lines as it depends on emerging processes and innovations. To sum up, the ideal way forward would be to integrate the most promising concepts and processes within battery assembly lines as and when it is more profitable and efficient than conventional methods. This can be made possible by identifying areas along the process chain of battery manufacturing where plasma-based technologies can add value in terms of performance, sustainability, scalability or cost-effectiveness. Such an approach of 'giving it a plasma touch' can contribute to an increased efficiency of the battery manufacturing sector.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: lithium metal battery · lithium passivation · plasma · plasma technology

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