1. Introduction

Energy storage is ever more important with the universal recognition of environmental issues. There are major concerns with regard to the present fossil fuel-based energy economy, which leads to depletion of nonrenewable energy sources and presumably dramatic climate changes associated with high CO₂ emission. Therefore, the use clean and renewable energy is advised in order to reduce greenhouse-gas emissions. Solar and wind energy technologies are promising and fairly mature. However, the intermittence of these resources limits their application, which also highly depends on high-efficiency energy-storage systems. Among the various types of available energy-storage modes, i.e., mechanical, electrical, chemical, and electrochemical modes, electrochemical energy storage based on batteries and supercapacitors is highly promising to effectively harvest these intermittent energy sources.[1–3]

In principle, electrochemical-energy-storage systems are divided into two types: high-energy and high-power systems. Batteries show a high energy, but their power density is relatively low. Therefore they usually suffer from a drastic capacity drop during fast charge and discharge. On the contrary, supercapacitors exhibit high power capability, and they can realize fast charge–discharge processes. However, the stored energy of a supercapacitor per unit mass is rather poor. In addition, combining the advantages of both batteries and supercapacitors is highly promising to effectively harvest these intermittent energy sources.[4]

Rechargeable lithium-ion batteries are one of the great successes of modern electrochemical-energy-storage devices, and they are widely used in cell phones, laptops, digital cameras, tablets, etc., owing to their high energy density (>180 Wh kg⁻¹, about 2–3 times the energy per unit weight and volume compared with other conventional rechargeable batteries).[5] Although lithium-ion batteries are also promising candidates for electric vehicles (EVs) and hybrid electric vehicles (HEVs) as the state-of-the-art technology, e.g., the lithium-ion battery in the Tesla, tremendous research efforts have been devoted to new energy-storage systems to overcome the shortcomings of the energy density of lithium-ion batteries for application in...
mobile transport. Lithium–sulfur (Li–S) batteries and lithium–air (Li–O₂) batteries represent next-generation energy-storage systems with high energy density. Lithium–sulfur batteries can offer a high theoretical energy density of 2500 Wh kg⁻¹ or 2800 Wh L⁻¹, and the abundance of sulfur in the earth crust also makes lithium–sulfur batteries a low-cost system. On the other hand, Li–O₂ batteries provide the highest theoretical energy densities (3500 Wh kg⁻¹) for all known battery systems, which is approaching the energy level of gasoline. In addition, oxygen is an environmentally friendly, no-cost, and unlimited source, which makes this system more attractive. Although lithium-based batteries have pronounced advantages due to economic and availability issues, sodium-ion batteries are realistic promising alternatives and draw current worldwide interest. Besides the various types of batteries, if we pursue a high power function, supercapacitors are a very suitable choice. Various energy-storage systems are available; however, no matter whether batteries or supercapacitors, the electrochemical performance is mainly determined by the electrodes.

There are, in principle, four storage modes for the battery electrodes: 1) Single-phase storage: In this mode, the storage is based on dissolution, and the phase stays constant. A pertinent example is lithium storage in LiCoO₂ and TiS₂. 2) Two-phase storage: In this case, the storage accompanies phase transformation, e.g., the LiFePO₄/FePO₄ system. 3) Conversion-reaction storage: This mode accompanies phase changes as well; however, it will lead to phase decomposition, which is actually multiphase storage. 4) Interface storage: Lithium can be stored at the interface or higher dimensional defects. No matter the kind of storage mode, the transport properties, such as electronic conductivity, ionic conductivity, and diffusion coefficient, are key parameters for high-performance battery electrodes. In the literature, it is clear that the diffusion coefficients of the most electrodes are fairly low, although the reliable data on the transport properties are rather scarce. As a result, it is significant to overcome the ion- and electronic-transport limitations by the following approaches: 1) Doping the electrodes: Doping the target material by foreign atoms can change the concentrations of electronic and ionic charge carriers, and hence leads to an increase in the electronic or ionic conductivity. Establishing defect models, i.e., concentration of defects in dependence of control parameters such as temperature, partial pressure, doping concentration, etc., is very helpful for achieving rational control of charge carriers. 2) Surface coating: Coating the electrode surface by electronically conducting materials, such as carbonaceous materials (amorphous carbon, carbon nanotubes (CNTs), graphene), metals or metal oxides (Ag, RuO₂), or conducting polymers. This method is highly effective for improving the electronic conductivity of the electrodes. 3) Size-reduction: According to the formula \( \tau = L^2/2D \) (where \( \tau \) is the diffusion time, \( L \) is the diffusion length, and \( D \) is the diffusion coefficient), due to the quadratic dependence of \( \tau \) on \( L \), reducing \( L \) can significantly shorten the diffusion time. 4) Morphology control: The transport properties and diffusion behaviors for each electrode materials are different. To design specific architectures for relevant electrode materials according to their transport properties is a highly effective approach.
According to the charge-storage modes, supercapacitors can be divided into two types. The first group is electrochemical double-layer capacitors (EDLCs), which adsorb/desorb ions from the electrolyte on the surface of the electrode during the charge/discharge process. Various types of carbon materials, such as activated carbon, carbon nanotubes, graphene, carbide-derived carbons, etc., are widely used as electrode materials for EDLCs. The key point for these carbonaceous materials is the porous structure with very high surface area. The second type of supercapacitors, known as pseudocapacitors (PCs), is based on the reversible Faradic redox reactions occurring on the surface or subsurface of electrodes. Metal oxides such as RuO$_2$, MnO$_2$, VO$_2$, etc., and conducting polymers, e.g., PPy and PANI, are representative pseudocapacitive materials. Since charges store in the first few nanometers from the surface, decreasing the particle size and increasing the surface area are effective methods to improve the performance.

Based on the discussions above, it is clear that nanostructured electrode materials with rationally designed architectures are significant in improving the electrochemical performance of both various types of batteries and supercapacitors. Nanostructures with different dimensionalities (nanodots, nanofibers, and nanosheets) are helpful for different situations. We have summarized the criteria for designing electrodes depending on transport and dimensional parameters. Such a strategy is to implement two different length scales over which ions and electrons must diffuse within the storage phase to reach the ionic (electrolyte) and electronic current collector phases. The optimal values of these two “wiring lengths” depend on the ionic and electronic conductivities of the storage material. As far as nanostructure realization, there are a wide variety of physical and chemical synthetic methods to fabricate nanostructured electrode materials for batteries and supercapacitors with designed architectures in the literature. Among these methods, the electrostatic spray deposition (ESD) technique is a simple but versatile approach to construct numerous electrode materials with various morphologies, e.g., dense, granular, 3D porous, sponge-like, interpenetrating 3D tricontinuous, and is attracting more and more attention in application toward electrochemical-energy-storage systems.

Here, first of all, we will give a comprehensive introduction to ESD, including setup and basic principles, various prepared materials, controllable prepared morphologies, advantages, new trends, and application potentials of ESD for energy storage. Afterward, we will focus on electrode materials applied in various energy-storage systems, i.e., Li-ion batteries, Na-ion batteries, supercapacitors, Li–S batteries, and Li–O$_2$ batteries, designed by the ESD technique. We will consider the unique structures generated by ESD and discuss how the specific morphologies improve the electrochemical performance for different types of electrode materials.

### 2. The Electrostatic Spray Deposition Technique

Since the invention of the ESD technique, which was first developed by Schoonman and co-workers at Delft University of Technology, this approach has found a great number of applications for various energy-storage devices (Li-ion batteries, Na-ion batteries, supercapacitors, Li–S batteries, and Li–O$_2$ batteries), with different typical structures and morphologies, such as particles, dense and porous thin film, as shown in Figure 1.

![Figure 1. Various electrochemical-energy-storage devices with typical structures and morphologies prepared by the electrostatic spray deposition (ESD) technique.](image-url)

Figure 1 also exhibits the experimental set-up of ESD. In principle, a typical setup includes three parts: 1) a metal nozzle, which is connected with a syringe and provides the precursor solution; 2) a substrate, whose temperature can be controlled by a thermocouple; and 3) a high-DC voltage supply. Briefly, in the ESD process, owing to the high DC electric field between the nozzle and substrate, the precursor solution is atomized into an aerosol. Afterward, the charged aerosol (composed of charged droplets) is attracted and deposited on the substrate. The solvent is evaporated and the relevant chemical reactions occur due to the controlled high temperature. Finally, thin-film materials with various characteristic morphologies are obtained. In addition, a particle suspension of the material can also be deposited onto a substrate to form a solid layer, besides forming a thin film from the precursor solution.

In a typical ESD process, there are several either sequential or simultaneous physical and chemical process involved, including mainly five steps: 1) spray formation, 2) droplet transport, evaporation, and disruption, 3) droplet preferential landing, 4) droplet spreading and penetration, and 5) decomposition, reaction, and surface diffusion. Each step is described below separately: 1) Spray formation: Due to the high voltage applied between the metal nozzle and the substrate, when the applied voltage is higher than a certain threshold, the precursor solution is drawn into a cone. The characteristic shape of the cone is often called the “Taylor cone.” If the voltage is high enough, the electrostatic force overcomes the surface tension...
of the precursor liquid, and a microjet will be extracted from the Taylor cone. This microjet elongates to a fine filament and disperses into small aerosol droplets.[41] Such a Taylor-cone-jet mode[42] is the most used, due to its capability to stably generate monodisperse particles. However, depending on the form of the meniscus, there are also several other modes in terms of the motion pattern of the jet, the way the jet disintegrates into droplets. For the cone-jet mode, the size of the droplets is usually determined by the following equation:[41]

\[ d = \alpha \frac{Q^2 \varepsilon_0 \rho^2}{\sigma^2 \gamma'} \]  

(1)

where \( d \) is the droplet diameter, \( \alpha \) is a constant determined by the permittivity of the liquid, \( Q \) is the liquid volume flow rate, \( \varepsilon_0 \) is the permittivity of the free space, \( \rho \) is the mass density of the liquid, \( \sigma \) is the liquid conductivity, and \( \gamma \) is the surface tension of the liquid. The exponents \( a, b, c, d \), and \( e \) in Equation (1) are constants, which vary slightly according to different authors.[41]

A conclusion can be drawn that three main factors determine the droplet size, i.e., the electric-field strength, the liquid flow rate, and the properties of fluid (including viscosity, surface tension, conductivity, and relative permittivity). The droplet or spray formed by the ESD technique is generally smaller than other atomization methods, and it will not aggregate due to its unipolar charged property, leading to a much narrower size distribution. To achieve atomization by ESD, the precursor solution need to be electrically conductive, and a high DC voltage in the range of 2–15 kV is usually applied. 2) Droplet transport, evaporation, disruption. The charged droplets are attracted to the ground substrate by a Coulombic force due to the electric field. Solvent evaporation during flight will occur, especially under heating. When the droplets move to the heated substrate, a temperature gradient is built between the metal nozzle and the substrate. The evaporation of solvent leads to the size reduction of each droplet with unchanged charges; therefore, the surface charge density of the droplet increases. The point when the Coulombic repulsion of the surface charge is equal to the surface tension of the droplet is the so-called Rayleigh limit, which can be expressed as Equation (2).

\[ Q_{m} = 6 \left[ \frac{\gamma s}{\rho} \right]^{\frac{1}{3}} \]  

(2)

where \( Q_m \) is the maximum attainable charge density, \( m \) is the mass of the droplet, \( \rho \) is the true density of the droplet, \( r \) is the radius of a liquid droplet, and \( \gamma \) is the surface tension of the liquid with respect to the surrounding gas. A charged droplet maybe disrupted into several smaller droplets after reaching the Rayleigh limit. Note that the Coulombic repulsion among smaller droplets will prevent smaller droplets aggregating into big droplets, resulting in a uniform morphology. 3) Droplet preferential landing. The charge distribution is generally not uniform. The position relative to the nozzle, and especially the local curvature of the substrate surface will influence such a charge distribution. In general, the place with the greater curvature has more charge concentration, leading to a stronger electric field than other places. When a charged droplet moves to the substrate surface, it will be attracted more to the place the greater curvature (so-called preferential landing). This indicates that the morphology will be influenced by the surface condition of the substrate. 4) Droplet spreading and penetration. The type and dynamics of spreading depend strongly upon the spreading coefficients:[39]

\[ S = \gamma_{sg} - \gamma_{al} - \gamma_{lg} \]  

(3)

where \( \gamma_{sg} \), \( \gamma_{al} \), and \( \gamma_{lg} \) represent the interfacial tensions between the substrate and the ambient gas, between the substrate and the liquid drop, and between the liquid drop and the ambient gas, respectively. If \( S < 0 \), only partial wetting occurs, with equilibrium being reached at a finite contact area. If \( S \geq 0 \), the drop spreads until it totally covers the surface. The value of \( S \) is related to the spreading rate. In principle, the substrate properties and the viscosity of the liquid are the main factors that affect the spreading rate. In general, the higher the viscosity, the lower the spreading rate. In addition, when defects (i.e., cracks or pinholes) are formed in the earlier deposited layer, the subsequent droplets may penetrate into them through capillary action. By this repair effect, a defect-free layer can be obtained by the ESD process. 5) Decomposition, reaction, and surface diffusion. Decomposition and reaction can occur before or after the droplets arrive at the substrate. If the temperature is relatively low, the solution droplets will reach the substrate, and the wet-chemistry process of a solvent and metal salt precursor will determine the morphology of the layer. Generally speaking, in the ESD process, the final morphology of the thin-film layer depends on the relative rates of the different processes, i.e., spreading, precipitation, decomposition, and reaction.

2.2. Various Materials Prepared by ESD

For a typical ESD process, the precursor solution is prepared by dissolving metal nitrates or acetates in water, ethanol, ethylene glycol, propylene glycol, 1,2-propanediol, butyl carbitol, or their mixtures. During the ESD process, the precursors are easily decomposed and form various metal oxide thin-film layers in an ambient atmosphere. In fact, ESD is a very powerful technique to prepare different oxides. A large number of oxides have been fabricated by such techniques for various functions, e.g., CeO₂,[43] LiCoO₂,[44] LiMn₂O₄,[45] SnO₂,[46] Mn₃O₄,[47] TiO₂,[48] V₂O₅,[49] LiCoO₂·Ni₃O₄,[50] Li₄Ti₅O₁₂,[51] Fe₂O₃,[52] Co₃O₄,[53] Fe₃V₂O₇,[54] etc. However, the other compounds can also be prepared by the ESD technique with some modifications in the precursors. If the metal precursor contains a sulfur source (e.g., (NH₄)₂MoS₄ for preparing MoS₂) or if additional sulfur sources such as (NH₄)₂CS or L-cysteine are added in the precursor solution, various metal sulfides can be obtained as well. The successful examples are CdS,[55] MoS₂,[57] WS₂,[56] ZnS,[57] SnS,[58] etc. Following the same method, selenides such as CdSe have been successfully prepared with an additional precursor (NH₄)₂CSe.[59] By controlling the precursor on purpose with the target elements or units, a great number of compounds, i.e., carbides,[60] metals or alloys,[61] phosphates,[62] titanates,[63] or silicates.[64] can be fabricated by the ESD technique as well.
compounds can be seen in Table 1. In addition, besides the dissolved precursors, suspensions are also suitable to grow thin-film layers by the ESD technique. Hence, some carbonaceous materials, i.e., CNTs or graphene have also been prepared. Moreover, by using a mixture of different types of precursors, a great deal of composite thin films can be fabricated which can be seen in Table 1 as well.

2.3. Various Controllable Morphologies by ESD

The typical morphologies obtained by ESD can be divided into three main categories: granular, dense, and porous. One of the pronounced highlights of the ESD technique is that the morphology is easily controlled by the ESD experimental parameters, such as the voltage, the distance between the metal nozzle and the substrate, the concentration of the precursor solution, the flow rate, the substrate temperature, the boiling point of the solvents and the surface tension and viscosity of the solution.

Understanding the rules as to how experimental parameters influence solution chemistry and how such parameters affect the final morphology and structure during ESD are very important to achieve rational morphology design by ESD.

(i) The Effect of Solvent: By using different solvents during ESD, various morphologies of LiMn$_2$O$_4$ have been obtained. For example, a low-boiling-point solvent such as pure ethanol leads to a dense LiMn$_2$O$_4$ sample; while a high-boiling-point solvent results in porous LiMn$_2$O$_4$, i.e., sponge-like porous or fractal-like porous. This can be attributed to the different evaporation rates of the solvents during the droplets travelling in air, according to Equation (1), and different spreading dynamics on the substrate according to Equation (3).

(ii) The Effect of Precursor Salts: Different precursor sources will also have different influences on the final morphology. Koike et al. investigated the various morphologies of the LiMn$_2$O$_4$ cathode by using different lithium sources in the precursor solution, e.g., Li$_2$CO$_3$, LiOAc, and LiOH. The reticular morphology obtained using LiNO$_3$ leads to a smaller pore diameter and thinner pore walls, which is different from LiOH and LiOAc sources. Li$_2$CO$_3$ is the only lithium source of the four that does not give rise to a reticular structure.

(iii) The Effect of Flow Rate: Chen et al. used ESD to prepare porous LiCoO$_2$ thin films and investigated the effect of flow rate on the final morphology. They found that at small flow rates, the average pore size was approximately proportional to the flow rate.
(iv) The Effect of Substrate Temperature: Shui et al. used a mixed alcohol solvent (15% ethanol + 85% butyl carbitol) to prepare reticular LiMn$_2$O$_4$ and investigated the effects of the substrate temperature on the morphology. The morphologies are reticular structure with thick pore walls (220 °C), reticular structure with thin pore walls (235 °C), bimodal porous reticular structure (250 °C), and dense particulate structure (270 °C).[46] A similar trend of the morphology evolution on substrate temperatures is also found for a MnO$_2$ thin film prepared using a single alcohol solvent by ESD.[46]

(v) The Effect of Deposition Time: Reticular MnO$_2$ films deposited for different times from 10 to 90 min have been studied. A reticular film by ESD needs a certain deposition time to form a relatively uniform pore size distribution.[46] Wang et al. investigated V$_2$O$_5$ film deposition times from 2 to 4 h by ESD. Layers of 2D reticular structure transformed to a 3D porous multideck-cage structure with increasing deposition time.[49]

(vi) The Effect of Electric-Field Strength: In order to work with a stable spray during ESD, the high DC voltage can be varied in a limited range. Different voltages (7.5, 8, and 9.5 kV) to prepare LiMn$_2$O$_4$ films by ESD have been investigated. A higher DC voltage leads to an increase in the shape regularity of the pores as well as porosity of the film.[46]

Table 2 summarizes several typical morphologies obtained by the ESD technique, such as dense,[70] nanoparticle,[71] nanosponge,[72] 3D porous,[66] interpenetrating porous 3D tricontinuous,[62] etc. The typical representative materials, together with the experimental parameters, such as relevant precursors, solvents, temperatures and substrates, are listed in Table 2 as well.

2.4. Advantages of ESD

There are several advantages of the ESD technique. First of all, ESD is a simple, cheap, and flexible method, by which morphology can be easily controlled at the nanoscale. Second, using this method, highly pure materials can be prepared. Third, ESD can produce extremely thin layers, and the quality of such thin films is high, which can be defect-free and more homogeneous compared to other approaches. Fourthly, the growth rate of the thin film by the ESD technique is relatively high compared to other thin-film techniques such as chemical vapor deposition (CVD) or physical vapor deposition (PVD).[40] For instance, the deposition rate of a 1 μm thin-film layer is 0.1, 0.006–0.06, 0.02–0.05 μm min$^{-1}$ by ESD, PVD, and CVD techniques, respectively.[40,73] Fifth, ESD can be carried out in an ambient atmosphere and at low temperature; especially, complex reactors and high-vacuum systems are unnecessary. In addition, the efficiency of the ESD process is very high, and almost 80–90% of base materials can be deposited onto the substrate.[40] Finally, if the ESD technique is applied to prepare electrodes for energy storage, one of the pronounced advantages is that the electroactive materials can be directly deposited on the various current collectors (also acting as a substrate) without any additional conductive additives and binders, which greatly simplifies the battery assembly process. Moreover, it can further increase the rate capability of electrodes (binders are usually nonconductive polymers) and improve the energy density of the electrode (without nonelectroactive parts).

2.5. New Trends of ESD

There are some new advances for the ESD technique. 1) Preparation of new compounds by ESD: As we discussed before, since ESD normally is carried out in an ambient atmosphere, it is a widely used method to fabricate various metal oxides. By carefully choosing appropriate precursors, new compounds, such as sulfides, have been prepared recently.[58] 2) Finding new applications: Since new compounds have been successfully prepared, the materials obtained by ESD have more and more applications. In terms of energy storage, previously, the materials prepared by ESD were mainly applied in Li-ion batteries and supercapacitors, while, lately they are also able to be applied in Na-ion batteries, Li–S batteries, and Li–O$_2$ batteries. 3) Combining ESD with other synthesis methods: The

| Morphology | Example material | Precursor | Solvent | T (°C) | Substrate | Refs. |
|------------|------------------|-----------|---------|--------|-----------|-------|
| Dense      | LiMn$_2$O$_4$    | CH$_3$COOLi, Mn(NO$_3$)$_2$ | Ethanol | 400 | Pt–Si | [70] |
| Nanoparticle | Sn–Co | SnCl$_2$, CoCl$_2$, NaBH$_4$ | Dimethyl sulfoxide | None | None | [192] |
| Nanosponge | VO$_2$–TiO$_2$ | NH$_4$VO$_3$, titanium (IV) isopropoxide | Oxalic acid, ethanol, acetic acid | 260 | Nickel foam | [72] |
| Nanotree   | Li$_4$Ti$_5$O$_{12}$ | CH$_3$COOLi, Ti(OC$_4$H$_9$)$_4$ | Ethanol, butyl carbitol | 300 | Platinum disks | [51] |
| 3D porous  | V$_2$O$_5$ | NH$_4$VO$_3$ | C$_2$H$_5$OH, water, ethanol | 230–275 | Stainless steel | [49] |
| 0D=3D porous | Sn | SnCl$_2$, l-cysteine | 1.2-propanediol | 238 | Ti foil | [58] |
| Porous spherical multideck-cage morphology | Li$_2$O–CuO–SnO$_2$ | Sn(NO$_3$)$_2$, Cu(NO$_3$)$_2$, LiNO$_3$ | Glycol, 1,2-propanediol | 300 | Cu foil, stainless steel | [66] |
| Porous 0D–1D–2D integration | MoS$_2$–CNT–rGO | (NH$_4$)$_2$Mo$_3$S$_2$O$_8$, GO, CNT | 1,2-propanediol | 238 | Nickel foam, stainless steel | [37] |
| Interpenetrating porous 3D tricontinuous | Na$_x$V$_2$(PO$_4$)$_3$–rGO–CNT | NaH$_2$PO$_4$, NH$_4$VO$_3$, GO, CNT | 1,2-propanediol, water | 190 | Stainless steel | [62] |
ESD technique can be applied together with other synthesis methods, e.g., the templating method,[74] the sol–gel method,[48] the solvothermal method,[75] the electrospinning method,[76] etc., to fabricate new and more complex morphologies. For example, when ESD is applied together with the soft-chemistry method such as the sol–gel and solvothermal methods, the building units of the final materials can be modified. When ESD is combined with the template method, the porosity can be carefully controlled. When ESD is applied together with the electrospinning method, unique 1D–3D composites can be prepared. Detailed information on such combined techniques will be discussed for the specific materials in the following text. 4) Combination of ESD with other characterization methods: The ESD technique can be combined with other advanced characterization approaches to realize in-depth characterization. For instance, change of mass of LiMn$_2$O$_4$ can be investigated in situ by electrochemical quartz crystal microbalance (EQCM) combined with ESD.[70]

2.6. Application Potential of ESD for Energy Storage

Generally speaking, frequently used approaches (e.g., doping, carbon-coating, size-reduction, and morphology control) that can improve the performance are all compatible with the ESD technique. First of all, rational doping is easily achieved during the ESD process. Second, ESD is an effective carbon-coating technique to coat various carbonaceous materials, such as CNTs, rGO, and amorphous or crystalline carbon. It is also an efficient method to prepare various electrode/carbon composites. Third, according to the principle of ESD, electrodes with nanoscale components are easily obtained. Finally, ESD is a simple and powerful technique that can easily control the morphology. Various morphologies such as dense, porous, and 3D porous tri-continuous composites, etc. obtained by ESD can just meet the different requirements of various energy-storage devices based on different mechanisms. In addition, ESD is a very suitable technique to fabricate self-supported thin-film or 3D electrodes without additional conductive additives and binders.

In terms of the design of nanoarchitectures, if we would like to improve the performance of electrode materials for different energy-storage devices (i.e., batteries and supercapacitors), the first step is to determine what kinds of structures or morphologies are preferred for various application aims. The energy-storage mechanisms of electrodes for batteries and supercapacitors can be generally divided into three types: the intercalation reaction, the alloying and conversion reaction, and the surface/interface reaction. 1) The intercalation reaction includes most cathode and some anode materials for lithium and sodium batteries. The transport properties, such as electronic conductivity, ionic conductivity, and chemical diffusion, are key issues for this type of reaction. The chemical diffusion coefficient is given by:[77]

$$D = \frac{\sigma_{ion} \sigma_{con}}{\sigma} \left( \frac{X_{con}}{X_{ion}} + \frac{X_{ion}}{X_{con}} \right)$$  \hspace{1cm} (4)

where $\sigma_{ion}$, $\sigma_{con}$, and $\sigma$ are the ionic conductivity, electronic conductivity, and total conductivity. $c_{con}$ and $c_{ion}$ are the concentrations of the electronic and ionic carriers. The $\chi$-factors describe the internal trapping reactions (usually crucial at the temperature of operation). For electrodes based on intercalation, pure materials with high crystallinity and an effective mixed conducting network are crucial for improving the performance. 2) The alloying and conversion reaction includes most anodes and some cathodes materials of lithium- and sodium-ion batteries, as well as Li–S and Li–O$_2$ batteries (the reactions from sulfur to Li$_2$S and from O$_2$ to Li$_2$O$_2$ can be considered as conversion reactions). Besides transport properties, how to buffer the huge volume change and prevent pulverization and cracks of the electrodes are highly significant and of wide concern for this type of reaction. As a result, the designed structures or morphologies of electrodes should have the abovementioned multifunctions (facile ion/electron transport, buffering of large volume changes, and preventing pulverization and cracks of the electrodes). 3) The surface/interface reaction relates to supercapacitors and Li–O$_2$ batteries. A high surface area is particularly important for both surface adsorption of supercapacitors and surface catalysis of Li–O$_2$ batteries. Structures that can improve the charge and mass transport and increase surface catalysis reactivity are desired. Table 3 summarizes the energy-storage mechanisms versus various devices, as well as different structure and morphology requirements for various batteries and supercapacitors.

In the following text, by collecting pertinent examples, we will show the great potential of ESD for energy storage. We will summarize the recent progress on electrode materials for Li-ion batteries, Na-ion batteries, supercapacitors, Li–S

Table 3. Summary of the energy-storage mechanisms, systems, and requirements for high-performance electrodes.

| Mechanisms                  | Devices and systems           | Requirements                                         |
|-----------------------------|-------------------------------|------------------------------------------------------|
| Intercalation reaction      | Cathodes and anodes for Li-ion batteries | 1. Pure materials with high crystallinity;             |
|                             | Cathodes and anodes for Na-ion batteries | 2. An effective mixed conducting network.             |
| Alloyning and conversion reaction | Cathodes and anodes for Li-ion batteries | 1. An effective mixed conducting network;             |
|                             | Cathodes and anodes for Na-ion batteries | 2. Buffering of the huge volume changes;              |
|                             | Li–S batteries                | 3. Preventing electrode pulverization and cracks.     |
|                             | Li–O$_2$ batteries            |                                                      |
| Surface/interface reaction  | Supercapacitors               |                                                      |
|                             |                               | 1. High surface area;                                 |
|                             |                               | 2. Facile charge and mass transport;                  |
|                             |                               | 3. Increase of the surface catalysis reactivity.      |
batteries, and Li–O₂ batteries prepared by ESD. The various designed nanostructures fabricated by ESD and the role that the unique advantages and aspects of ESD plays on the electrochemical performance of various specific electrodes will be discussed and emphasized.

3. Cathode Materials for Lithium-Ion Batteries Prepared by ESD

Since the invention of the lithium-ion battery, LiCoO₂ has been the dominant cathode material.⁹⁸ In order to further decrease the high cost and environmentally unfriendly element Co, other layered transition-metal oxides materials with the formula of LiMO₂ (M: Mn, Co, Ni, or a mixture of them) or lithium-rich transition-metal oxides with the formula of xLi₂MnO₃ + (1-x)LiMO₂ have also been investigated. Other developments regarding the cathodes have focused on lithium manganese oxides spinel and lithium transition-metal phosphate, such as LiFePO₄. Because most lithium cathodes are based on the intercalation reaction, pure materials with high crystallinity and sufficient lithium diffusion are the most critical (Table 3). In this direction, ESD can be applied due to its impurity-free synthesis properties and its effective mixed-conducting-network solution.

3.1. Layered (Lithium) Transition-Metal Oxides

3.1.1. Layered Lithium Transition-Metal Oxides

In the past two decades, intense effort has been devoted toward layered LiCoO₂ cathodes and relevant LiCoO₂, LiMnO₂, and LiNiO₂ systems. Replacing Co with relatively cost-effective and abundant Ni or/and Mn is a widely used method to increase the market potential. Research has been focused on increasing the power capability and cycling stability, especially on elevated temperatures or at higher potentials. The solutions include surface coating,⁹⁹ core–shell structures,⁰₀ metal doping,⁰₁ and new electrolytes.⁰₂ ESD uses a precursor solution including Li and Co elements, which can be mixed on the atomic scale, resulting in final products with high purity and designed composition and morphology.

The ESD technique was first developed to prepare 4 V LiCoO₂ cathode materials by Schoonman and co-workers.⁴⁴ The morphology of LiCoO₂ can be easily controlled during the ESD process. LiCoO₂ with morphologies of dense layer, dense layer with incorporated particles, porous top layer with a dense bottom layer, and fractal-like porous layer can be obtained by carefully controlling the experimental parameters, such as the deposition time, deposition temperature, precursor solution concentration, electric-field strength, substrate, and solvent.⁰₃ Especially, by using a solvent mixture of ethanol (15 vol%) and butyl carbitol (85%), LiCoO₂ thin films with a unique 3D crosslinked structure, having a high porosity and a narrow pore size distribution, are obtained.⁰₄

The crystallinity of LiCoO₂ can be controlled during the ESD process by changing the substrate temperature and post-annealing temperature. When the substrate is 280 °C, amorphous LiCoO₂ is formed; while above 340 °C, crystalline hexagonal LiCoO₂ is obtained.⁴⁴ For a Li cathode, a high crystallinity is important, as we discussed before. Yoon et al. found that a LiCoO₂ thin film by ESD, with a stable cycling performance, can be obtained by annealing at temperature as low as 600 °C.⁰₅ ESD can also be applied as a coating technique to increase the performance of LiCoO₂. For example, Yu et al. synthesized nano-SiO₂-modified LiCoO₂ thin films by the ESD technique.⁰₆ The texture of the film is porous, with a LiCoO₂ (shell)/SiO₂ (core) structure. This LiCoO₂–SiO₂ (15%) exhibits the highest discharge capacity of 130 mAh g⁻¹ at the current density of 0.1 mA cm⁻², and the lowest impedance. SiO₂ helps to improve the cycling stability, i.e., the capacity of LiCoO₂–SiO₂ (15%) hardly fades over 60 cycles. In addition, an LiMnO₂-coated LiCoO₂ thin-film electrode has been successfully prepared as well.⁰₇

In terms of electrochemical performance, a highly porous LiCoO₂ thin film without binder and conductive additives prepared by ESD is a good choice.⁰₈ Koike et al. were able to use an aluminum substrate with a low temperature of 650 °C to prepare LiCoO₂ by ESD. Walls a few micrometers thick and ~5 µm holes were observed, as shown in Figure 2a. The capacity of the first cycle is 140 mAh g⁻¹ and the capacity is still 93% of the first cycle after 100 cycles at a 1C rate. The rate performance is good for this film, and the capacity is around 79% and 57% at high rates of 10 C and 20 C, respectively (Figure 2b).

Furthermore, in order to further increase the energy density, besides LiCoO₂, other layered lithium transition-metal oxides, such as LiNiO₂, LiMₓNi₁₋ₓO₂ (M = Co, Al) have also been successfully prepared by ESD.⁰⁰

![Figure 2](image-url)  a) SEM image of a LiCoO₂ thin film prepared by ESD and after heat treatment at 650 °C for 2 h. b) Rate capability of such an HT-LiCoO₂ film. Reproduced with permission.⁰⁸ Copyright 2007, Elsevier.
3.1.2. Layered Transition-Metal Oxides

Among the layered transition metal oxides, great attention has also been paid to V2O5 and other relevant compounds with a layered structure, due to their pronounced advantages, such as abundance, low cost, and ease of fabrication. In terms of the electrochemical performance, they have high energy efficiency and high theoretical capacity (≈294 mAh g−1 corresponding to 2 lithium insertion), which are comparable to other commonly used cathodes, such as LiCoO2.[89,90] The major concerns for these materials are the poor transport properties and the structure stability, which lead to limited rate performance and cycling stability. A great number of nanostructured designs have been devoted to these concerns, i.e., synthesizing nanotubes, nanofibers, nanoparticles, and so on.[91,92]

ESD is a suitable technique to prepare porous V2O5, which greatly increases the transport properties. Kim et al. used the ESD technique to prepare a V2O5 thin-film electrode on a platinum substrate.[93] The porous V2O5 thin film showed a high capacity of 270 and 260 mAh g−1 at current densities of 0.2 C and 1 C, showing no fading after 25 cycles in the voltage range of 2–4 V. Furthermore, a unique 3D porous multideck-cage V2O5 thin film with very high rate capability and cycling stability was achieved by Wang et al. by using the ESD technique.[49] The morphology-formation mechanism was investigated (Figure 3a).

First of all, on a stainless-steel substrate, a 2D reticular layer is formed. As the deposition time increases, such 2D layers will stack together and the thickness will increase. Finally, the new spray droplets prefer to be deposited on some standing-out spots to form spherically shaped structures, leading to 3D multideck-cage microspheres. Such 3D porous structures are very stable, even after annealing in air at 350 °C for 2 h. In the voltage range of 2.5–4.0 V, the ESD V2O5 film will transform to LiV2O5 with a capacity of 142 mAh g−1, which is nearly the theoretical capacity. The rate capability is excellent: the capacities are 120 and 86.7 mAh g−1 with current densities of 8 C and even 56 C, respectively (Figure 3b). The cycling performance is good as well, i.e., it can at least maintain 110 mAh g−1 during 200 cycles (Figure 3c). This demonstrates that the 3D porous structure from ESD is effective to increase the transport of both electrons and ions.

ESD can be applied as a doping method to further increase the performance. Li et al. prepared a Fe0.1V2O5.15 thin film by the ESD technique.[94] They found that Fe3+ can act as a stabilizing agent in the layered V2O5 and delay the ε → δ → γ phase transition at a potential close to 2 V, leading to better reversibility and cycling stability in the voltage range of 2–4 V. Porous Fe/V oxides, including crystalline Fe2V2O13 and amorphous Fe2V2O12.29 thin film, were prepared through ESD by the same group as well.[54] They found that amorphous Fe/V oxide shows better rate capability and cycling performance compared to its crystalline counterpart.

In addition, the ESD technique can be combined with the solvothermal method to further tune the morphology. For example, micrometer-sized agglomerates of primary V2O5 particles have been prepared, for the first time, by an oil-bath method. Afterward, by using ESD and subsequent heat treatment, such particle suspensions are deposited on carbon plate substrates as a thin film comprising interconnecting walnut-like particles.[79]

3.2. Lithium Manganese Oxides Spinels

Lithium manganese oxide spinel (i.e., LiMn2O4) is another attractive alternative to commercialized LiCoO2, due to its advantages such as abundance, low cost, environmental friendliness, high safety, and high power capability. However, the major issue of this material is the severe capacity fading with cycling.[95] The reasons for that are as follows: 1) dissolution of LiMn2O4 into acidic electrolyte, especially at elevated temperatures, according to the disproportion reaction: 2Mn3+ → Mn4+ + Mn2+; 2) in the high-voltage region, transformation of an unstable two-phase structure to a more stable single-phase structure via the loss of MnO;[96] and 3) some electrochemical reactions occurring in the electrolyte at a high voltage. There are some effective approaches that are applied to overcome such issues, for example, doping LiMn2O4 with a lower valence state (such as Li or Al)[97] surface coating,[86] and choosing suitable electrolyte additives.[98] LiNi0.5Mn1.5O4 is another promising spinel with capacity close to the theoretical maximum (148 mAh g−1) and a high voltage of ≈4.8 V, which is very suitable for high-energy applications. How to enhance the compatibility between such a high-voltage cathode and common nonaqueous electrolyte is a significant issue.

ESD is applied to prepare spinel LiMn2O4 cathodes with good crystallinity and controlled nanostructures. For example, LiMn2O4 thin films with various morphologies can be obtained by changing the experimental...
parameters during ESD; namely, sponge-like porous (15% ethanol + 85% butyl carbitol), fractal-like porous (80% ethanol + 20% glycerol), and dense structures (pure ethanol). Among these various morphologies, the sponge-like porous LiMn$_2$O$_4$ cathode has a lower resistance and better rate capability compared to the dense film, which can be attributed to the large active surface area.

ESD offers the possibility of combination with advanced electrochemical techniques to achieve in-depth characterization. For the LiMn$_2$O$_4$ cathode, it is important to investigate the surface films that surround the LiMn$_2$O$_4$ particles in situ. The EQCM is an in situ mass-sensitive detector based on the measurement of resonant-frequency changes induced by mass or viscosity changes of a film attached to a quartz-crystal substrate during electrochemical measurement. This EQCM technique can be applied to investigate the mass change of LiMn$_2$O$_4$ due to the formation of a surface film. The key point of EQCM is the fabrication of LiMn$_2$O$_4$ thin film on the EQCM electrode, which can be effectively achieved by the ESD technique at relatively low temperature without any conductive additives and binders. Shu et al. used EQCM combined with the ESD technique to investigate an electrode with a surface layer around LiMn$_2$O$_4$.[70] They found that the mass of the surface layer around LiMn$_2$O$_4$ was 1.2%.

In order to increase the energy density of LiMn$_2$O$_4$, ESD is also suitable for the preparation of phase-pure and high-voltage LiNi$_{0.5}$Mn$_{1.5}$O$_4$ thin-film electrodes, which deliver a capacity of 135 mAh g$^{-1}$.[100] It can be controllably deposited on various substrates, e.g., flat or 3D-architected substrates, demonstrating the great potential to fabricate 3D all-solid-state batteries by the ESD technique.

### 3.3. Lithium Transition-Metal Phosphates

Lithium transition-metal phosphates such as LiMPO$_4$ (M = Fe, Co, Ni, Mn) and Li$_2$M$_2$(PO$_4$)$_3$ (M = V, Fe) have attracted great attention, owing to their competitive energy density and outstanding thermal stability. LiFePO$_4$ first reported by Goodenough and co-workers,[11] has obtained great success in the last two decades, and was considered the safest cathode material for lithium batteries. Nonetheless, the major shortcomings of LiFePO$_4$ are its intrinsic sluggish mass and charge transport.[101,102] In order to overcome the electronic- and ionic-transport limitations, doping,[20,22,103–105] particle-size reduction,[106,107] coating with electronic (or ionic) conductive materials,[23,108] and control of shape morphology[109,110] are widely used approaches. ESD is an effective coating and morphology-control approach to increase the transport properties of different lithium transition-metal phosphates.

Thin-film olivine structure phosphates have been successfully prepared. Ma and Qin synthesized LiFePO$_4$, LiMnPO$_4$, and LiMn$_{0.4}$Fe$_{0.6}$PO$_4$ thin-film cathodes with nanocrystalline morphology by the ESD technique.[111] They found that LiMn$_{0.4}$Fe$_{0.6}$PO$_4$ has better electrochemical performance compared to pure LiFePO$_4$ and LiMnPO$_4$. Shui et al. prepared pure LiCoPO$_4$ and LiCoPO$_4$–Li$_2$PO$_4$–Co$_3$O$_4$ ternary composite thin films with different ratios by the ESD technique for 5 V lithium electrode materials.[112] For the LiCoPO$_4$–Li$_2$PO$_4$–Co$_3$O$_4$ ternary composite, Li$_3$PO$_4$ and Co$_3$O$_4$ are able to be homogeneously distributed in the LiCoPO$_4$ matrix. Co$_3$O$_4$ will increase the electronic conductivity and capacity, while Li$_3$PO$_4$ may act as a separation layer to prevent direct contact between the LiCoPO$_4$ and the commonly used electrolyte (LiPF$_6$, EC-DEC, 1:1 v/v), resulting in improved cycling stability.

The poor electronic conductivity is a key issue for phosphates. ESD is powerful to realize carbon coatings or build phosphate–carbon composites by simply adding some carbon sources during the ESD process, which can reduce the particle size of the phosphate as well. Wang et al. used the ESD technique by adding glucose as a carbon precursor to prepare Li$_3$V$_2$(PO$_4$)$_3$/C thin films.[113] The thickness of the film was about 3 µm, and it was composed of ≈10 µm walnut-kernel-like clusters. Such clusters are further composed of small ≈50 nm Li$_3$V$_2$(PO$_4$)$_3$ crystals, which are distributed in a continuous carbon matrix. The carbon content is ≈10%. The rate capability of the Li$_3$V$_2$(PO$_4$)$_3$/C thin film is excellent. In the voltage range of 3.0–4.3 V, the specific capacity is 118, 115, and 80 mAh g$^{-1}$ at current densities of 1, 6, and 24 C, respectively. The Li$_3$V$_2$(PO$_4$)$_3$/C thin film exhibits stable capacity retention, i.e., the capacity maintains 113 mAh g$^{-1}$ (initially 118 mAh g$^{-1}$) after 100 cycles. This demonstrates that the 3D porous structure of phosphate/carbon is a very useful approach to overcome the shortcomings of mass and charge transport for these materials.

### 4. Anode Materials for Lithium-Ion Batteries Prepared by ESD

Based on the electrochemical reaction mechanism, anode materials for lithium-ion batteries can be divided into three categories: intercalation–deintercalation, alloying–dealloying, and conversion reactions. Except for the intercalation reaction, which is similar to that for cathode materials, most anode materials suffer from a large volume change and cracks during the lithiation process (Table 3). The ESD technique has great potential for the preparation of high-rate, long-cycle anode materials with various designed nanostructures, which are able to accommodate the huge volume change and prevent electrode pulverization.

#### 4.1. Intercalation–Deintercalation

The classic electrochemical reaction mechanism for an anode material is intercalation and deintercalation, such as graphite, mostly used in the commercial lithium-ion batteries. TiO$_2$ is another promising anode based on this mechanism, where a phase-pure material and an effective mixed conducting network are very important. ESD is applied to carry out impurity-free synthesis and morphology control. Chen et al. used the ESD technique in combination with the sol–gel process to synthesize TiO$_2$ thin film with nanostructures on various substrates, which combined the advantages of both ESD and the sol–gel method.[48] Titanium tetraisopropoxide was dissolved in absolute ethanol. Afterward, the vessel was sealed and the solution was aged until it became a semitransparent sol. The sol was taken and diluted to prepare the precursor sol for ESD. Al
Figure 4. a) SEM image and b) rate capability of 3D porous core–shell Sn@carbon composite by ESD and postheat-treatment at 900 °C. Reproduced with permission.© 2011, Wiley-VCH.

disks, ITO, and Pt disks were chosen as substrates. The deposition temperature determined the surface morphology of the ESD-derived TiO2 films. For instance, at 100 °C, a very dense and smooth film can be prepared, which cannot be obtained with an ethanolic precursor solution by ESD; at 220 °C, densely packed submicrometer TiO2 particles were obtained.

Li4Ti5O12 is a promising zero-strain electrode material involving two phases with the same symmetry (Li4Ti5O12–Li7Ti5O12), with the voltage ~1.5 V.114 This anode material delivers a specific capacity of 175 mAh g−1 with excellent cycling stability. It can be either coupled with a high-voltage cathode, such as LiMn2O4 or LiCoO2, to offer a working voltage of ~2.5 V, or coupled with LiFePO4 to provide a cell with high safety. The main issues for this anode material are its low electronic conductivity and the low lithium-ion diffusion coefficient. ESD is an effective method to prepare high-performance Li4Ti5O12 porous thin films to overcome these transport issues. Phase-pure Li4Ti5O12 is obtained after annealing at 700 °C with a porous nanotree morphology by using lithium acetate and titanium butoxide as the precursor.110 The Li4Ti5O12 thin film exhibits a specific capacity of 150 mAh g−1 (close to the theoretical capacity) with a Coulombic efficiency nearly 100% and excellent capacity retention for 70 cycles.

4.2. Alloying–Dealloying

4.2.1. Sn Prepared by ESD

Anode materials based on alloying–dealloying, such as Sn, Si, and Ge, are able to offer higher capacity compared to commercialized graphite anode (372 mAh g−1). For Sn anode materials, Li4.4Sn can be formed, with a corresponding capacity as high as 994 mAh g−1, which is a serious candidate to replace the graphite anode.115 However, it also has several problems for Sn anodes. When Sn reacts with Li to form Li4.4Sn, it will lead to large volume change (259%).116 Pulverization and cracks of the Sn anode during cycling result in a poor cycling stability.116 The main approaches to overcome such issues include reducing the size of the Sn to the nanoscale117 and preparing Sn–carbon composites or Sn–metal alloys.1118

ESD is a suitable method to tune the nanostructure of Sn and achieve carbon-coated Sn composites, leading to high-capacity and long-cycling anode materials. Li et al. fabricated 3D porous core–shell Sn@carbon composite anodes directly on a Ni foam substrate by the ESD technique (Figure 4a).61 Tin (IV) acetate and PVP was applied as the precursor. During the ESD process at 270 °C, tin (IV) acetate decomposes into SnO2, leading to PVP-coated SnO2. After annealing at 900 °C, SnO2 was reduced to crystalline Sn metal and the PVP was transformed into a conductive carbon layer. The thickness of such a carbon layer is 3.2 nm, with the carbon content in the Sn–carbon being around 35% by weight. The capacity is 672 mAh g−1 at a current density of 25 mA g−1, and the values of capacity retention are 86%, 77%, 71%, 61%, and 52% relative to the capacity at 25 mA g−1 at the current density of 100, 150, 200, 250, and 300 mA g−1, respectively (Figure 4b). Such a designed 3D porous structure and carbon shell can buffer the large volume change during the charge–discharge process and enhance the electric conductivity, resulting in a high-performance Sn anode.

4.2.2. Si Prepared by ESD

Si is another promising anode material based on the alloying process, whose capacity is as high as 4212 mAh g−1, almost 10 times higher than the commercial graphite anode.119 However, the poor electronic conductivity of Si limits the power density; while the huge volume change (>300%) results in pulverization and electric disconnection of the Si particles, leading to poor cycling performance. In order to solve such issues, designing various nanostructures for Si anodes, such as nanoparticles, nanowires, and nanotubes, and porous or hollow structures are proved to be effective approaches to improve the performance.120–122 Synthesis of Si/carbon composite is another widely used method as well.123,124

ESD offers different ways to fabricate various Si/carbon composites, which can be used independently or applied together with other techniques to prepare high-performance Si anodes. Yin et al. used electrospay to synthesize Si/carbon nanoporous microspheres.125 Si nanoparticles were dispersed into an aqueous solution of sodium alginate to form the precursor solution, which was electrospayed in to CuCl2 aqueous solution to form microspheres. After calcination, carbon coating, and a HF etching process, the target Si/carbon was obtained.
Such microspheres exhibited a pear-like morphology with a 30–70 µm diameter, with a surface area of 57 m² g⁻¹ and a pore size of 30 nm (Figure 5b). The Si/C nanoporous microspheres exhibited a capacity larger than 1000 mAh g⁻¹ and greatly improved cycling stability compared with pure nano-Si due to the controlled manner of ESD in terms of pore size, carbon coating, and porosity.

ESD can also be applied as a layer-by-layer synthesis technique to fabricate Si/C composites (Figure 5c,d).[126] First of all, a well-dispersed GO suspension is deposited on a copper substrate by ESD to form a thin film of GO sheets (A layer). Afterward, a mixture precursor of Si nanoparticles, PVP, CB, and MWCNTs is used to form a B layer by the same ESD technique. The A layer and B layer are deposited alternately, leading to a target thin film with alternatively stacked Si-porous carbon layers and graphene layers. By heat treatment, Si nanoparticles are embedded in the porous carbon layer composed of a nitrogen-doped carbon framework, carbon black, and carbon nanotubes, which are further sandwiched by flexible and conductive graphene sheets (Figure 5e,f). The porous carbon layer and graphene layer will accommodate the volume change of the Si particles, enhance the electronic conductivity, facilitate ion transport by the void space, and prevent the agglomeration of Si nanoparticles. Hence, such an electrode exhibits a reversible capacity of 1020 mAh g⁻¹ with 75% capacity retention after 100 cycles and a good rate capability on the basis of the total electrode weight.[126]

The combined ESD/electrospinning technique is an effective approach to fabricate Si/C composites with high performance. Currently, Si electrodes are prepared by casting slurries consisting of Si, conductive carbon, and a binder onto Cu metal current collectors. Since the Si loading is normally less than 1 mg cm⁻², in spite of the Si anode with a high reported capacity (>2000 mAh g⁻¹), the overall capacity of the entire anode is less than 100 mAh g⁻¹, considering the weight of the current collectors. As a result, high-capacity Si and lightweight current collectors can be used to increase the overall capacity of the anode. Xu et al. prepared a 3D Si/C fiber paper electrode by a combined ESD and the electrospinning technique.[76] Such a paper electrode was prepared by simultaneously electrospraying a nano-Si-PAN dispersion and electrospinning a PAN solution to uniformly distribute PAN-coated nano-Si clusters into a PAN nanofiber paper, followed by heat treatment in Ar (Figure 6a). After carbonization, the paper electrode still shows good flexibility (Figure 6b). The PAN nanofiber with a diameter of ≈200 nm built a continuous carbon network with microsized void spaces, and Si nanoparticles were bonded together by coated carbon to form 1–2 µm clusters (Figure 6c). The continuous carbon fiber network provides a fast electronic pathway, while the void space is beneficial for ionic transport through the electrolyte. In addition, the unoccupied fiber cages offer free space to accommodate the volume change of the nano-Si and alleviate stress/strain, leading to a long cycle life.
Si content in the paper electrode is ≈72 wt%. The electrode exhibits an overall high capacity of 1600 mAh g⁻¹ and good capacity retention of 840 mAh g⁻¹ after 600 cycles. The rate capability is good as well for such paper electrodes with a mass loading of 1.7 mg cm⁻², with a current density from 0.2 to 4 A g⁻¹ (Figure 6d). The success of the Si/C electrode highlights the great potential of the combined electrospinning/ESD technology as a suitable mass-production technique with low cost for flexible batteries or electronics.

4.2.3. Oxides Prepared by ESD

SnO₂-based oxide is another extensively investigated anode for lithium batteries based on the alloying reaction. SnO₂ will first react with lithium to form Sn metal and Li₂O (step I, conversion reaction), and then the Sn metal will further react with lithium to form a lithium tin alloy (step II). Since step I is irreversible, tin-oxide-based anodes are, in principle, anodes based on alloying–dealloying. Besides Sn and Si anodes, ESD is an effective method to improve the performance of SnO₂-based oxides or composites. Yu et al. fabricated a few nanostructured carbon-free anode materials, such as SnO₂, Li₂O–SnO₂, CuO–SnO₂, and LiO₂–CuO–SnO₂ composite, by the ESD technique, which exhibit a special porous, multideck-cage morphology (Figure 7a,b).[66] The hollow porous spheres with diameter of ≈5 µm are randomly arranged, and the diameters of pores are in the range of 200 nm to 1 µm. The thickness of the interconnected piled-up porous spheres is ≈10–15 µm. Among the tin-based composites, Li₂O–CuO–SnO₂ shows the highest reversible capacity of 1158 mAh g⁻¹ at 0.5 C, and it still maintains 525 mAh g⁻¹ at high rate of 8 C. The excellent performance of the SnO₂-based composite can be attributed to the LiO₂ and CuO components and porous structure. The inactive Li₂O component and the porous structure can accommodate the volume change, while the Cu nanoparticles introduced by the CuO component can improve the electrical contact.

Oxide anodes based on alloying, with various morphologies, crystallinities, and components, have been extensively investigated by the ESD technique; for example, amorphous tin oxide,[127] SnO₂–CoO,[128] SnO₂–MnO,[129] SnO₂–iron oxide,[130] SnO₂–Fe₂O₃,[131] SnO₂–SiO₂,[132] SnO₂/graphene composite,[133] etc. Nanoporous tree-like SiO₂ film was prepared by the ESD technique combined with the sol–gel method.[45] Spherical SiO₂ with a size of 300–500 nm sized is monodisperse with pore size of ≈7.5 nm.

4.3. Conversion Reactions

Conversion-reaction anodes have pronounced advantages and disadvantages compared with the ones based on intercalation.[16,134] On the one hand, the theoretical capacity of a conversion anode is very high, but on the other, the kinetic problems associated with it are extraordinarily severe. We will take RuO₂ as a relevant example. It will reduce to Ru metal and a Li₂O matrix according to the following equations: RuO₂ + 4Li → Ru + 2Li₂O.[17] It is clear to note that it involves 4 Li per transition metal, compared to 1 Li per metal in LiFePO₄ (two-phase mechanism) and 0.5 Li per metal in LiCoO₂ (single-phase mechanism), which corresponds to a much larger theoretical capacity. According to reaction equation of the conversion reaction, the initial oxides, i.e., RuO₂ will decompose into complex phase mixtures of RuO₂, Ru, and Li₂O, which will lead to severe kinetic problems, not only on discharge, but even more strongly on charging, whereby nucleation and diffusion are necessary to form the electroactive material again. Usually, for the conversion reaction, polarization and reversibility are extremely

Figure 6. a) Schematic illustration of the synthesis process of the flexible 3D Si/C fiber paper electrode. b,c) Photographs and SEM image of 3D Si/C fiber paper electrode. d) Voltage profiles at current density from 0.2 to 4 A g⁻¹ for such an electrode. Reproduced with permission.[76] Copyright 2014, Wiley-VCH.
serious. Due to the phase decomposition and multiphase mixture properties, a large volume change occurs during the charge–discharge process, which results in a poor cycling stability for the conversion reaction. Increasing the reversibility, cycling stability, and rate capability for high-energy conversion anodes is still a challenging task.

4.3.1. Oxides Prepared by ESD

Metal oxides based on the conversion reaction are considered as potential anode materials for Li-ion batteries. The ESD technique is an ideal approach to prepare carbon-free and binder-free conversion anodes in order to overcome the above-mentioned issues. Yu et al. fabricated a reticular CoO–Li2O composite on a conducting nickel-foam substrate by the ESD technique (Figure 8a).[36] Such a porous nickel-foam substrate can make sure of the maximization of the contact area between the electrode and the electrolyte compared to a dense metal foil. The reticular film with the thickness of 30 µm had a good adherence to the substrate (Figure 8b). In the composite film, CoO is crystalline and Li2O is amorphous. Introduction of Li2O has several advantages. 1) Li2O limits the growth of CoO particles. 2) Li2O as an oxidant can convert CoO to the higher-valency Co oxide, which will lead to extra capacity. 3) Li2O can buffer the stress due to the volume change of CoO during the cycling, resulting in good cycling stability. The reticular composite film shows good cycling stability and rate capability compared to the dense film (Figure 8c,d). It delivers a capacity of 650 mAh g⁻¹ at 5 C for the reticular film, while the value is 250 mAh g⁻¹ for a dense film under the same conditions. In principle, pristine metal oxides normally have low electronic conductivity. In order to overcome this issue, a porous NiO–Ni nanocomposite can be prepared by ESD.[135] The introduction of Ni can offer a highly electronic conductive medium and facilitate a more complete decomposition of Li2O during charging.

In order to further improve the performance, ESD can be used together with other synthesis methods (i.e., solvothermal method) to prepare conversion anodes.[53] Cobalt oxide thin films composed of interconnecting hollow spherical Co3O4 particles (≈300 nm) can be prepared through two steps: 1) Hollow cobalt alkoxide particles in a stable suspension are synthesized as a precursor by the solvothermal method from mixed polyalcohol solutions of cobalt acetate in an oil bath. 2) A thin film is prepared by ESD using the above precursors combined with heat treatment. Such a film shows a capacity of ≈1000 mAh g⁻¹ up to 50 cycles and good rate capability.

A series of oxides anode based on conversion reaction have been successfully fabricated by ESD to enable fast electron/ ion transport and buffer the volume changes, leading to an improved performance, i.e., Co3O4–graphene composite,[136] 3D porous ZnO thin film,[137] porous Fe2O3 thin film,[53] Fe2O3 thin film,[138] Mn2O3 nanoparticle,[139] 3D porous MnO thin film,[140] MnO/CNT composite film,[141] MnO/graphene composite
film.\footnote{3D porous ZnMn$_2$O$_4$ thin film.} and 3D reticular pomegranate-like CoMn$_2$O$_4$/C.\footnote{3D reticular pomegranate-like CoMn$_2$O$_4$/C.}

Normally the ESD technique is a facile method to fabricate conductive additive-free and binder-free electrodes. However, on the other hand, a binder can also be added to prepare an electrode during ESD. For instance, metal-oxide/PVdF nanocomposites can also be obtained by electrospraying precursor solutions containing metal salts dissolved in NMP together with PVdF as binder.\footnote{Metal-oxide/PVdF nanocomposites can also be obtained by electrospraying precursor solutions containing metal salts dissolved in NMP together with PVdF as binder.} In this way, small oxide nanoparticles can be prepared and dispersed in situ in the binder, creating oxide (e.g., Fe$_2$O$_3$, CuO, SnO$_2$, CoO)/PVdF nanocomposites.\footnote{Metal-oxide/PVdF nanocomposites can also be obtained by electrospraying precursor solutions containing metal salts dissolved in NMP together with PVdF as binder.}

ESD together with electrochemical cycling can be applied to synthesize single-crystalline metal nanoparticles with various morphologies, based on the conversion reaction.\footnote{ESD together with electrochemical cycling can be applied to synthesize single-crystalline metal nanoparticles with various morphologies, based on the conversion reaction.} For a 3D reticular Li$_2$O–Cu$_2$O composite film prepared by ESD, if the cell of Li$_2$O–Cu$_2$O/Li is discharged, Cu nanospheres (On Ni foam) and pyramid-like Cu particles (on Cu foil) can be successfully obtained. Furthermore, the shape of the Cu particles can be controlled by changing the cycle numbers of the cell; for example, Cu pyramids can change to Cu truncated pyramidal nanoparticles after 50 cycles.

### 4.3.2. Sulfides Prepared by ESD

Besides metal oxides, metal sulfides have been extensively investigated as high-capacity lithium anodes as well. By using the ESD technique, various oxide-based conversion electrodes can be prepared easily, whereas it is not so straightforward to obtain conversion sulfide by ESD. Recently, by choosing an appropriate precursor of (NH$_4$)$_2$MoS$_4$, MoS$_2$ has been prepared by conventional ESD, according to: (NH$_4$)$_2$MoS$_4$ + H$_2$ → MoS$_2$ + H$_2$S + NH$_3$.\footnote{MoS$_2$ has been prepared by conventional ESD, according to: (NH$_4$)$_2$MoS$_4$ + H$_2$ → MoS$_2$ + H$_2$S + NH$_3$.} In addition, a 3D porous interconnected nanocomposite was constructed by ESD, integrating nano-2D graphene, nano-1D CNT, and nano-0D MoS$_2$ (Figure 9a).\footnote{A 3D porous interconnected nanocomposite was constructed by ESD, integrating nano-2D graphene, nano-1D CNT, and nano-0D MoS$_2$.} Depending on annealing or not, either amorphous MoS$_2$ (0.5–5 nm) or nanocrystalline few-layered MoS$_2$ (5–10 nm) can be obtained. Such 0D–1D–2D integration has several advantages. MoS$_2$ nanodots (0D) are beneficial for more reversible conversion reactions. 1D CNT as an electronic connector between MoS$_2$ and the carbon skeleton will also prevent the agglomeration of graphene. 2D graphene is a suitable matrix to constitute an effective, 3D, porous, and integrated conductive network. Finally, an efficient electrochemical circuit is constructed for both electrons and lithium ions by ESD. The composite shows an excellent rate capability, especially for annealing samples. The capacities are 949, 883, 858, 737, and 652 mAh g$^{-1}$ at current densities of 100, 500, 1000, 5000, and 10 000 mA g$^{-1}$ respectively (Figure 9b), and the good capacity retention is maintained for at least 100 cycles (Figure 9c).

For the purpose of the synthesis of MoS$_2$, the key point is to choose the precursor of (NH$_4$)$_2$MoS$_4$, which limits the application to other metal sulfides. In order to solve this problem, we have also proposed a general strategy to fabricate 3D porous interconnected carbon-coated metal sulfides by ESD and without adding expensive carbon materials such as graphene and CNT.\footnote{A general strategy to fabricate 3D porous interconnected carbon-coated metal sulfides by ESD and without adding expensive carbon materials such as graphene and CNT.} Taking SnS/C as an example, the key strategy is to choose L-cysteine together with a SnCl$_2$. The L-cysteine is...
not only the sulfur source for the sulfide formation, but it also acts as a complexing agent for Sn\(^{2+}\) ions in the 1,2-propanediol solvent\([58]\). The L-cysteine molecule has different functional groups, such as \(-\text{NH}_2\), \(-\text{COOH}\), and \(-\text{SH}\), and has a strong tendency to coordinate Sn\(^{2+}\). During ESD and post-heat-treatment in Ar, the Sn\(^{2+}\)–L-cysteine complex decomposes to form SnS, and the extra L-cysteine and 1,2-propanediol convert to amorphous carbon. In this way, small nanorods of SnS with a size of 10–20 nm embedded in amorphous carbon are formed, which further self-assemble into a 3D porous interconnected composite (Figure 10a,b). The nanocomposite shows excellent rate capability and cycling stability due to the 0D⊂3D porous interconnected structure, which improves the transport properties and buffers the volume change during cycling. The reversible capacity is around 953 mAh g\(^{-1}\) at 100 mA g\(^{-1}\), and it still has a capacity as high as 329 mAh g\(^{-1}\) at very high current density of 10 A g\(^{-1}\) (Figure 10c). At a current density of 1 A g\(^{-1}\), the capacity maintains 535 mAh g\(^{-1}\), which is 80% capacity retention (Figure 10d).

5. Electrode Materials Prepared by ESD for Sodium-Ion Batteries

In view of the abundance and the low cost of elemental sodium, sodium-ion batteries are considered as a realistic promising alternative compared to its lithium counterpart\([8,148]\). However, due to the larger ionic radius and greater molecular mass, it leads to several disadvantages, such as lower theoretical capacity, lower cell voltage, less-rapid transport, more-severe volume change, and structure impact, when compared to its lithium analogues. In spite of such shortcomings, there are several arguments in favor of sodium storage, as well as in terms of kinetics. 1) For some specific materials, such as NASICON materials, sodium transport is even higher than lithium. 2) The charge-transfer reaction from liquid electrolyte to solid electrode is even easier for Na\(^+\) due to the less extensive solvation of the bigger cation\([149]\). Referring to cathode materials for sodium batteries, layered transition-metal oxides\([150,151]\), polyanionic materials\([152–155]\), and Prussian Blue materials\([156]\) have been extensively studied. For anode materials, hard carbon\([157]\), alloys\([158]\), conversion anodes\([159]\), and low-voltage transition metal oxides, and phosphates\([160]\) are most commonly investigated anode materials. The ultimate goal for sodium storage is to improve the specific performance of sodium batteries, i.e., capacity, rate capability, cycling stability, etc., to compete or even exceed lithium batteries. As shown by various examples of lithium electrodes, ESD has several pronounced advantages. For example, it can prepare phase-pure materials with high crystallinity; it is an effective method to construct an efficient mixed conducting network; and it can build a robust and porous structure to accommodate the volume changes. Hence, more and more high-performance electrodes for sodium storage have been prepared by ESD recently.

5.1. Sodium Cathodes Prepared by ESD

NASICON-type Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) (NVP) is a promising sodium cathode material due to its high sodium conductivity, high thermal stability, and energy density\([161,162]\). However, the main issue is its poor electronic conductivity\([163]\) which limits the chemical diffusion of this material. To construct an effective mixed conducting network, especially, an electronic conducting network is very important. A bicontinuous network (current collector, electrolyte) is an optimized solution, and for NASICON
materials with high ionic conductivity, a tricontinuous network (current collector, electrolyte, electroactive mass) is even helpful. Besides the commonly used templated method or template-free approaches to prepare 3D electrodes, the ESD technique is also a general strategy to prepare self-supported interpenetrating 3D tricontinuous cathodes. By using this technique, we fabricated an interconnected 3D tricontinuous NVP–rGO–CNT, which was directly deposited on a stainless-steel current collector without any conductive additive and binder (Figure 11a–c). This electrode shows a much more ordered structure than the ones achieved by other template-free methods, which is even comparable to the tedious templating method. Such an electrode exhibits an excellent electrochemical performance when used for both cathode (2.3–3.9 V) and anode (1.3–2.0 V), as well as full NVP symmetric cell (1–2.2 V). For example, as far as for cathodes, up to 30 C, the specific capacity is still as high as 109 mAh g\(^{-1}\), which is quite comparable to the theoretical capacity of NVP. Even at an ultrahigh C rate of 100 C (11 A g\(^{-1}\), full charge–discharge in 36 s), the capacity still maintains 82 mAh g\(^{-1}\), which is 70% of the theoretical capacity (Figure 11d). Such rate capability is quite comparable to supercapacitors, but with the much higher energy density of batteries. After 2000 cycles at 10 C, the capacity is still as high as 96% of its initial capacity, with high Coulombic efficiency (Figure 11e). For the anode part, such a 3D tricontinuous NVP:rGO:CNT can deliver 70% of its theoretical capacity at 20 C, and its capacity shows almost no decay (maintains 99%) after 2000 cycles at 10 C. A full sodium battery using 3D tricontinuous NVP:rGO:CNT as both the cathode and anode was assembled as well, which delivered a capacity of 90 mAh g\(^{-1}\) at 10 C with voltage of 1.7 V. The excellent performance is due to the unique 3D tricontinuous structure constructed by ESD, i.e., continuous electronic phase (rGO–CNT), continuous electroactive (here also ionic) phase (NVP), and continuous ionic phase (electrolyte in pores), which ensures fast electron and Na\(^+\) transport in the entire electrode. Hence, the ESD technique is a simple but powerful method to prepare high-power–high energy 3D or 2D thin-film batteries.

5.2. Sodium Anodes Prepared by ESD

Besides NASICON-type sodium anodes such as Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) (1.3–2 V), self-supported 3D porous reticular Nb\(_2\)O\(_5\)@carbon composites based on the intercalation reaction were also prepared by ESD. The nanosized Nb\(_2\)O\(_5\) encapsulated in the carbon matrix facilitates the electrochemical kinetics between the Nb\(_2\)O\(_5\) and electrolyte. The 3D interconnected hollow structure buffers the volume change during cycling. Therefore, the Nb\(_2\)O\(_5\)@carbon obtained by ESD exhibits improved sodium-storage performance.

An alloying anode such as Sb was also successfully fabricated by ESD to improve its performance. Sb is a promising anode candidate for sodium batteries due to its low reaction potential and high theoretical capacity of 660 mAh g\(^{-1}\). Nonetheless, similar to alloy anodes used for lithium batteries, the large volume change will lead to a poor cycling stability. To solve this problem, Sb nanoparticles encapsulated in a 3D reticular carbon
network were prepared by ESD with a postheat treatment. The diameter of pores in the reticular structure are 100 nm to 20 µm, and the width of the wall is ∼8 µm (Figure 12a). Sb nanoparticles are ∼20–40 nm, and they are embedded in the reticular carbon matrix (Figure 12b). The electrode exhibits a high rate capability up to 5 C (Figure 12c). At 0.2 C, it still delivers 404 mAh g⁻¹ after 100 cycles (Figure 12d), which shows good cycling stability. Such a 3D porous structure effectively buffers the volume change during the sodiation/desodiation process.

ESD is a powerful method to prepare metal sulfides based on the alloying reaction for sodium storage as well. As we have already shown in the part on lithium anodes, a carbon-coated 3D porous interconnected SnS/C composite can be prepared by the ESD technique. Such a SnS/C composite as an alloying anode also shows a good sodium-storage performance. The capacities are 419, 334, 310, 205, and 145 mAh g⁻¹ at current densities of 100, 500, 1000, 5000, and 10 000 mAh g⁻¹. At 1 A g⁻¹ current density, the capacity is still as high as 266 mAh g⁻¹, which maintains more than 80% capacity retention with almost 100% Coulombic efficiency.

Conversion anodes such as sulfides are also extensively investigated for sodium batteries. 3D porous WS₂ and 3D porous WS₂/C nanocomposites was successfully fabricated by the ESD technique. WS₂/C nanocomposites include nano-0D WS₂, nano-1D CNTs, and nano-2D rGO. Depending on annealing, WS₂ can be amorphous or nanocrystalline. An effective electrochemical integrated circuit was constructed by ESD with the combination of 0D–1D–2D nanostructures, leading to good electrochemical performance for sodium storage. It delivered capacity of ∼400 mAh g⁻¹ at 0.2 C and 81 mAh g⁻¹ at 10 C. After 300 cycles at 1 C, the capacity still maintained 219 mAh g⁻¹.

6. Electrode Materials for Supercapacitors Prepared by ESD

No matter whether for electrical-double-layer capacitors (EDLCs) or pseudocapacitors, electrode materials with a high surface area are extremely significant. At this point, the various porous structures obtained by the ESD technique are very suitable to improve the electrochemical performance of supercapacitors.

6.1. Electrical-Double-Layer Capacitor Materials Prepared by ESD

Various carbon materials with high surface area are widely used for EDLCs, which exhibit high power density compared to pseudocapacitors. Graphene is one of the materials of interest for supercapacitors owing to its high surface area and high electronic conductivity. Various morphologies constructed with graphene are achieved by ESD. A graphene-nanoplatelet thin film was prepared by dispersing graphene nanoplatelets with a surface area of 600–750 m² g⁻¹ and a diameter of 2 µm in 1,2-propenediol solvent as a precursor. The film shows capacitances of 55 and 53 F g⁻¹ for the 1 and 6 µm thick films, respectively, at a discharge rate of 1 A g⁻¹. A crumpled reduced graphene oxide (C-rGO) thin film was also fabricated by ESD. The C-GO thin film was first prepared by dissolving GO in water/absolute ethyl alcohol solution and depositing them on the stainless steel by ESD. The C-GO film was further reduced to C-rGO by exposure to hydrazine hydrate vapor at 85 °C for 10 h. Such C-rGO shows a high capacitance of 366 F g⁻¹ at 1 A g⁻¹ in 6 M KOH aqueous solution and 108% capacitance retention to 40 000 cycles.
Besides graphene, CNTs are also applied for supercapacitors. Compared to pristine CNTs, surface-modified CNTs have better dispersion stability in a polar solvent and better electrochemical performance due to the exposure of edge sites by the partial opening of the nanotube structure.[170] Through chemical etching by KMnO₄, surface-unzipped CNTs with oxygen-containing functional groups were obtained, making them highly dispersible in a polar solvent. Hence, binder-free unzipped multiwalled CNT electrodes were prepared by ESD using this precursor, which delivered a capacitance of 133 F g⁻¹ at a scan rate of 10 mV s⁻¹ in 1 m H₂SO₄ aqueous electrolyte.

In order to realize a unique morphology with high surface area, rGO/CNT composites can be prepared through ESD. Micropatterned interdigitated electrodes combining both rGO and CNT composite thin films by ESD have also been reported.[65] Single-layer GO and COOH-functionaized CNT were dispersed by sonication in 1,2-propanediol as a precursor solution. GO can be reduced to rGO during the ESD process at 250 °C without a further thermal or chemical reduction process. Figure 13a schematically describes the procedure to integrate supercapacitor electrodes on interdigital Ti/Au microelectrodes and how to fabricate microsupercapacitors by the ESD technique. As shown in Figure 13b,c, a typical micro-supercapacitor with 20 in-plane interdigital microelectrodes (100 µm in width, 2500 µm in length, distance between adjacent microelectrodes 50 µm) was constructed. The obtained rGO–CNT hybrid electrode exhibits porous morphology, and CNTs uniformly appear between the rGO sheets, which prevents the stacking of the rGO sheets and maintains a porous structure (Figure 13d,e), thus offering a high surface area for the microelectrodes. Among the samples of rGO, rGO–CNT (9:1), and rGO–CNT (8:2), the best performance is achieved for rGO–CNT (9:1). The capacitance of 5.1 mF cm⁻² at a 3 mA cm⁻² current density is obtained, and it drops by about 30% at current density of 100 mA cm⁻² (Figure 13f). Similar work combining rGO and CNT to prepare a thin-film electrode for supercapacitors was also performed using a mixed solution of water and ethanol (volume ratio 1:1) instead of high-boiling-point solvent such as 1,2-propanediol at 300 °C by the ESD technique.[171]

6.2. Pseudocapacitor Materials Prepared by ESD

Conducting polymers and transition oxides are widely used examples for pseudocapacitive materials, which exhibit a promising energy density. In order to increase the surface area and control the porosity, ESD combined with a template method is promising. A CNT/PPy composite film with controlled pore sizes was prepared by this strategy.[74] CNTs and nanosize silica were first deposited by ESD, and then PPy was electrochemically deposited on to the CNTs to anchor them in an entangled structure. Finally, the silica was removed, leaving a 3D entangled structure of a CNT/PPy film. The pore size can be controlled by the amount of silica. The capacitance of such a film (80% PPy) is 250 and 211 F g⁻¹ at scan rates of 10 and 500 mV s⁻¹, respectively, in 1 m KCl.

RuO₂ is one of the best electrode materials with high capacitance and long cycle life for supercapacitors, due to its high conductivity and electrochemical reversibility. Hydrous RuO₂·xH₂O[172] and anhydrous RuO₂[173] were successfully prepared by the ESD technique, with specific capacitances of...
650 F g\(^{-1}\) and 500 F g\(^{-1}\), respectively, at a scan rate of 20 mV s\(^{-1}\). The capacitance of the anhydrous RuO\(_2\) can be further improved by ESD followed by electrochemical lithiation and delithiation. Based on the reversible conversion reaction, the as-prepared ESD RuO\(_2\) with primary particle sizes of 15–30 nm will be converted to nanostructured RuO\(_2\) ranging from 2 to 5 nm. The specific capacitance will be increased to 653 F g\(^{-1}\) at 20 mV s\(^{-1}\).

ESD allows homogeneous mixing of different precursors at the atomic scale, so that phase-pure metal oxides composites can be constructed by ESD for supercapacitors, and the performance can be improved with synergistic effects. Benefiting from the high capacity of VO\(_2\) and high stability of TiO\(_2\), a unique interconnected pore network of VO\(_2\)/TiO\(_2\) nanosponges was successfully prepared by ESD. The binder-free electrode exhibited a specific capacitance of 86.2 mF cm\(^{-2}\) (=548 F g\(^{-1}\)) and a good cycling stability with 84.3 retention after 1000 cycles.

7. The ESD Technique for Li–S Batteries

Li–S batteries are considered as one of the most promising next-generation batteries owing to their high theoretical energy density (2600 Wh kg\(^{-1}\)) and low cost. However, they still suffer from several serious issues. One disadvantage is the low electronic and ionic conductivity of sulfur, which results in low sulfur utilization and poor rate performance. The other problem is the shuttle effect of polysulfides. The produced intermediate polysulfides are easily dissolved in the organic electrolyte and then diffuse to the anode part to react with the Li anode, which leads to a worse cycling performance and a low Coulombic efficiency.

ESD can be applied to design a unique structure for the sulfur cathode in order to further improve the performance of Li–S batteries. For example, a 3D interpenetrating sulfur-impregnated MWCNT microball cathode was prepared by using the ESD technique as follows. An MWCNT/organic binder compact sphere with a uniform size of 3–6 µm was prepared by the ESD process. After burning out the binder at 400 °C, mesoporous MWCNTs were obtained with a specific surface area of 175 m\(^2\) g\(^{-1}\). Finally, on impregnation of sulfur, a sulfur-impregnated MWCNT microball cathode was achieved. This cathode can improve the electronic and ionic transport of active materials and overcome the volume change during cycling, leading to good cycling stability and rate performance.

Suppressing the shuttle effect is the most important issue for Li–S batteries. As a thin-film preparation technique, besides the 3D porous structure, ESD can also prepare dense thin
films. Hence, ESD is a suitable method to construct an inter-blocking-layer between the cathode and the separator to solve the shuttle effect.\[177]\) As shown in Figure 14a, a multifunctional polysulfide blocking layer (MPBL) including a conductive polymer and carbon is coated on the cathode by ESD. On the one hand, PEDOT:PSS offers a high electronic conductivity and reacts with polysulfide by strong chemical binding. On the other hand, nanosized carbon black with a high surface area will increase the conductivity and reacts with the polysulfide by physical adsorption. An integrated and compact layer with a controlled thickness, by easily changing the spray time and concentration of precursors, can be achieved by ESD. As displayed in Figure 14b, the electrode is fully wrapped by a smooth and dense MPBL, whose thickness is only 100 nm, thinner than the ones prepared by other methods. The rate performance of such an MPBL-coated cathode is superior. It exhibits the capacity of 1034 mAh g\(^{-1}\) at 0.3 C, and the capacity is still 615 mAh g\(^{-1}\) when the current increases to 3 C (Figure 14c). The cycling stability of MPBL-coated cathode is also sufficiently improved compared to the PEDOT:PSS coated cathode and uncoated cathode. The capacities are 879, 645, and 473 mAh g\(^{-1}\), respectively, after 200 cycles at 0.3 C (Figure 14d).

8. The ESD Technique for Li–O\(_2\) Batteries

Li–O\(_2\) batteries provide even higher theoretical energy densities (3500 Wh kg\(^{-1}\)) compared to Li–S batteries, and represent a very promising system for various devices based on energy storage.\[178]\) The design of highly effective oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) catalysts are key issues to improve the battery performance.\[179,180]\) In order to increase the kinetics of the ORR and OER, the enhancement of the electronic conductivity and catalytic activity is crucial. The ESD technique can be applied to design suitable components and structures of catalysts. For example, a porous Co\(_3\)O\(_4\)/Ketjenblack cathode film was directly deposited on Ni foam by the ESD technique as the cathode of a Li–O\(_2\) battery.\[181]\) The optimized Co\(_3\)O\(_4\)/Ketjenblack (80%) composite film exhibited the best performance. The discharge capacity was 2044 mAh g\(^{-1}\) at a current density of 100 mA g\(^{-1}\), with the lowest overpotential of less than 1.0 V. This unique cathode prepared by ESD has a high surface area and facile charge and mass transport, and hence results in increased surface catalysis reactivity.

9. Outlook and Conclusions

Fabrication of designed structures and morphologies for energy-storage materials is essential to meet the targets of energy-storage applications. Among the various synthesis methods, the ESD technique attracts intense interest and undergoes pronounced advances. ESD is a simple but versatile method, which can be applied to prepare a large number of compounds for various energy-storage systems (Li-ion batteries, Na-ion batteries, supercapacitors, Li–S batteries, and Li–O\(_2\) batteries) with different energy-storage mechanisms (intercalation reaction, alloying and conversion reactions, and surface reaction), leading to a pronounced improvement of the electrochemical performance (i.e., capacity, rate capability, and cycling stability). The highlight of this technique is that it can offer various morphologies, such as granular, dense, porous, 3D interpenetrating...
tricontinuous, etc. with a controllable manner, easily achieved by adjusting the experimental parameters, such as the voltage, the concentration of the precursor solution, the flow rate, the substrate temperature, the deposition time, etc. In addition, ESD is also a fast thin-film deposition method compared to PVD or CVD, which can prepare an extremely thin and defect-free layer homogeneously, only in an ambient atmosphere and at low temperature without complex reactors and high-vacuum systems. Furthermore, electroactive materials can be directly deposited on the current collector by ESD without any additional conductive additives and binders, which greatly simplifies the battery/supercapacitor assembly process and increases the rate capability and energy density of the electrodes.

However, several challenges remain for the ESD technique. At the moment, not all compounds with designed structures and morphologies can be prepared by the ESD technique. The detailed mechanisms as to how the experimental parameters of the ESD process affect the morphologies of specific materials are still not fully understood. In addition, scale-up of the ESD technique for industrial applications in terms of various energy-storage systems is still a challenge. Great efforts still need to be devoted to the ESD technique in order to further improve this powerful and versatile method. All in all, pronounced advantages and the brilliant perspective of the ESD technique will make a great contribution to energy storage in both the academic and industrial fields in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

batteries, electrostatic spray deposition, energy storage, nanostructure, supercapacitors

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