Thin-Film Techniques for Advanced Energy Conversion and Storage Systems

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Received September 10, 2004; Accepted November 22, 2004

Abstract: Energy conversion and storage is more and more important nowadays. Organic solar cells, solid oxide fuel cells (SOFCs), and rechargeable lithium batteries are three key electrochemical systems that can meet these demands. Two thin-film techniques, i.e. electrostatic spray deposition (ESD) and chemical vapor deposition (CVD) have been extensively and successfully used for the deposition of ceramic thin films for lithium batteries, organic solar cells, and SOFCs. A large variety of layer morphologies including unique structures have been obtained by ESD and CVD. Both the working principles of the three energy-related electrochemical systems and the basics of ESD and CVD are reviewed in this paper. Experimental results are selectively presented as well.

Keywords: thin film, deposition, lithium battery, solid oxide fuel cell, solar cell

Introduction

When history has just passed the transition point between two centuries, our human society has entered such an era that we seem to be able to create almost everything both in matter and in spirit. People may take the rapid expansion and application of the internet, and the artificial cloning of sheep and other animals as two of the most exciting and representative examples. This reminds us of a popular saying in the turbulent late 1960s and early 1970s in China. It said that “there is nothing that people are unable to achieve; there is only something that people don’t think of yet”. However, the truth of the matter is that we now more and more realize that the fast consumption of non-renewable energy resources and environmental pollution may be the two largest barriers to hinder further advancement of our society. It is even worse that these two problems would most likely cause catastrophe to the human being if we are not able to solve them with enough effort.

There are basically two ways to deal with the energy problem and, to a substantial extent, the environmental problem, (1) exploiting all of the current energy sources, and (2) improving the energy conversion and storage [1]. The first way involves utilizing more efficiently and cleanly the traditional non-renewable energy sources (nuclear energy and fossil fuels like oil, coal and natural gas) and making use of renewable energy sources (hydroelectric energy, biomass energy, geothermal energy, solar thermal energy, photovoltaic solar energy, wind energy, and ocean energy). The second way involves the storage of an energy form, for instance, electricity, heat or hydrogen, and the conversion of energy from one form into another (electricity in most cases). The classification of energy sources and the facilities or devices for energy conversion and storage are schematically illustrated in Figure 1. Of the hardware, organic solar cells, solid oxide fuel cells (SOFCs), and rechargeable lithium batteries are among the research subjects in our laboratories. Solar cells convert sunlight, the most powerful and free energy source, directly into electricity. Fuel cells generate electricity by converting the chemical energy via the oxidation or “flameless burning” of fuel gases either from nature (e.g. natural gas) or from man made (e.g. hydrogen, carbon monoxide). Rechargeable batteries are the devices to convert electricity into chemical energy during charging for storage, and to convert the chemical energy...
back to electricity during discharging.

For the success of developing and commercializing these electrochemical systems advanced ceramic materials, especially in the form of thin films, play a very important role. The syntheses of ceramic thin films of high quality and diversity have been the goal and practice in our laboratories in the past years. We have used a variety of thin-film techniques including chemical vapor deposition (CVD), electrostatic spray deposition (ESD), physical vapor deposition (PVD), and sol-gel processes to prepare the thin-film components for the third generation solar cells, rechargeable lithium batteries, and SOFCs. The first two deposition techniques, i.e. CVD and ESD, are the main techniques currently used. We have gained a lot of expertise on CVD [2-11], while the ESD technique was developed in our laboratory recently [12-27] and has been adopted by other research groups worldwide [28-37]. Therefore, these two techniques will be reviewed in this paper. The working principles of the rechargeable lithium batteries, the dye-sensitized solar cells, and SOFCs will also be presented here.

**Energy Storage and Conversion Systems**

**Rechargeable Lithium-ion Batteries**

Electrical energy is most typically stored in batteries for everyday use. Batteries consist of one or more electro-

chemical cells, which contain an electrically conductive medium called electrolyte and two electrodes, one positive (cathode) and the other negative (anode). The electrolyte can be liquid, solid, or a gel through which preferably only ions can migrate. The cathode and the anode are usually solid where (semi)electrochemical reactions take place separately with reduction on the cathode and oxidation on the anode. Depending on whether or not a freshly fabricated battery can deliver electricity, it may be either a primary battery or a secondary battery. If a battery can be recharged and will recover its initial open circuit voltage after discharging, it is called a rechargeable battery. A secondary battery is always a rechargeable one, but a rechargeable battery is not necessarily a secondary one.

Some battery systems can be used as primary as well as rechargeable batteries. However, a rechargeable battery has generally smaller energy density than its corresponding primary battery because a discharge run of a rechargeable battery should be terminated well before its theoretical energy density is reached in order to attain a good rechargeability. For example, the energy densities of a primary and a rechargeable zinc/silver oxide (Zn/AgO) battery are 120 and 80 Wh/kg, respectively [38]. Owing to the unrivalled electronegativity and lightness of lithium, the lithium batteries generally deliver relatively large single-cell voltages and consequently relatively high energy densities. This makes the research and development of lithium batteries particularly attractive for practical applications.

However, there are two main problems which limit the use of metallic lithium in rechargeable batteries, i.e. the short life cycle due to the irreversible electrochemical reactions at the metallic lithium anode, and the safety issue due to the very high reactivity of lithium with air or water, which is a direct consequence of the high potential of the lithium. The problems have partly been solved by the use of so-called four-volt cathodes and the development of so-called lithium-ion rechargeable batteries. Currently four-volt cathodes are made of LiCoO₂, LiNiO₂, or LiMn₂O₄. Lithium batteries (with metallic lithium as the anode) are working at about 4 V after extraction of Li from these cathodes upon charging [39]. The materials are able to accept lithium again in the charged state and, therefore, called intercalation compounds. In addition, it has been shown that a lithium metal anode can be replaced with a lithium-based alloy such as Li-Al [40-43], LiCu₂Sn [44,45] or a material into which Li can be easily inserted and extracted, such as the most well-known C₆₀Li₆ [46-48] and can also be referred to as intercalation compounds. They are found to have a potential difference less than 1 V versus Li. Therefore, a cell comprised of a four-volt cathode and such an alloy or a lithium intercalation anode has an OCV around 4 V. Within such a
Figure 2. Schematic representation of a lithium-ion battery.

cell, only lithium ions, rather than metallic lithium, are involved within the internal circuit (both electrodes plus electrolyte) during charge-discharge, while electrons only move along the external circuit. Hence, they are referred to as rechargeable lithium-ion batteries.

To illustrate the electrochemical reactions taking place in a lithium-ion battery more clearly, the cell C (graphite)/LiCoO₂ is taken as an example (Figure 2).

During charge,
\[
\text{Cathode, LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x \text{Li}^+ + x e^- \quad (1)
\]
\[
\text{Anode, } \text{C}_6 \text{(graphite)} + x \text{Li}^+ + x e^- \rightarrow \text{Li}_x\text{C}_6 \quad (2)
\]

During discharge,
\[
\text{Cathode, } \text{Li}_{1-x}\text{CoO}_2 + x \text{Li}^+ + x e^- \rightarrow \text{LiCoO}_2 \quad (3)
\]
\[
\text{Anode, } \text{Li}_x\text{C}_6 \rightarrow \text{C}_6 \text{(graphite)} + x \text{Li}^+ + x e^- \quad (4)
\]
\[
\text{Total, } \text{C}_6 + \text{LiCoO}_2 \leftrightarrow \text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{CoO}_2 \quad (5)
\]

Note that, to achieve a long cycle life, a practical battery seldom reaches the fully-charged composition CoO₂.

For some applications such as in the chips industry for miniaturization of electronic devices and for implantation in "smart" credit cards, thin-film lithium batteries or sometimes-called microbatteries are required. In these batteries, all the components including the cathode, the electrolyte, and the anode have to be made in thin-film form. Therefore, thin-film techniques play an important role in this field.

Dye-sensitized Solar Cells

After absorption by the atmosphere natural sunlight consists of mainly photons in visible range, i.e. 430-700 nm (corresponding to 2.88-1.77 eV) together with a small fraction of photons in infrared and ultraviolet range. In order to convert the solar energy into electricity, several types of solar cells have been used in which a semiconductor is usually a key component. These solar cells may distinguish from each other either by the types of semiconductors used or by the working principle to convert the solar energy. Up to now, solar cells made from single crystalline, polycrystalline, and amorphous Si have dominated the market owing to decades of scientific research and development. Basically, when such a solar cell is subjected to sunlight, absorption of photons with energy exceeding the bandgap of the semiconductor results in the separation of holes and electrons into valence band and conduction band, respectively. Many semiconducting materials such as TiO₂, ZnO and SnO₂ have wide bandgaps (>3 eV) beyond the photon energy of visible light. They cannot be simply used in above mentioned solar cells.

One solution to the wide-bandgap problem lies in the use of sensitizers to reduce the optical absorption threshold [49,50]. With the help of suitable sensitizing chromophores, liquid-junction photovoltaic (PV) devices can be constructed [51,52]. However, the efficiency of these PV devices is usually very low due to the fast recombination of electron-hole pairs in the polycrystalline semiconductors. The major breakthrough in this type of solar cells, i.e. dye-sensitized solar cells, has been made in the past decade when thin layers of a nano-structured oxide semiconductor sensitized by organic dyes were used [53,54]. The efficiency of the solar cells has been raised to 10-12% due to the large surface-area-enhancement factor of 1000 by using porous nanostructured semiconducting electrodes. The structure and the working principle of a dye-sensitized solar cell are schematically shown in Figure 3 and Figure 4. It consists of a negative electrode, a liquid electrolyte medium, and a positive electrode. The negative electrode is made from a porous layer of nano-sized powders of an oxide semiconductor (e.g. anatase TiO₂ here) that is coated on a transparent conducting glass. A monolayer of organic dye molecules (e.g. chlorophylls, porphyrins, rose bengal, or ruthenium bipyridyl complexes) is adsorbed on the powder particles. The positive electrode can simply be a transparent conducting glass. The liquid electrolyte containing a redox couple (e.g. I⁻/I³⁻) provides an intimate electrical contact to the two electrodes.

In this solar cell structure, a so-called Schottky barrier is formed at the interface between the semiconductor particles and the liquid electrolyte, resulting in band bending of the semiconductor and the build-up of an electric field (Figure 4). The presence of this electric field is responsible for the PV effect. When the sunlight irradiates the cell from either side of the transparent electrodes, the dye molecules (D/D⁻) are excited into a higher energy state (D⁺/D⁻) by absorbing photons. Sub-
the system at the negative electrode, where they reduce oxidizing species (I in Figure 3) of the redox couple. Simultaneously, the oxidized dye (D') is regenerated by acceptance of an electron from the reducing species (I) of the redox couple. This completes the charge transport and transfer in the total circuit.

Obviously, the preparation of the porous nano-sized semiconductor layer is crucial for the success of this type of solar cells. Naturally, instead of a layer from nanoparticles, other nanostructured semiconductor layers should also work similarly as long as large surface areas are obtained. Such a nanostructure has been achieved by a CVD technique in our laboratory, as will be shown below.

**Solid Oxide Fuel Cells (SOFCs)**

Fuel cells are electrochemical devices for the continuous production of direct-current electric power by electrochemical reaction of a fuel with an oxidant. They belong to the family of primary batteries. Therefore, similar to any other batteries, each fuel cell consists of at least a cathode, an anode, and separated by a gas-tight electrolyte. Depending on the type of electrolyte used, they are classified into five types, (i) alkaline fuel cell (AFC), normally with KOH as electrolyte; (ii) phosphoric acid fuel cell (PAFC), with H₃PO₄ as electrolyte; (iii) molten carbonate fuel cell (MCFC), with e.g. Li₂CO₃/K₂CO₃ (62/38) mixtures as electrolyte; (iv) solid polymer fuel cell (SPFC), with a proton conducting membrane as electrolyte; and (v) solid oxide fuel cell (SOFC), with yttria-stabilized zirconia (YSZ) as state-of-the-art electrolyte. The AFC, PAFC, and SPFC operate at low temperature ranging from 60 to 200°C, while the MCFC operates at about 650°C, and the SOFC at about 1000°C.

The SOFCs are all-solid-state devices for the direct conversion of the free energy variation due to the oxidation (“burning”) of a fuel gas into electric energy. A SOFC using hydrogen (H₂) as the fuel and oxygen (O₂) as the oxidant is schematically shown in Figure 5. Catalysts (e.g. porous or mesh platinum) are usually used on both electrodes and are indicated in the figure. At the cathode (e.g. La₀.₆Sr₀.₁₄MnO₃₋ₓ) oxygen accept electrons coming from the external circuit and form oxygen ions (O²⁻). The oxygen ions diffuse through the oxygen ion-conducting electrolyte (e.g. YSZ) to the anode (e.g. Ni/YSZ cermet), where they react with hydrogen to form water vapor and simultaneously electrons are released and supplied to the external circuit. The electrochemical reactions can be written using the Krgrer-Vink notation as follows,

\[ \frac{1}{2} O_2(g) + V_O + 2e^- \rightarrow O_2^- \]

Figure 3. The structure of a dye-sensitized solar cell.

Figure 4. The working principle of a dye-sensitized solar cell.
anode, $H_2(g) + O_2^\circ \rightarrow H_2O(g) + V_0 + 2e^-$ 

(7)

cell, $H_2 + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$

(8)

The cathodes and anodes are usually porous and in thin-film forms so that the fuel gas and oxidant gas (oxygen or air) can easily be adsorbed and subsequently reach the interfaces with the electrolyte. This electrolyte must be gas-tight in order to prevent direct reactions of the fuel and oxygen and even explosion. The electrolyte is preferably thin in order to reduce the internal resistance of the cell. Therefore, again, thin-film techniques play a key role in the fabrication of the SOFCs.

**Thin-film Techniques**

**Electrostatic Spray Deposition (ESD)**

The Electrostatic Spray Deposition (ESD) technique was first developed in our laboratory about ten years ago for the preparation of thin films of LiMn$_2$O$_4$ and YSZ [55,56]. Recently, it has been developed further and applied extensively to deposit a variety of functional ceramic materials, especially those for energy conversion and storage [12-27,57].

**Working Principle**

If a liquid is forced to flow through a small metal nozzle that is subjected to an electric field, the liquid will leave the outlet of the nozzle in different forms or modes due to different electrohydrodynamic mechanisms. These modes include among others dripping mode, cone-jet mode, and spindal mode [58]. In which mode a spray operates depends mainly on the electric potential ($\varphi$), the electrical conductivity ($\sigma$), and the surface tension ($\gamma$) of the liquid influence the mode as well [59]. If a spray of a precursor liquid is generated electrostatically and used for film deposition, the basis of the ESD technique has been set. For film deposition, the cone-jet mode is the most suitable because it is a continuous mode and the formation of homogeneous fine spray droplets is possible. In this mode, the liquid takes up a conical shape with 49.3° half-angle at the outlet of the nozzle. In memory of G. I. Taylor's great contribution to the study of liquid behaviour under an electrostatic field [60], this cone is referred to as a Taylor cone. Moreover, a jet of the liquid is extended from the Taylor cone and breaks up into fine droplets that can be subsequently directed to a heated substrate to form thin films.

**Set-up**

An ESD set-up may be designed with either a vertical or a horizontal configuration. Similar deposition results can be obtained with both configurations, but the vertical configuration is preferred as it reduces the equipment size. The schematic view of a vertical set-up is shown in Figure 6. The set-up consists mainly of the following parts, (1) an electrospraying unit, including a high DC voltage power supply capable of providing voltages up to 15-30 kV, a nozzle made of a metal (e.g. stainless steel) needle with a diameter usually smaller than 1.0 mm, a substrate holder mounted on an x-y table, whose motion is controlled by a computer, and a high-intensity halogen lamp (not shown in Figure 6); (2) a liquid feeding unit, including a liquid container, and a liquid-driving mechanism which can be a pump, hydraulic pressure as shown in Figure 6, or compressed air; (3) a temperature control unit, including a heating element, and a temperature controller; and (4) other supporting elements, including electronic connection cables suitable for high voltage operation, a digital ruler to measure the nozzle-to-substrate distance, and a drain collection container.
Precursors

One of advantages of the ESD technique is the extremely large choice of precursors. In our studies, a variety of chemicals has been used as precursors, such as hydrated metal nitrates (e.g. Co(NO$_3$)$_2$·6H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O), hydrated acetates (e.g. Li(CH$_3$COO)·2H$_2$O, Co(CH$_3$COO)$_2$·4H$_2$O), chlorides (e.g. SnCl$_4$, TiCl$_4$), metalorganic compounds (e.g. Ti[OCH(CH$_3$)$_2$]$_4$, Zr(O$_2$C$_2$H$_5$)$_4$), and even non-metal compounds (e.g. H$_3$BO$_3$, P$_2$O$_5$). The basic considerations here are that, (1) a precursor must be relatively soluble in an alcoholic solvent, (2) it must be decomposed and converted into a desired product at the deposition temperature, and (3) no contaminant or impurity will be introduced to the deposited thin films.

It should be addressed that sols instead of solutions can be used as precursors in ESD as well, i.e. a modified ESD technique which we referred to as electrostatic sol-spray deposition (ESSD) [23].

Processes During ESD

There are several physical and chemical processes involved in the ESD of layers, occurring either sequentially or simultaneously. Possible sequential steps are (viz. Figure 7) described as follows [13].

1. The formation of spray containing fine droplets of the precursor liquid, preferably working in the cone-jet mode.

2. Droplet transport from the nozzle to the substrate surface accompanied by the evaporation of solvent and possible disruption of the droplets.

3. The impingement of the droplets on the substrate surface, preferentially on the sites with relatively large (local) surface curvatures owing to the relatively large (opposite) charge densities there.

4. The discharge of the impinged charged droplets, the spreading of droplet solution on the surface, the penetration of the solution into the being-formed layer, and a drying process.

5. The surface diffusion of solid particles, and chemical reactions between these particles.

Generally speaking, all these processes can influence the morphology of the deposited layer. Among many deposition parameters, substrate temperature and the composition of the precursor liquid are the main factors determining the layer morphology [13]. The higher the substrate temperature and the lower the boiling-point of the solvent, the more porous layers are deposited. Even unique reticular structures have been obtained by using suitable precursor solutions and substrate temperatures [14,19].

Deposition Kinetics

The deposition kinetics of the ESD is rather simple. At a sufficiently high substrate temperature (or deposition temperature) the rate determining step of film growth by ESD is usually the feeding of precursor liquids rather than the steps taking place on the substrate surface (diffusion, solid state reactions, etc.) because (1) there is a proportional relationship between the weight of a deposited layer and the deposition time, and (2) the deposition rate is independent of the substrate temperature as long as the temperature is high enough to decompose the precursor solutes. This is a clear indication of a high deposition efficiency of this technique. Therefore, the film growth rate is determined by the concentration as well as the feeding rate (i.e. flow rate) of the precursor liquid. Based on our study of LiCoO$_2$ deposition, the maximal growth rate of a dense film can be as high as 12 µm/h.

Chemical Vapor Deposition (CVD)

The CVD technology is well-established and widely used in micro-electronics and materials science and engineering. In CVD processes, usually more than one gaseous precursor is carried by a carrier gas to a deposition zone where chemical reactions between these precursors take place on or above the surface of a substrate to form a thin film. The advantages of CVD are relatively cheap equipment, relatively easy up-scaling, and a large number of available precursors. Disadvantages are difficulties in controlling the compositions of thin films of ternary and more complex materials and achieving good reproducibility. It should be mentioned that in some PVD processes such as reactive sputtering, chemical reactions are also involved in the film deposition. They may be regarded as a special case of CVD.

Set-up

A CVD set-up contains mainly three parts, (1) a gas-line unit, including precursor evaporators, gas pipelines,
valves, and flowmeters; (2) a reactor unit, including a space for deposition reactions to take place, substrates mounted on a substrate holder, and the equipment for providing activation energy (e.g., a furnace); and (3) an exhaust unit, including filters, cold traps, and gas scrubbers. In addition, a rotation pump (or together with other pumps) is usually equipped to provide vacuum conditions and to better control the total gas flow. As an example, a scheme of the CVD set-up for TiS₂ deposition is shown in Figure 8, where TiCl₄ is the titanium precursor, H₂S gas or a liquid sulfur compound (e.g., C₆H₅SH) is the sulfur precursor.

Precursors
In principle, a gaseous reactant or a liquid or solid with sufficiently high vapour pressure can be used as CVD precursor to form solid products via one or more chemical reactions with other reactants. The precursors should also be (a) stable between evaporation and decomposition temperatures, and (b) not leaving contaminating species in the solid deposit after decomposition. Gaseous precursors are preferred because their integration in the gas line is easy. Volatile liquid precursors are also convenient but solids, particularly those having low vapour pressures, require special treatment to evaporate and to carry to the reactor. In practice, following chemicals are usually used as precursors,

I. Halides.—Examples are AlCl₃, AlBr₃, BCl₃, CCl₄, SiCl₄, TiCl₄, ZrCl₄, and VCl₄.

II. Carbonyls of certain refractory transition metals and a few noble metals.—Examples are Cr(CO)₆, Ni(CO)₄, Fe(CO)₅, Mo(CO)₆, W(CO)₆, Ru(CO)₅, Os(CO)₅, Fe₂(CO)₉, Mn₃(CO)₁₂, Re₂(CO)₁₀, Ir₂(CO)₉, Ru₃(CO)₁₂, Co₃(CO)₁₂, Rh₃(CO)₁₂, and Ir₃(CO)₁₂.

III. Carbonyl halides or nitrosyls.—Examples are Ru(CO)Cl₂, Os(CO)Cl₂, Rh₂Cl₆, RhCl₃(NO)(CO)₃, IrCl₃(CO)₃, PtCl₃, PtCl₃, and CoCl₃(NO)(CO)₃.

IV. Hydrides.—Examples are AsH₃, B₃H₆, PH₃, SiH₄, GeH₄, SbH₃, SeH₄, H₂S, and NH₃.

V. Metal organic compounds.—Examples are Al(CH₃)₃, As(CH₃)₃, In(CH₃)₃, Mg(C₂H₅)₂, Mg(C₆H₅)₂, Pb(CH₃)₄, Si(CH₃)₄, Sn(CH₃)₄, Sn(C₂H₅)₄, and Zn(C₂H₅)₂.

VI. Alkoxides.—Examples are Si(OC₂H₅)₄, Ti(OC₂H₅)₄, and Zr(OC₂H₅)₄.

VII. Acetylacetonates (acac) and derivatives.—Examples are acetylacetonates of Ba, Ca, Ce, Cr, Co, Cu, In, Fe, Pb, Li, Mg, Mn, Ni, Pd, Pt, the rare earths, Rh, Sc, Sr, Ag, V, Y, Zn, and Zr.

CVD Classifications
CVD can be classified into many types according to different process conditions,
I. Reactors.—There are two types of CVD, (i) cold-wall CVD, if reactors are heated internally, and (ii) hot-wall CVD, if reactors are heated externally.

II. Activation methods.—One distinguishes several ways of activation of the chemical reactions. Among them are (i) thermally-activated CVD (TA-CVD), if resistive heating alone is used for activation, (ii) plasma-enhanced CVD (PECVD), if an electrical or microwave plasma is applied, (iii) laser CVD (LCVD), if a laser is applied, and (iv) photo-CVD, if a lamp is used to generate the photons. These modes of activation are used in order to reduce deposition temperatures compared to TA-CVD.

III. Pressures.—There are two types, (i) low pressure CVD (LPCVD), if deposition occurs under reduced pressures, and (ii) atmospheric pressure CVD (APCVD), if deposition occurs at atmospheric pressure.

IV. Precursors.—Metal organic CVD (MOCVD) using metal organic precursors is frequently used, because a wide variety of precursors is available to date. In addition, MO-CVD requires moderate deposition temperatures.

Processes During CVD [61]

Figure 9 presents the eight elementary steps in CVD. They are described briefly as follows.

1. and 8. Bulk reactant gas flow into the reactor and flow of excess reactants and gaseous reaction products out of the reactor.

2. Reactions of precursors in the gas phase to form either reactive gases or solid products (homogeneous nucleation).

3. and 7. Diffusion of reactants and gaseous waste products through the stagnant boundary layer, respectively.

4. and 6. Adsorption of reactants on the surface and desorption of gaseous products, respectively.

5. Diffusion and chemical reaction of surface species to form the product, including nucleation and crystallite growth.

Deposition Kinetics

In CVD kinetics, the film growth rate and morphology are determined by the related rates of the elementary steps mentioned above. According to the rate limiting step(s), the CVD process may operate in three different regimes, diffusion-limited regime, feed-rate limited regime, and surface-reaction limited regime.

Diffusion-limited regime.—If diffusion (step 3 or 7 in Figure 9) is slow compared to the slowest surface reaction step, CVD is operating in the diffusion-limited regime because the diffusion determines the overall deposition rate. High pressures (e.g. atmospheric pressure), high temperatures, and small flow rates favour this regime. The growth front is unstable and usually rough surfaces are formed.

Feed-rate limited regime.—If bulk reactant gas supply flow is slow with respect to both diffusion (steps 3 and 7) and chemical reaction steps (steps 2, 4-6), CVD is operating in the feed-rate limited regime since the overall deposition rate is determined mainly by the mass flow rate of input reactant(s). This regime occurs also at high temperatures. Dense crystalline films are usually formed.

Surface reaction limited regime.—If surface steps (4-6) are slow compared to the transport steps (1-3, 7-8), CVD is operating in the surface reaction limited regime since the overall deposition rate is determined by the slowest surface step. Low pressures, low temperature, and high gas velocity favour the appearance of this regime. Dense amorphous films are usually formed under these conditions. The growth front is very stable and smooth surfaces are obtained.

Besides, when more than one (independent) precursors is used simultaneously, the CVD process may operate in a mixed-reactivity regime to form special film morphologies. Actual fractal-type nanostructured TiO2 films have been obtained in our laboratory (see next section). Furthermore, in the feed-rate limited regime the solid product may be formed as particles through homogeneous nucleation in the gas phase (step 2) if high supersaturation is reached in the gas phase rather than through the surface steps (4-6). This results in either powder synthesis or so-called particle-precipitation aided CVD (PP-CVD) [4,7,62,63], if a temperature gradient exists between the gas phase and the substrate, the substrate being cooler than the gas phase.
Thin-film Materials Prepared by ESD and CVD

Battery Materials
LiCoO$_2$ and LiMn$_2$O$_4$ are the most widely used cathode materials in commercial rechargeable lithium-ion batteries. Our study on the ESD of LiCoO$_2$ thin films has shown that totally five different layer morphologies can be obtained with suitable deposition conditions [13]. Four of them are shown in Figure 10. They are, (i) dense layer (Figure 10a); (ii) dense layer with incorporated particles (Figure 10b); (iii) porous top layer with dense bottom layer (Figure 10c); and (iv) fractal-like porous layer (Figure 10d). The fifth morphology is the reticular porous structure as shown in Figure 11. Of these five morphologies, the fractal-like porous layers are not suitable to be used as cathodes in batteries because of their poor mechanical strength. The other four have proved to be useful although the reticular structures seem to be the best [18].

The ESD has also been used to prepare thin films of other battery materials such as LiMn$_2$O$_4$, Li$_2$O-BPO$_4$ [17], and Li$_3$PO$_4$ [64].

In addition to the above-mentioned four-volt cathode materials LiCoO$_2$ and LiMn$_2$O$_4$ prepared by ESD, CVD techniques are also used to prepare films of the electrode material TiS$_2$. The scanning electron micrograph of a TiS$_2$ film made by the APCVD technique is shown in Figure 12.

Organic Solar Cell Materials
The most useful electrode material for organic solar cells is a nanostructured anatase TiO$_2$ thin film. Both ESD and CVD have been used to prepare nanostructured TiO$_2$ films [19,65]. The CVD layers reveal very inter-

Figure 10. Four types of layer morphologies obtained in ESD LiCoO$_2$ films, (a) dense layer; (b) dense layer with incorporated particles; (c) porous top layer with dense bottom layer; and (d) fractal-like porous layer.

Figure 11. A reticular LiCoO$_2$ layer made by ESD.

Figure 12. A TiS$_2$ layer made by APCVD with the set-up shown in Figure 8.
esting morphologies which look like trees, bushes, and grasses on a micro-scale. They are all anatase phase which is desired for solar cell operation. Two of such layers are shown in Figure 13. All of these morphologies can only be formed by using titanium tetrachloride (TiCl₄) and titanium isopropoxide (Ti(OCH(CH₃)₂)₄) simultaneously together with O₂ and H₂O as precursors in the temperature range between 300 and 400°C. It is believed that the CVD of these layers occurs in a mixed-kinetics regime, i.e. the diffusion-limited regime for TiCl₄, and the surface reaction limited regime for Ti(OCH(CH₃)₂)₄. The dye-sensitized solar cells constructed with these TiO₂ layers as semiconductors exhibit photovoltaic effects.

Another nanostructured semiconductor ZnO film for organic solar cells has been prepared by electrostatic sol-spray deposition (ESSD). The scanning electron micrographs of such a ZnO film are shown in Figure 14.

The nano-sized (about 100 nm) particles can be clearly seen from Figure 14b.

**SOFC Materials**

As mentioned before YSZ is the state-of-the-art electrolyte for SOFCs operating at about 1000°C. The relatively small ionic conductivity of YSZ limits the effort to lower the working temperature down to the medium temperature range of 600 to 800°C. One has to use other electrolyte materials with higher ionic conductivities for this purpose. Gadolinia-doped ceria (GCO) is suggested as the most promising alternative. However, GCO exhibits a significant electronic conductivity in a reducing atmosphere [66]. An obvious solution to this problem is coating a thin, under reducing atmosphere stable and purely ionically conducting, YSZ layer on top of GCO. Figure 15 shows such a composite structure made by ESD [16]. The ESD has also been used to prepare Tb-doped YSZ and Ti-doped YSZ coatings on a
YSZ substrate [57]. In fact, the Ti-YSZ || YSZ || Tb-YSZ constitutes a single SOFC cell.

Summary

At the beginning of the 21st century energy conversion and storage are of paramount importance for the sustainable development of human society. Rechargeable lithium batteries, organic solar cells, and solid oxide fuel cells (SOFCs) are chosen to be the best devices to deal with this problem. Among the thin-film techniques, the novel technique electrostatic spray deposition (ESD) and the conventional technique chemical vapor deposition (CVD) may play an important role in the manufacture of these energy-related conversion and storage systems.

Acknowledgments

The authors would like to thank Dr. E. M. Kelder, Dr. A. Goosens and Dr. A. A. van Zomeren, C. H. Chen would like to express thanks to the 100 Talents program of Academia Sinica and National Science Foundation of China (grant no. 50372064).

References