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Functionalization of Particles by Atomic Layer Deposition for Energy Storage Applications

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Resumen

Los materiales en forma de pequeñas partículas son uno de los principales ingredientes en diversos procesos y aplicaciones industriales. Generalmente, estos materiales están clasificados en función de su tamaño y sus funcionalidades: mientras que las partículas en tamaño milimétrico son usadas principalmente en la industria alimentaria, farmacéutica y en sectores de limpieza y construcción, aquellas de tamaño micrométrico y nanométrico son generalmente empleadas en aplicaciones de almacenamiento de energía, catálisis o electrónica.

Las investigaciones pioneras han centrado su atención en partículas de tamaño micrométrico y nanométrico, debido a sus propiedades relevantes con relación a su pequeño tamaño y su gran área superficial. La funcionalización de dichas partículas podría mejorar considerablemente su comportamiento y otorgarles valor añadido. Entre los muchos métodos de funcionalización, cabe destacar la generación de partículas “core-shell”, ya sea encapsulando las partículas con un recubrimiento, o bien depositando pequeñas “islas” de un determinado material en su superficie, protegiéndolas, activándolas químicamente, o modificando su comportamiento inicial. En la actualidad, existen diversas técnicas de recubrimiento, las cuales puedes clasificarse principalmente en dos grupos: técnicas de recubrimiento en seco y técnicas de recubrimiento en húmedo. Los métodos de recubrimiento en húmedo se caracterizan principalmente por emplear disolventes durante el proceso de revestimiento. Aunque su aplicación es sencilla, no muchos procesos industriales hacen uso de esta tecnología debido a varios inconvenientes. Entre ellos, destaca el proceso de secado de los disolventes residuales, que requiere largos tiempos de procesado, genera una gran cantidad de residuos y consume mucha energía. Es por ello que en los últimos años, los métodos de recubrimiento

en seco han atraído mucho interés a la hora de depositar películas delgadas. Su ventaja principal reside en el control preciso del espesor del recubrimiento generado, incluso a escala nanométrica. Una de las tecnologías más conocidas en este campo es la deposición química de fase vapor (*Chemical Vapor Deposition*, o CVD), aunque posteriormente se desarrolló una técnica derivada del CVD conocida como deposición de capa atómica (*Atomic Layer Deposition*, o ALD), que permite una mayor precisión en el control del espesor y en la composición de la película depositada.

La aplicación de ALD en diferentes campos, incluyendo microelectrónica, sistemas de almacenamiento de energía y aplicaciones biológicas, ha adaptado esta tecnología a substratos con una gran variedad de formas geométricas; desde substratos planos hasta materiales en forma de partículas. A la hora de recubrir partículas mediante ALD se pueden encontrar dos tipos de reactores en función de cómo se manipulen las partículas: los reactores de partículas estáticas y los reactores de lecho fluidizado. Los reactores de partículas estáticas se utilizan para recubrir pequeñas cantidades. No son adecuados para grandes cantidades, ya que las partículas quedarían menos recubiertas a medida que aumenta la profundidad del lecho. Por otro lado, los reactores de lecho fluidizado mantienen las partículas en constante movimiento durante el proceso de recubrimiento, y por tanto son aptos para procesar mayores cantidades de partículas. En este tipo de reactor se introduce un gas inerte por su parte inferior provocando un movimiento del lecho de partículas similar al de un fluido, manteniéndolas en suspensión y recubriéndolas homogéneamente. Este tipo de reactor permite recubrir grandes cantidades de partículas mediante ALD, y puede ser escalado para su uso en aplicaciones industriales.

La aplicación de la tecnología ALD para la fabricación y/o recubrimiento de componentes de sistemas de almacenamiento de energía se ha investigado intensamente en los últimos años, ofreciendo grandes avances tecnológicos. Las formas más convencionales de producción de energía, principalmente mediante el uso de combustibles fósiles, están siendo sustituidas por tecnologías de producción de energías renovables, que requieren sistemas de almacenamiento de energía eficientes y fiables. Las baterías son uno de los sistemas de almacenamiento de

energía más importantes, gracias a su excelente densidad de energía y tasa de liberación de la misma. Las baterías de iones de litio (*Lithium-Ion Batteries*, LIB) son actualmente el tipo de batería más común en una amplia variedad de aplicaciones. Estas baterías dominan el mercado de la electrónica portátil y la electrificación del transporte, proporcionando una excelente ciclabilidad, una larga vida útil y una alta estabilidad de la densidad de energía, llegando a una densidad de energía de 300 $\mathrm{Wh \cdot kg^{-1}}$. Sin embargo, su capacidad específica limitada y los materiales catódicos empleados han llevado a los investigadores a buscar otros tipos de sistemas de baterías alternativas.

Las baterías de litio-azufre (*Lithium-Sulfur*, Li-S) se han convertido en una alternativa prometedora debido al fácil manejo y extraordinarias propiedades del azufre como material catódico activo. Concretamente, las baterías de litio-azufre muestran una densidad de energía teórica de 2600 $\mathrm{Wh \cdot kg^{-1}}$ (mucho más alta que la de las baterías de ion litio convencionales). Además, el azufre es ecológico y uno de los elementos más abundantes en el mundo. Sin embargo, las baterías Li-S presentan varios inconvenientes, entre los que destacan la naturaleza aislante del azufre, el efecto de cambio de volumen del cátodo entre la carga y la descarga, el 'shuttle effect' de los polisulfuros y el peligro de seguridad asociado al ánodo de litio. Todos estos inconvenientes han impedido la implantación de esta tecnología, y conducen a los investigadores a encontrar soluciones emergentes para el desarrollo de baterías de Li-S con alta densidad de energía, ciclabilidad y estabilidad a largo plazo. La aplicación de ALD en sistemas de almacenamiento de energía ha demostrado aportar muchas mejoras hasta el momento. De hecho, la deposición de ciertos materiales a escala nanométrica sobre los distintos componentes de una batería se ha erigido como una línea de investigación relevante en la mejora de la densidad de potencia y reversibilidad de las baterías de Li-S.

El objetivo de esta tesis se basa en el estudio y la comprensión de la generación de recubrimientos mediante ALD en materiales en forma de partículas, prestando especial atención a materiales aptos para dispositivos de almacenamiento de energía. Para ello, se han recubierto partículas de tamaño micrométrico y

nanométrico con óxidos metálicos, mostrando resultados prometedores y nuevas funcionalidades que no se habían observado con anterioridad.

En la primera parte de la tesis se realiza un estudio inicial de recubrimiento de partículas mediante ALD en un reactor de partículas estáticas. Para ello se recubren partículas de óxido de hierro (γ-Fe_2O_3) con dióxido de titanio (TiO_2), generando partículas "core-shell" de FeO_x-TiO_2. Este estudio demuestra que mediante la aplicación de ALD no solo se consigue recubrir las partículas, sino que, dependiendo de los reactivos (precursores) utilizados, también se pueden reducir químicamente para formar nanopartículas 'core-shell' de tipo Fe_3O_4-TiO_2. Este estudio demuestra que la elección del ligando apropiado del precursor de metal puede conducir a un enfoque novedoso de recubrimiento y reducción química de las partículas. En este caso, el ligando del precursor organometálico aplicado, $(CH_3)_2N^-$, desencadena la reducción del Fe^{3+} presente en el substrato (γ-Fe_2O_3), mientras se oxida y se recombina formando tetrametilhidrazina como subproducto de la reacción tal y como se muestra en la Figura I. Además, el catión del precursor también desempeña un papel importante, ya que cuanto mayor es su electronegatividad, más energía se requiere para liberar los ligandos, lo cual es condicionante para la recombinación de estos últimos. Por lo tanto, el diseño apropiado de precursores y la selección de substratos adecuados allanarán el camino para la formación de nuevos compuestos, mientras que el proceso ALD empleado permitirá un fácil escalado a nivel industrial de grandes cantidades de partículas, recubiertas y reducidas químicamente al mismo tiempo.

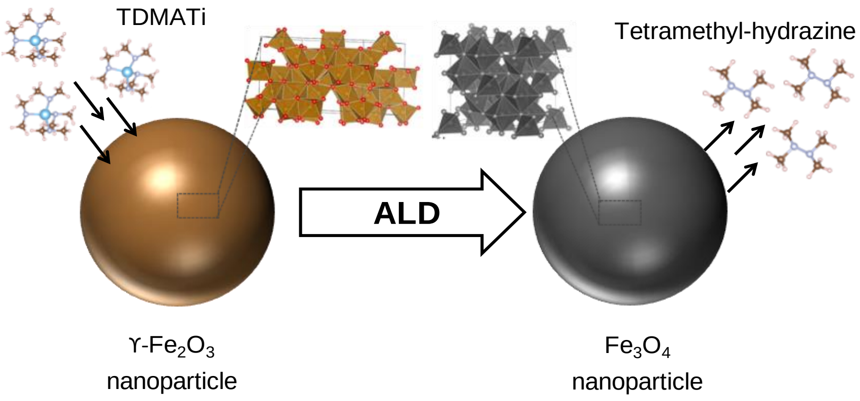

Figura I. Esquema del proceso de ALD desencadenado sobre las partículas de óxido de hierro.

En la segunda parte de la tesis se lleva a cabo el estudio de recubrimientos ALD en dispositivos de almacenamiento de energía, específicamente, en baterías de litio-azufre. Para ello, se realiza la modificación mediante ALD del material catódico de las baterías de Li-S haciendo uso de un reactor de ALD convencional (de partículas estáticas). Como parte del trabajo, se evalúan los parámetros óptimos de aplicación de la película delgada depositada por ALD sobre los electrodos de azufre. Los procesos de ALD se realizan a baja temperatura y se analiza el efecto del material depositado sobre el material catódico tras varios ciclos de deposición. Durante el proceso ALD se deposita óxido de aluminio o alúmina (Al_2O_3) sobre cátodos prefabricados (Figura II), mejorando la capacidad de los sistemas, principalmente a elevadas intensidades de corriente, es decir, a cortos tiempo de carga y descarga. Como resultado, se determina que aplicando únicamente dos ciclos de ALD a 85 ^{o}C, la capacidad de las baterías Li-S aumenta en un 13 % a bajas densidades de corriente (C/5), y en un 50 % a altas densidades de corriente (>1C).

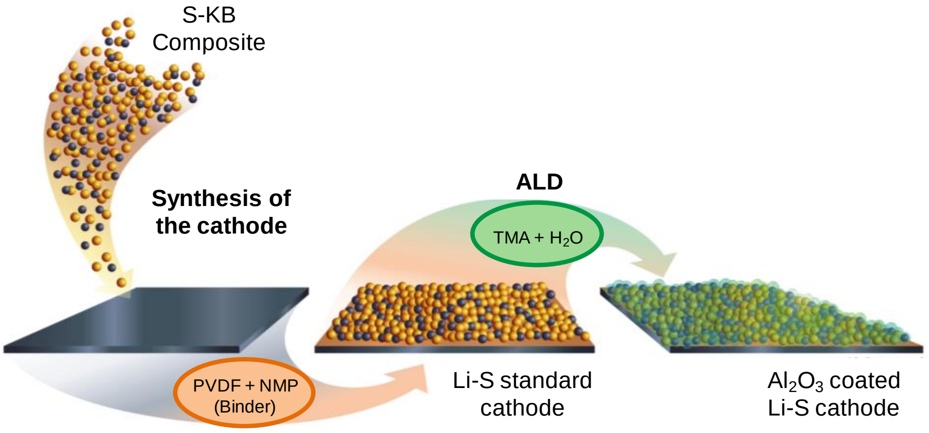

Figura II. Ilustración esquemática de la fabricación del cátodo de azufre y la posterior deposición de alúmina mediante el proceso ALD.

Finalmente, en la última parte de esta tesis, se emplea la técnica ALD como tecnología prometedora para el recubrimiento de composites de azufre-carbono presentes en baterías Li-S, mejorando su rendimiento. En este caso, las partículas compuestas de azufre y carbono son encapsuladas o cubiertas con "islas" de alúmina en su superficie por medio de la técnica ALD en un reactor de lecho fluidizado, que ofrece enormes ventajas para recubrir grandes cantidades de partículas. De esta forma se consiguen unir las partículas antes de la fabricación del cátodo, mejorando su cohesión. Los mejores resultados se obtienen después de aplicar 5 ciclos de ALD, aumentando la capacidad del sistema un 30 % a bajas densidades de corriente, y un 50 % a altas densidades de corriente, con respecto a una batería Li-S estándar. Además, gracias a la mejora morfológica proporcionada por la alúmina depositada (cohesión de partículas) la cantidad de azufre en los cátodos se puede duplicar, fabricando electrodos uniformes y sin grietas con mayor cantidad de azufre, imposibles de fabricar con el composite convencional. Estos nuevos electrodos exceden significativamente el rendimiento de los electrodos estándar, y aumentan la capacidad de las baterías litio-azufre en un 60 %.

Abstract

Powders are essential ingredients for many processes and applications. They are usually classified with relation to their particle sizes and functionalities. While particles in the millimeter size range are intensely used in alimentary, pharmaceutical, cleaning and construction sectors, micrometer and nanometer sized particles are commonly used in energy storage applications, catalysis and electronics.

Recent research has focused its attention on micrometer and nanometer sized particles due to the special properties arising from their high surface area to particle size ratio. Functionalization of those particles can greatly improve their performance. In this way, providing added value, like protecting and activating them, or changing their performance. Among the most promising ways of functionalization is the generation of core-shell particles through coating, or the deposition of islands or clusters on the surface of the particles. Nowadays, a wide variety of coating technologies are applied for this purpose. Among those coating technologies, chemical vapor deposition (CVD) became attractive in the recent years thanks to its great thickness control over the deposited coating. However, more recently, atomic layer deposition (ALD) was developed, allowing for ultimate thickness and compositional control of the deposited film in a large variety of geometries. The application of ALD in different fields, including microelectronics, energy storage systems or bioapplications, pushed the application of this technology to materials with diverse geometries, among those being particles. The need for coating powders resulted in the modification of reactors for carrying out ALD processes on such materials. The various reactors are distinct in the way of handling particles; namely, static particle reactors and fluidized bed reactors. While static particle reactors are used to coat small amounts of particles, fluidized bed reactors (FBR) can be used to coat large amounts of particles, allowing the scale-up of the technology for its use in industrial applications.

The application of ALD to fabricate or coat materials and components for energy storage systems is intensely investigated and it is beginning to deliver breakthroughs. Batteries belong to the most important energy storage systems thanks to their excellent energy density and energy release rate. Lithium-ion batteries (LIB) are currently the most common battery types for a large variety of applications. In fact, they offer a theoretical energy density of around 300 $Wh \cdot kg^{-1}$. However, their limited specific capacity and the precious cathode materials made researchers looking into other kinds of battery systems as alternatives. Lithium-sulfur (Li-S) batteries became a promising alternative due to their better handling and extraordinary properties of sulfur as cathodic material. Namely, it shows a theoretical energy density of 2600 $Wh \cdot kg^{-1}$, higher than that of Li-ion batteries. Moreover, sulfur is environmentally friendly and one of the most abundant elements in the world. However, Li-S batteries suffer from several drawbacks that affect their application and have driven researchers to develop solutions to enable the practical use of lithium-sulfur batteries and in this was increase the energy density and long-term stability. The application of ALD in energy storage systems has shown many improvements by now. In fact, the deposition of certain materials at the nanometric scale has many unique benefits for improving the behavior of Li-S batteries.

The objective of this thesis is the study and understanding of ALD coatings on powders, paying special attention to materials that can be used for energy storage devices. Micrometer and nanometer sized particles have been coated with metal oxides, which showed promising alterations and functionalities of powders that have not been observed before.

In the first part of the thesis, an initial study of coating particles by ALD is done. For this aim, iron oxide nanoparticles (γ-Fe_2O_3) are coated with titanium dioxide (TiO_2), generating FeO_x-TiO_2 core-shell nanoparticles. This study shows that the application of ALD not only coats the particles, but also, depending on the reactants (precursors) used, can also reduce them to form core-shell nanoparticles of Fe_3O_4-TiO_2. This study demonstrates that choosing an appropriate ligand of the metal source can unveil a novel approach to concertedly coat and reduce γ-Fe_2O_3 nanoparticles. Moreover, it is found that the more electronegative the cation of the precursor is, the more energy is necessary to release the ligands, which is conditional for their recombination. Thus, the appropriate design of precursors and selection of substrates will pave the way for numerous new compositions with more and improved functionalities.

In the second part of the thesis, the study of ALD on energy storage devices, specifically on lithium-sulfur batteries, is carried out. The modification of the cathode material of lithium-sulfur batteries is done by ALD in a conventional static ALD reactor. The optimal parameters for the ALD application to sulfur-based electrodes are evaluated. Aluminum oxide (Al_2O_3) is deposited on prefabricated cathodes, improving the capacity of the systems. In fact, applying only 2 ALD cycles at 85 °C increases the capacity of a lithium-sulfur battery by 13 % for low current densities and by 50 % for high current densities.

Finally, a promising powder coating technology is applied in order to coat sulfur-carbon composite powders of cathodes of lithium-sulfur batteries by ALD and in this way considerably improving the performance of those batteries. For this aim, a fluidized bed reactor was constructed. The best results are obtained after applying 5 ALD cycles of Al_2O_3, sufficient to increase the capacity of the system by 30 % at low current densities and by 50 % at high current densities, with respect to a standard battery system. Besides, the sulfur loading in the cathodes can be doubled thanks to the morphological improvement provided by the aluminum oxide. After coating, uniform and crack-free electrodes can be fabricated, which significantly exceed the performance of standard electrodes increasing the capacity of lithium-sulfur batteries by 60 %.

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Chapter 1

Introduction

This chapter gives an introduction to the main topics studied in this thesis, namely, particle technology and energy storage devices. The most relevant works developed so far are highlighted and its contribution to this thesis is explained.

1.1. Particle Technology

1.1.1. Background

Since the industrial revolution, powders have been essential parts of processes. Over 75 % of raw materials and around 50 % of products from the chemical industry fall into the category of particles.[1] Powders are very useful in a wide range of applications and processes. They are usually classified according to their particle size and functionality. Particles in the millimeter range are typically found in alimentary and pharmaceutical sectors, cleaning and construction. In contrast, micrometer- and nanometer-sized particles are more commonly used in energy storage systems, catalysis or electronics.[2], [3] Given the continuous need for improved materials for emerging applications, the research and development of powders for industrial use is growing considerably.

Recent research focuses on micrometer and nanometer scale particle-based technologies due to the special properties associated to the particle size and their large specific surface areas. Powders are intensely investigated for the production of drugs, food, electronics, catalysts and energy storage devices.[4]–[7] In many of those applications, functionalization of particles can greatly improve their performance. One of the most promising ways for improving the performance of particles is the application of a coating around them, forming core-shell nanoparticles as shown in Figure 1,[8] or even the deposition of islands or clusters of further materials on their surface, which brings additional functionalities to the powder, protecting them, activating or changing their performance.

For instance, a facile way to enhance the performance of catalysts was developed by Goulas *et al.*, who deposited platinum (Pt) clusters on TiO_2 particles to increase the active surface area of the Pt catalyst.[9] In another case, for energy storage applications, Beetstra and coworkers deposited a thin film of alumina on the cathode material of Li-ion batteries ($LiMnO_2$ nanoparticles). The film prevented the dissolution of the cathode material into the electrolyte, thus reducing the aging of the battery.[10]–[12] For various applications, SiO_2 nanopowders have been coated with TiO_2 to obtain core-shell nanoparticles.

Thanks to the synthesis of the core-shell structure with its increased surface area, the performance of the TiO_2 is enhanced, and therefore, its photocatalytic and optical properties.[13], [14] All those examples demonstrate that modifying properties of a material at nanometric or micrometric scales can result in macroscopic effects, improving the performance of the material for its final application.

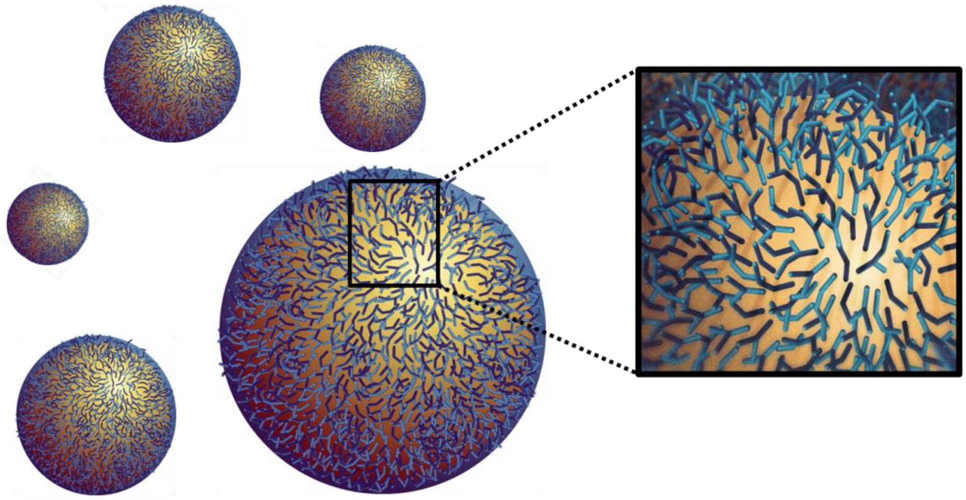

Figure 1. Core-shell particle structure with functional groups on a particle surface.

1.1.2. Coating Technologies

Coating of powders is a straightforward pathway to obtain functional particles. Indeed, in pharmaceutical, biological, food, energy or chemical industries, new materials are achieved by altering the surface properties and/or functionalities of fine particles.[15] Such surface modifications not only enhance the performance of particles, but also lead to the design of advanced and novel materials.

Coatings of particles are typically performed in either of the two ways, wet or dry. The wet particle coating technology, also known as liquid coating, involves solvents in the coating process. The coating agent is dissolved or suspended in a solvent and the resulting liquid is then progressively applied to the particles to be coated. Once the solvent is evaporated, it leaves behind a solidified coat on the particles. Not many industrial coating processes rely on the liquid coating technology, since the drying stage of solvent evaporation involves long processing times, generates large amounts of waste and considerably consumes energy.[16], [17] Besides, it is difficult to control the thickness of the deposited layers accurately and to assure that they are pinhole-free. Nowadays, the most prominent liquid coating techniques include spray drying,[18] sol-gel coating,[19] or fluid bed coating.[20]

As an alternative, gas-phase processes, also known as dry particle coating, have been developed for coating particles. In this case, the coating agent is dispersed in a gas and added to the system in form of solid particles. The adhesion of the particles to the substrate is achieved by van-der-Waals or electrostatic forces. The particle size of the coating agent is small enough to allow adhesive forces to generate thinner coatings with high accuracy.

A promising technology among the gas phase techniques is the chemical vapor deposition (CVD).[21], [22] This deposition technique is based on the simultaneous injection of two or more vaporized molecular reactants (precursors) into a reaction chamber, which will react with the surface of a substrate. Thus, a coating with a precise control over its thickness, even down to hundreds of nanometers, is deposited. During the 1960s, some initial experiments were done by Russian and Finnish researchers modifying CVD towards ultimate growth control, which marked the beginning of the era of atomic layer deposition (ALD), originally called atomic layer epitaxy (ALE).[23]

1.1.3. Atomic Layer Deposition

Atomic layer deposition (ALD) was intensely investigated and developed during the 1970s by Suntola *et al.* in order to produce high quality ZnS films for thin film electroluminescent (TFEL) flat panel displays.[24] In the early development stage it was called Atomic Layer Epitaxy (ALE), but it was soon realized that the films rarely show epitaxial growth, but were rather amorphous or polycrystalline. Therefore, this new deposition method was renamed to Atomic Layer Deposition

(ALD). The interest in this technology increased in 1990s, especially for microelectronic devices, but it was not until 2000s, when its use grew exponentially, triggered by the need of mass production of thin conformal coatings on high aspect ratio structures.[25]

Atomic layer deposition is a vapor phase thin film deposition technique to create conformal, pinhole free and homogeneous coatings. Similar to CVD, the process is based on the reaction between two or more gaseous precursors, whose surface chemical reaction results in the desired coating material.[26], [27]

In ALD processes one of the precursors, typically an organometallic, metal organic or metal halide molecule, acts as the metal source for the final coat. The other reactant is a counter precursor, like water, ozone, ammonia, hydrogen, or similar, which defines the nature of the deposited material; a pure element, an oxide or a nitride, etc. In ALD processes, the substrate is exposed to each precursor separately, which stands in contrast to CVD, where all precursors are supplied simultaneously to the reaction chamber. Consequently, ALD precursors do not react with each other in the gas phase, but the reaction takes place exclusively at the solid-gas interface. The high precision and controllability of the film growth of ALD is based on the self-terminating nature of the chemical reactions in each cycle. Once the surface is saturated with one precursor, no more reactions take place, even if excess precursor is available in the reaction chamber. The supply of the counter precursor will consequently react with only one layer of the bound primary precursor, thus assuring that a maximum of one monolayer of precursor is formed on the surface in each cycle.[26], [28]–[30]

Aluminum oxide or alumina (Al_2O_3), deposited using trimethylalumininum (TMA), $Al(CH_3)_3$, and water, H_2O, is one of the most studied ALD systems mainly for the following three reasons: (1) alumina can be deposited in a wide range of temperatures and pressures given by the high reactivity of TMA, (2) the deposition of alumina shows the typical linear layer-by-layer growth mechanism of ALD, and (3) it is a facile and economic process if compared to other ALD processes. Figure 2 illustrates the aluminum oxide (Al_2O_3) ALD deposition step by step, described as follows: (1) TMA pulse into the chamber. TMA molecules are supplied to the reaction chamber by an inert carrier gas, in this case, nitrogen. The molecules react with available functional groups on the surface of the substrate, usually hydroxyl groups (-OH), until surface saturation is reached. (2) Purging of the excess precursor and byproducts (methane, CH_4) out of the reaction chamber by an inert gas. Nitrogen gas is used to remove the excess of TMA and methane molecules. (3) Water vapor supply to the reaction chamber. Using nitrogen as carrier gas, water vapor molecules react with the chemisorbed TMA molecules on the substrate surface, generating the first layer of alumina. (4) Purging of the excess second precursor and the reaction byproduct, methane. This purging step completes an ALD cycle, eliminating the excess of water and methane from the reaction chamber. In each cycle, one alumina layer is deposited; enabling the control of the final thickness of the coating with the number of the applied ALD cycles.

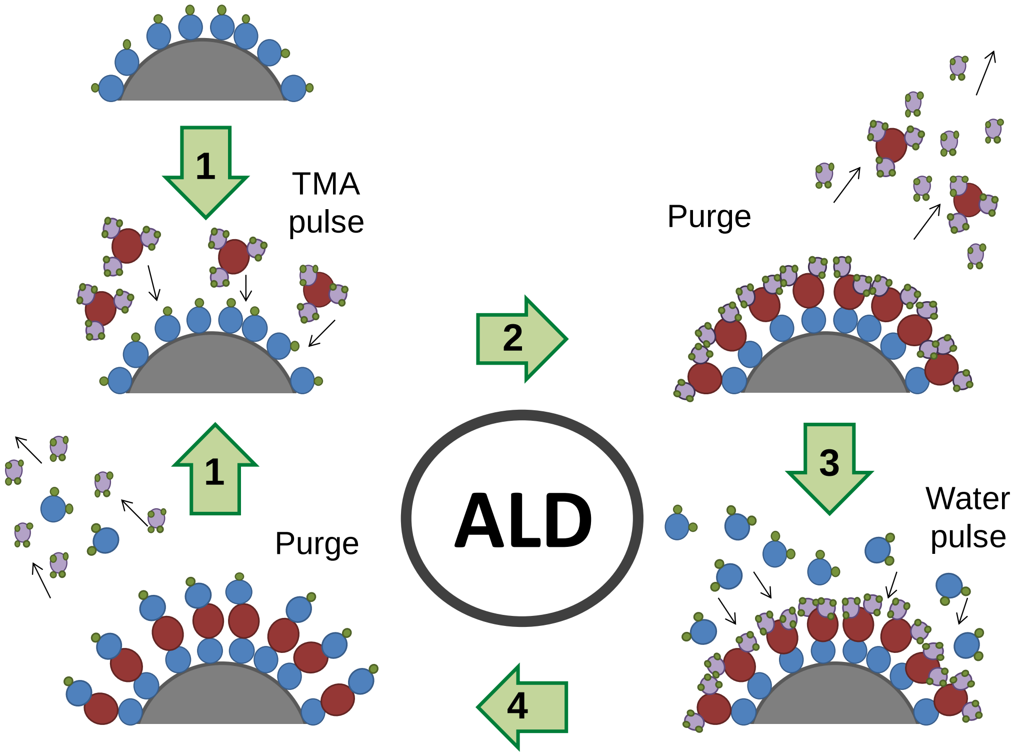

Figure 2. Schematic of the ALD deposition of Al_2O_3 using trimethylaluminium (TMA) and water as precursors.

ALD has been dominantly used to functionalize microelectronic devices, mainly in order to deposit homogeneous and pinhole free high-k dielectric coatings to prevent current leaks through the gate oxide.[31]–[33] More recently, its use was extended to many other applications, such as improved photovoltaic devices [34] or energy storage systems with increased electrochemical performance.[35], [36] The spread of ALD into different fields also brings about the evolution and adaptation of this technology towards substrates with a large variety of geometries, ranging from flat substrates to fine particles.[37]–[39]

The application of ALD to particles, being it continuous or semi-continuous, is increasingly attracting attention thanks to the high surface area of particles and thus their enhanced functionality in comparison to flat substrates. Meanwhile, a variety of reactors have been developed which are suitable for a deposition of nanometer-scaled layers on particles.[40]

1.1.4. ALD reactors for coating particles

The reactors for coating individual particles by means of ALD can be classified as a function of powder particle motion; namely, as static particle reactors and as agitated or fluidized particle reactors.

ALD on static particles

The first experiments for coating powders by ALD were conducted as early as 1992 by Suntola and coworkers in a flow-type ALD reactor, with the goal to obtain active catalyst materials. They used a top-flow reactor with static particles as substrates. The precursor gases were fed from the top of the reactor and then diffused through the bed of particles, before their excess and byproducts were purged through the pumping system connected to the bottom of the reactor.[41] Another experiment was carried out by Ferguson *et al.* in a pump-type ALD reactor at the University of Colorado in the early 2000s. Successful deposition of Al_2O_3 and SiO_2 on boron nitride (BN) particles for thermal applications was obtained using a sample holder as support for the particles.[42]

ALD reactors, where the deposition is carried out on static particles, have shown very good results for a wide range of coatings. However, experiments performed with such configuration are only applicable to small amounts of powders. Figure 3a schematizes such a process, where for small amounts of powders individual particles are coated by ALD, since the precursors reach each particle easily. However, if the amount of particles is large, only the upper fraction of the powder will be completely coated (Figure 3b), since those are rapidly exposed to the precursor gases, similar to a planar substrate. With increasing depth of the powder bed, the coating thickness will decrease, eventually leaving particles in the bulk of the bed uncoated. This effect can be attributed to two factors, namely i) the limited diffusion of the precursor into the bulk of the bed due to more tortuous diffusion paths and therefore longer exposure times required, and ii) the higher consumption of the precursor due to the much larger surface area of the particles if compared to flat substrates. Additionally, if the number of deposited ALD cycles is high, the lack of mobility of the particles will generate continuous and thick coatings, specially on the surface of the bulk, that act as a glue connecting and agglomerating particles to each other. Therefore, conformal coatings are successfully deposited on individual particles by ALD using this technique, but the nature of the set-up is not suitable for up-scaling.[43]

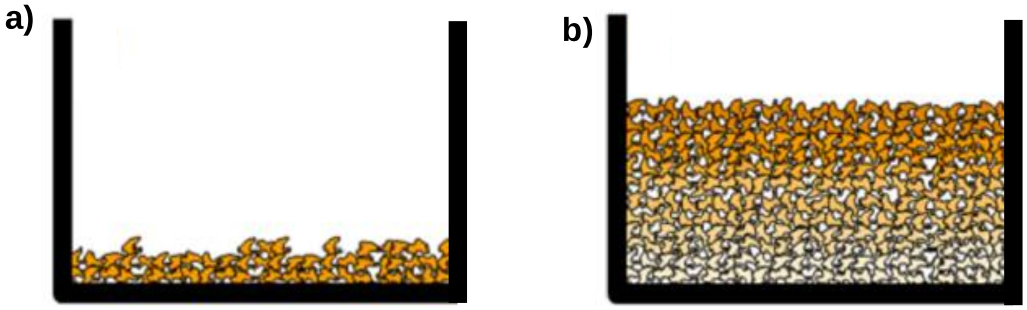

Figure 3. Schematic of static particles coated in a pump-type ALD reactor. The intensity of the coloration indicates the efficiency of the coatings. Image adapted from D. Longrie *et al.*, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces and Films,* **32**, 1 (2014).

In order to uniformly coat large amounts of particles, homogeneous agitation or fluidization of the particles is needed to improve gas and precursors diffusion and reduce the necessary exposure times. One of the most efficient and well-known techniques for this aim is the fluidized bed reactor (FBR), where particles behave like a fluid. More recently, McCormick *et al.* developed also rotatory reactors for ALD.[44] In this case, thanks to the agitation of the particles due to the rotatory movement of the reactor chamber, particles are also coated in a homogeneous manner. While fluidized bed reactors are commonly used for coating microsized or larger particles, rotatory reactors are mostly used for coating nanoparticles with very high surface area, which require very large quantities of precursors. Moreover, depending on the porosity and the tortuous paths for the diffusion of the precursors along the nanoparticles to be coated, much longer residence times are needed to saturate the sample surface.[40] For this reason, a cost effective way for coating nanomaterials with high surface areas and without wasting too much precursor is the use of ALD rotatory reactors.

Given the nature of the materials to be coated in this thesis, the study is performed in a fluidized bed reactor.

ALD on fluidized particles

The fluidization of particles is obtained with a gas introduced upwards with an appropriate flow into the reactor. This process is characterized by a good gas-solid mixing that shows an efficient mass and heat transfer.[40] Fluidized bed reactors (FBR) were studied first by Wank *et al.* for processing large amounts of powders, specifically for coating fine nickel particles with alumina by ALD.[45]

FBRs are well established in industrial applications whenever there is a need for modifying particles, even though those conventionally do not use ALD, but other chemical coating processes like chemical vapor deposition (CVD). The amount of powder which can be processed in an FBR is significantly higher than in static-type ALD reactors. Appropriate design for an ALD process ensures a scale-up of ALD-type of powder coatings for industrial applications.

However, the fluidization behavior of the particles is dependent on their size and density. The Geldart diagram, shown in Figure 4, describes four main groups of particles. (1) Type A particles are characterized by uniform fluidization. A typical example would be cracking catalysts. (2) Type B particles have larger sizes than type A particles. As soon as the fluidization starts, bubbling occurs. Sand is the most prominent example of this class of particles. (3) Type C particles are very fine, at the nanometer scale, which tend to fluidize in a homogeneous manner. Usually, agglomerates are generated due to the small particle size and the resulting stronger cohesion forces. (4) Type D particles are the largest particles among this classification, with high densities, like grains or beans. Strong gas flows are required to fluidize this type of particles and usually, spouting occurs during the fluidization process.[46]

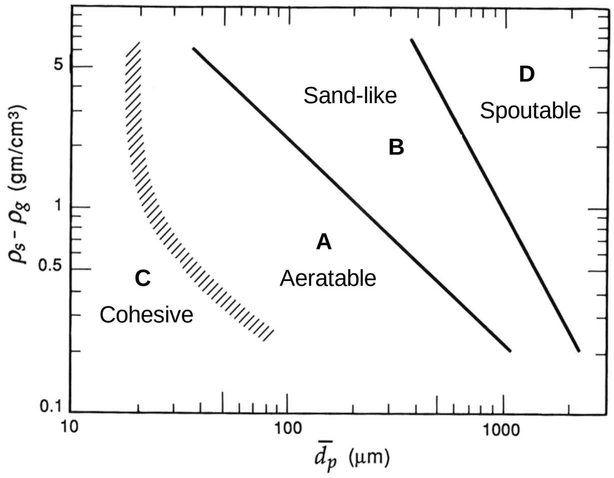

Figure 4. Geldart diagram of the particle fluidization behavior as a function of particle size and density. Figure adapted from H.A. Khawaja*, International Journal of Multiphysics* **9**, 4 (2015).

During the fluidization process agglomerates may be formed, which occurs due to van-der-Waals interactions, liquid or humidity bridging, or electrostatic forces. Thus, the coating process may result in a poor fluidization behavior, in which the particle bed is not homogeneously mixed, and therefore, channels and dead zones, that decrease the fluidization of particles, can appear.[47] As solution to overcome this issue, additional assistive methods are attached to the reactor, which should help to break agglomerates during the process, thus improving the fluidization efficiency. The most efficient techniques are mechanical stirring,[48] mechanical vibration[49] and ultrasound.[50] In such cases, particle fluidization happens dynamically, ensuring that agglomerates break and recombine continuously as a result of agglomerate-agglomerate and agglomerate-wall collisions.[46] In this way, a proper coating (continuous or semi-continuous) of each particle is ensured.

The good processing properties of fluidized bed reactors, and its versatility and precise control over the film thickness, make ALD-FBR an interesting approach for powder coatings, not only for research purposes, but also for scale-up and industrial production. The application of this technology to fabricate materials for energy storage systems is intensely investigated and it is beginning to deliver breakthroughs in a large variety of battery systems.

1.2. Energy storage

1.2.1. Background

Combustion of fossil fuels has been for many years, the main source of energy, a process that releases greenhouse gasses (CO_2, CO or CH_4) as byproduct to our atmosphere. This effect leads to abnormal overheating of the planet and the currently discussed climate change.[51], [52] Renewable energy generation technologies can be a solution to satisfy the growing energy requirements of our society. Solar, wind, hydropower and geothermal technologies, among others, can effectively substitute the conventional methods for energy generation without emission of further greenhouse gases.[53] However, these renewable energy technologies often require specific locations of the plants or do not generate electricity continuously, requiring efficient and reliable energy storage and transport methods.

Energy storage (ES) systems constitute an essential element in the development of sustainable energy technologies, providing great potential to overcome our energy needs in a sustainable way.[54] By now, there is a broad range of developed ES systems that can be classified in mechanical, thermal, chemical, electrochemical and electrical energy storage devices.[55]

The electrochemical energy storage is the most versatile ES system, with applications ranging from stationary plants to small electronic devices. Nowadays, four general types of electrochemical energy storage systems are in use, as shown in Figure 5. Those include capacitors, supercapacitors, batteries and fuel cells.[56], [57] Each system has its own characteristics regarding the storage capacity or energy density, and energy release rate (power density).

Batteries offer an excellent energy storage technology for a better integration of renewable energies into our society. As schematically shown in Figure 6, a battery cell consists of two electrodes, separated by a separator and an electrolyte between the electrodes. Both electrodes are connected through an external circuit. During the discharge, the negative electrode (anode) is oxidized, thereby releasing cations into the electrolyte. Simultaneously, the positive electrode (cathode) is reduced by binding those ions from the electrolyte. During this process the electrons travel from the anode to the cathode through the external circuit, generating the electrical current.[58] In other words, a battery or voltaic cell is a concept of two half cells bridged with each other to permit the ion transfer. It is based on two half reactions; oxidation in one half cell (electrode) and reduction in the other, resulting in a final redox reaction where energy is converted from chemical to electrical.

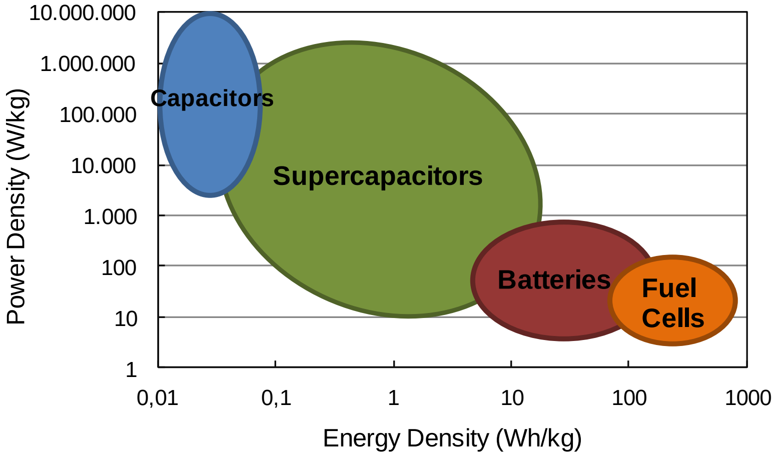

Figure 5. Classification of electrochemical storage systems by energy density vs power density (Ragone plot). Figure adapted from B. K. Kim *et al.*, *Electrochemical Supercapacitors for Energy Storage and Conversion. Handbook of Clean Energy Systems,* (2015).

Considering the reversibility of the redox processes, batteries can be divided into two categories. On the one hand, there are primary batteries, such as zinc-carbon, silver-zinc or lithium primary batteries, where the electrochemical reaction is not reversible. These batteries are not rechargeable and are for a single use only. They provide high energy densities at a low production cost.[59] On the other hand, there are secondary or rechargeable batteries, where the discharge process can be reversed by passing an equivalent current in the opposite direction. The most common rechargeable batteries are lead-acid and nickel-cadmium batteries. More recently, the development of nickel-metal hydride and li-ion batteries has allowed the revolution of portable electronics (smart phones, laptops, electric cars, etc.). Those battery systems are more compact and have a high energy density along with long cycle life.[60]

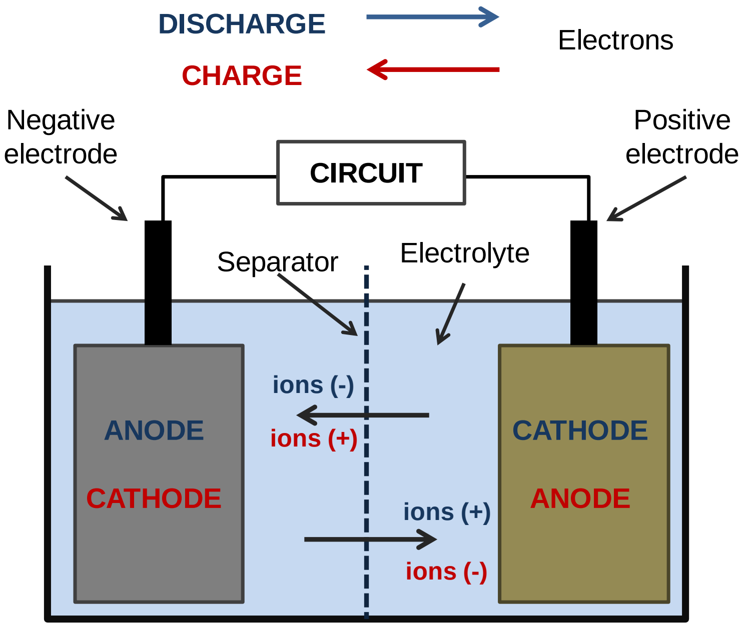

Figure 6. Schematic of the basic constituents of a rechargeable battery in its charge-discharge processes, marked red and blue, respectively.

Lithium-ion batteries (LIB) are currently the most used batteries for portable applications. Their naming indicates their mechanism. Namely, lithium ions are exchanged between the typically graphitic anode and the cathode, usually a ternary lithium-transition metal oxide, like $LiCoO_2$.[61]–[63] With a theoretical energy density of around 300 Wh · kg^{-1}, this kind of batteries provides excellent cycling stability, long cycle life and a high C-rate stability.[64] Nowadays, LIBs dominate the market of portable electronics and transport electrification. However, they also suffer from several drawbacks. Firstly, the electrode materials have a limited specific capacity, limiting the energy density of the battery. Secondly, the cathode materials are composed of rare metals, which have impact on the large-scale usability and, consequently, the price in future applications.

These limitations are a driving force to develop further battery technologies, suitable to replace the currently implanted LIB technology.

Lithium has excellent properties, including low density ($0{,}59\ \mathrm{g \cdot cm^{-3}}$), high theoretical specific capacity ($3860\ \mathrm{mAh \cdot g^{-1}}$), and a sufficiently negative redox potential (-3,04 V), which made the researchers focusing on alternative lithium metal based batteries.[65] In recent years, lithium-air (Li-O_2) and lithium-sulfur (Li-S) batteries have become promising solutions for the next generation of energy storage systems.[66], [67] Although Li-O_2 exhibits higher theoretical energy density than Li-S, the latter one is closer to the real market. This is attributed to the better handling and the exciting properties of sulfur as cathode material in energy storage systems.

1.2.2. Lithium-Sulfur batteries

Sulfur shows an outstanding theoretical specific capacity of $1672\ \mathrm{mAh \cdot g^{-1}}$, and a theoretical energy density of $2600\ \mathrm{Wh \cdot kg^{-1}}$. Moreover, sulfur is environmentally friendly and one of the most abundant elements on earth, which considerably lowers its price compared to the cathode materials in lithium-ion battery systems.[68]

A conventional lithium-sulfur battery comprises a sulfur-based cathode, a lithium metal anode and a separator soaked in electrolyte as it is shown in Figure 7. The cathode is the most complex part of the battery. It is composed of the active material (here, sulfur), conductive additives (conductive carbon), and a binder. In contrast, as anode a metallic lithium foil is commonly used. A porous polymer is usually used as separator. The electrolyte is a mixture of ether based solvents, namely, 1,3-dioxolane (DOL) and dimethoxyethane (DME) with lithium bis(trifluorosulfonyl imide) (LiTFSI) salt dissolved in it.[69], [70]

During the discharge of the cell, the oxidation happens at the anode, where lithium is oxidized and lithium ions (Li^+) are released to the electrolyte, and the electrons are released into the external circuit (Reaction 1).[71]

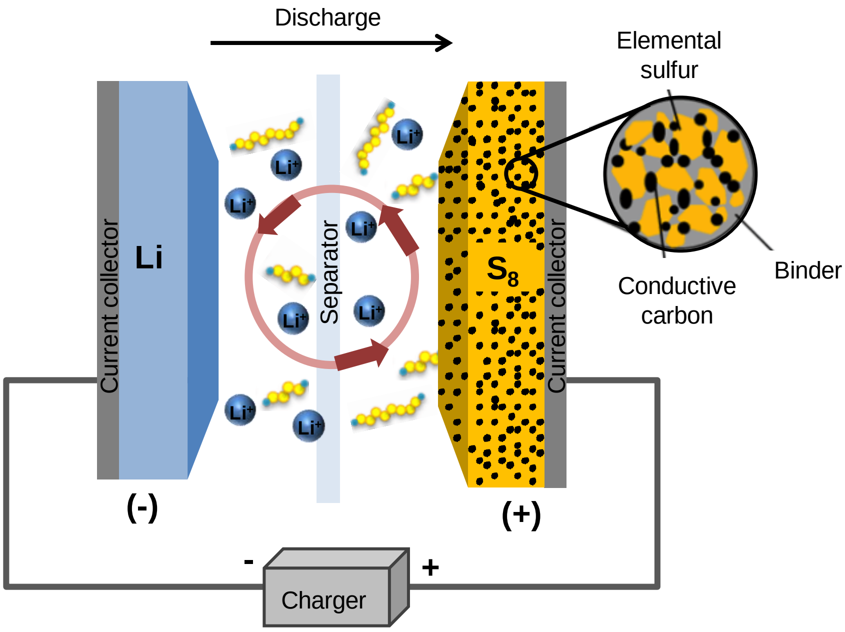

Figure 7. Schematic representation of a lithium-sulfur cell. Figure adapted from *Oxis Energy. Next Generation Battery Technology (https://oxisenergy.com/products/* taken on 02/01/2020*)*

Both, lithium ions and electrons travel to the cathode where the reduction of elemental sulfur occurs (Reaction 2). Following the half reactions (oxidation (1) and reduction (2)) the redox reaction of the whole process is shown in Reaction 3:

$$Li \rightarrow Li^{+} + e^{-} \qquad \text{E=0 V (vs Li/Li}^{+}\text{)} \qquad (1)$$

$$S + 2e^{-} \rightarrow S^{2-} \qquad \text{E=2,2 V (vs Li/Li}^{+}\text{)} \qquad (2)$$

$$S + 2Li^{+} + 2e^{-} \rightarrow Li_2S \qquad \text{E=2,2 V (vs Li/Li}^{+}\text{)} \qquad (3)$$

The most stable form of elemental sulfur in nature is the octasulfur ring, S_8. Considering this, the redox Reaction 3, can be adjusted as follows (Reaction 4):

$$S_8 + 16Li^{+} + 16e^{-} \rightarrow 8Li_2S \qquad \text{E=2,2 V (vs Li/Li}^{+}\text{)} \qquad (4)$$

From this reaction, the theoretical specific capacity of sulfur vs lithium is calculated to be 1672 mAh · g^{-1}. Considering that the average potential is around 2,2 V, the theoretical energy density of sulfur vs lithium is around 2600 Wh · kg^{-1}.[69] However, the reduction mechanism of sulfur is more complex than shown in Reaction 4.

As shown in Figure 8, during the discharge process the reduction of sulfur undergoes disproportion reactions of the octasulfur ring, forming higher order lithium polysulfides, Li_2S_8 (Reaction 5).

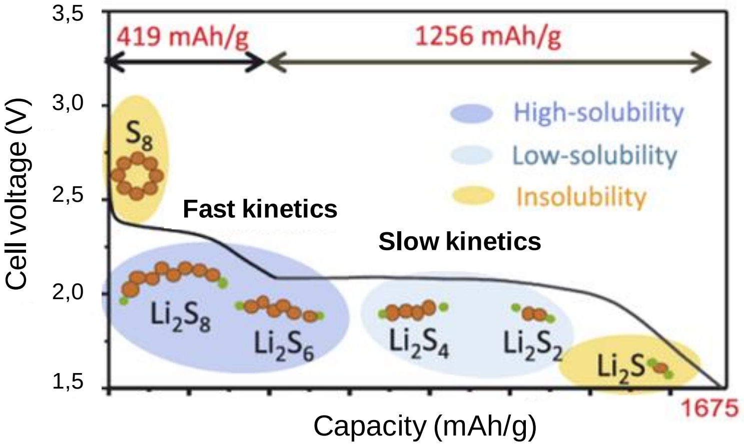

Figure 8. Discharge voltage profiles of sulfur and intermediately formed lithium polysulfides. Image adapted from B. Yan *et al.*, *Journal of Power Sources*, 338 (2017).

The discharge continues via the reduction of Li_2S_8, to further higher order lithium polysulfides, Li_2S_x, where 8>x>6, and subsequently into lower order lithium polysulfides, Li_2S_n, where 6>n>2, both described by the Reaction 6 and Reaction 7, respectively. Finally, the discharge finishes with the products of the reaction of reduced sulfur with lithium, forming lithium disulfide (Li_2S_2) or lithium sulfide (Li_2S) (Reaction 8).

$$S_8 + 2Li^+ + 2e^- \rightarrow Li_2S_8 \qquad E=2,5\ \text{V} \quad (\text{vs Li/Li}^+) \qquad (5)$$

$Li_2S_8 + nLi^+ + ne^- \rightarrow Li_2S_x$ 8 >x>6 E=2,4 V (vs Li/Li$^+$) (6)

$Li_2S_x + nLi^+ + ne^- \rightarrow Li_2S_n$ 6>n>2 E=2,0 V (vs Li/Li$^+$) (7)

$Li_2S_x + nLi^+ + ne^- \rightarrow Li_2S$ E=1,7 V (vs Li/Li$^+$) (8)

Even if there is an agreement of the researchers regarding the general redox Reactions (5) to (8), the exact species formed during the battery charge-discharge cycles is controversial. The disproportion reactions that take place are strongly dependent on many details of the battery, such as, the amount of electrolyte, salts, battery configuration, and operating voltage, among others.

1.2.3. Drawbacks in Lithium-Sulfur batteries

Lithium-sulfur batteries stand out due to their exciting theoretical electrochemical properties. However, there are several factors that negatively affect this battery system:

Insulating nature of sulfur

The most important drawback to overcome in lithium sulfur batteries is the insulating nature of sulfur, the active material. Its electrical conductivity is around 10^{-30} S · cm^{-1}, which is a true obstacle for the electrochemical utilization of a high percentage of this active material in the cathode.[72] The common strategy to solve this issue is to confine sulfur in a conductive matrix like carbon, polymers or other organic materials, and afterwards disperse and fix it in the conductive matrix by thermal treatments. This approach adds complexity to the cathode and implies a need to investigate secondary problems, including processing of the cathode, its scalability, and the sulfur loading.

Polysulfides dissolution "Shuttle effect"

When the battery discharge is taking place, the reduction of sulfur passes through several lithium polysulfides intermediates (see Figure 8).[73], [74] Those intermediate polysulfides are soluble in the electrolyte and tend to migrate towards the anode, where they become reduced by reacting with lithium to lower order lithium polysulfides. Some of those polysulfides can be further reduced to Li_2S, becoming insoluble and forming an ionically insulating and irreversible interface, the so-called Solid Electrolyte Interface (SEI), thus passivating the anode's surface. This effect leads to a self-discharge of the battery and a low Coulombic efficiency, as well as cathode degradation, due to the active material loss and passivation of the anode.[75]

Structural changes

The structural changes during charge-discharge processes of the battery (sulfur solid to liquid and vice versa) and density differences between elemental sulfur (2,07 $g \cdot cm^{-3}$) and lithium sulfide (1,66 $g \cdot cm^{-3}$) lead to a mechanical stress in the cathode, resulting in cracking, delamination and loss of the integrity of the cathode structure, eventually ending in a cell failure.[76], [77]

Lithium anode

The lithium metal, used as anode of Li-S batteries, easily reacts with the solvents in the electrolyte, resulting in a decrease of the Coulombic efficiency of the system.[78] Moreover, the non-homogeneous deposition and dissolution of lithium during the charge-discharge processes leads to the growth of lithium dendrites. Those dendrites can grow perpendicular to the anode into the electrolyte, through the separator and further to the cathode. Upon physical contact with the cathode, a short circuit of the battery will occur. Furthermore, the inhomogeneous dispersion of lithium in the formed dendrites, can cause breaks and result in inactive lithium in the electrolyte, reducing the efficiency and stability of the lithium anode and reacting with the electrolyte by consuming it, thus causing a lower cycle life.[79]

1.2.4. ALD on Lithium-Sulfur batteries

With the significant obstacles that have been found in lithium-sulfur batteries, it is imperative to focus the attention on developing Li-S batteries with high energy density and long-term stability by suppressing, overcoming or minimizing the described drawbacks. The design of effective strategies to address the insulating nature of sulfur, the volume effect of the cathode, the shuttle effect of soluble polysulfides and safety hazard of the Li metal anode is becoming very challenging.[80]

ALD has exceptional capabilities in developing conformal films with precise control. It has demonstrated to be a promising strategy for solving emerging issues in advanced energy storage devices via surface modification and fabrication of various functional materials. Badot *et al.* successfully deposited V_2O_5 films by ALD that served as LIB cathodes.[81] Thereafter, more extensive ALD coatings were done for components in Li-ion batteries. More recently, ALD experiments were performed to improve Li-S batteries. Kim *et al.* conducted the first study of applying ALD-Al_2O_3 on a sulfur cathode.[82] In that work, sulfur-carbon composite cathodes were fabricated and further coated with alumina using a plasma-enhanced chamber-type ALD reactor. The ALD-modified cathodes exhibited an evident increase in the system capacity, doubling it after a certain number of cycles, if compared to untreated cathodes. In a similar work by Yu *et al.* graphene-based sulfur composites were coated with Al_2O_3 by ALD. The circularly shaped composite pellets were coated in a chamber-type ALD reactor, where the assembly of pellets was static. The alumina coating reduced the dissolution of lithium polysulfides and increased the stability of the graphene-sulfur composite.[83]

In order to improve the conductivity of the sulfur-containing cathode and in this way maximize the utilization of sulfur, Meng *et al.* prepared nanoscaled sulfur particles by ball-milling of micrometer sized sulfur particles, thereby achieving higher efficiency and capacity of the battery system. In their work they deposited Al_2O_3 on the sulfur nanoparticles in a chamber-type ALD reactor with a static particle assembly. The deposition of Al_2O_3 by ALD showed different kinds of coverages of the sulfur cathodes as a function of the number of ALD cycles; dispersed nanoparticles (5-20 ALD cycles), porous nanofilms (50 ALD cycles) and uniform dense nanofilms (100 ALD cycles). Very interestingly, the morphology of the deposited coating revealed two different mechanisms for improving the performance of the resulting sulfur cathodes, which are resulting from the alumina coating. For low ALD cycle numbers (<20 cycles), alumina was deposited on sulfur discontinuously, as islands, acting as exceptional absorbent of polysulfides. For larger numbers of ALD cycles (≥ 50 cycles) Al_2O_3 formed a porous film over the cathode and acted as a physical barrier, inhibiting polysulfides from contacting and dissolving into the liquid electrolyte. In the case of thick alumina coatings (100 cycles) the electrochemical reactions of the sulfur electrode were restricted due to the uniform and dense coating of insulating alumina. As a result, they identified that 5 ALD cycles of Al_2O_3 deposition were sufficient to increase the capacity of Li-S batteries by 50% in comparison to the bare sulfur cathode.[84]

In all mentioned cases, ALD was used to improve the lithium-sulfur battery system by altering the cathode materials. The deposition of a specific material at the nanometer scale has many and unique benefits for improving the behavior of Li-S batteries, increasing its capacity and power density, in addition to its excellent properties over the control of the materials growth given by ALD.

1.3. Overview of this thesis

The aim of this thesis is to study and understand the functionalization of powders by ALD, especially for energy storage applications in lithium-sulfur batteries. Micro- and nano-sized particles of inorganic materials have been coated with metal oxides, showing promising results and new functionalities that have not been observed before. The thesis is composed of 6 chapters:

Chapter 1 shows an overview of the topical area. Both, particle coating technologies and energy storage devices are introduced. The state-of-the-art of each technology and the combination thereof is reviewed as introduction to the work performed in the course of the present thesis.

Chapter 2 describes the experimental techniques and methods utilized in this thesis for the physicochemical characterization of the studied samples.

Chapter 3 describes an initial study of particle coatings by ALD. For this aim, iron oxide particles (γ-Fe_2O_3) are coated with titanium dioxide (TiO_2), generating

FeO_x-TiO_2 core-shell nanoparticles. The study shows that ALD technology not only grows TiO_2 coatings around particles, but also a reduction of γ-Fe_2O_3 particles to Fe_3O_4 occurs as a side effect, which is analyzed in more detail theoretically and experimentally.

Chapter 4 presents the modification of cathode materials of lithium-sulfur batteries by ALD in a conventional static reactor. Alumina is deposited on prefabricated cathodes applying various processing temperatures. The results show an improved performance of the resulting ALD modified batteries in form of an increase of the efficiency and capacity of the battery.

Chapter 5 describes the coating of sulfur-carbon composite powders, which are subsequently used to assemble cathodes for lithium-sulfur batteries. Al_2O_3 is deposited by ALD in a home-made fluidized bed reactor. This novel experiment has not been done before and it shows promising results for the scale-up of the process to coat large amounts of composite powders. The coated powders show improvements in the efficiency and capacity of the assembled battery.

Chapter 6 summarizes the main results and conclusions obtained from this thesis and proposes further steps, which are necessary to further develop the line of study of this thesis.

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Chapter 2

Experimental techniques and methods

In this chapter the experimental techniques and methods used in this thesis are overviewed. All applied characterization tools related to physical, chemical, structural and electrochemical characterization, are briefly described. The specific experimental conditions of each method are detailed in the corresponding sections of the Chapters 3, 4 and 5.

2.1. X-ray Diffractometry (XRD)

X-ray diffractometry (XRD) characterization allows the analysis of the crystallinity of a material. Commonly, it is used for the identification of a crystalline material, for the determination of different phases in a polymorphic material and for the quantification of a crystalline phase. In XRD constructive interferences of monochromatic X-rays that interact with a crystalline sample, are analyzed. During the measurement, a monochromatic X-ray beam irradiates the sample at a grazing incident angle θ and the detector collects the reflected beam at an angle 2θ with respect to the incident beam, as schematically shown in Figure 9.

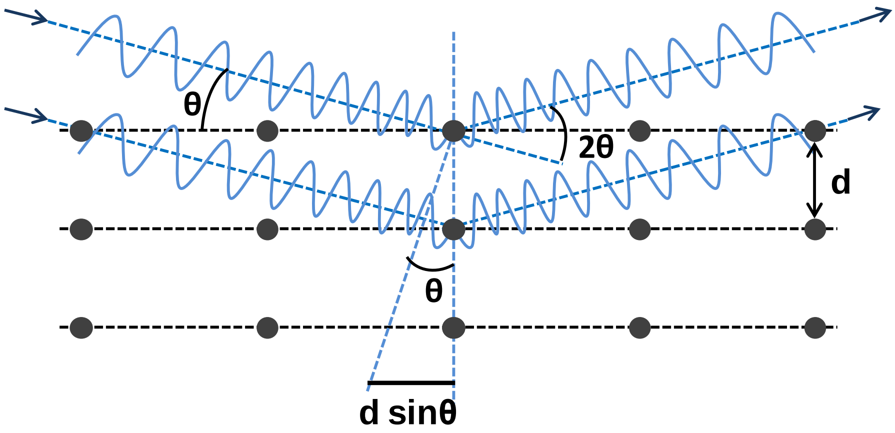

Figure 9. Schematic of the XRD principle. An X-ray beam irradiates a crystal at a grazing incident angle θ and it is scattered by the atoms in the crystal. When the Bragg's condition is fulfilled, characteristic peaks, resulting from constructive interferences, create a reflected peak characteristic of the crystalline material.

The interaction between the incident X-ray beam with the sample produces constructive interferences. When the conditions are in agreement with Bragg's law (Equation 1) a peak will appear in the reflected beam.[1]

$$2d\sin\theta = n\lambda \tag{1}$$

where *d* is the spacing between the diffracting planes, θ is the incident angle of the beam and λ is the wavelength of the beam. Thus, analyzing the information provided by the reflected peaks, the different crystalline planes present in the analyzed samples are obtained.

In this thesis, the XRD measurements were carried out by using the X-ray diffractometer X'Pert PANalytical, with a Cu Kα (λ=0,154 nm) radiation source. During the measurements, the working voltage and current were 45 kV and 40 mA, respectively. Since all measured samples were powders, the equipment was used in the X-ray powder diffraction mode, where the sample is rotated during the measurements to increase the probability of obtaining diffraction patterns.

2.2. Magnetometric measurements

Magnetometry refers to a broad class of experimental techniques that are used for the macroscopic characterization of magnetic properties. Magnetometers can be classified as (i) AC types, which measure magnetic properties using fields that vary relatively rapidly in time, and (ii) DC types, which measure in quasi-static fields. In this thesis, DC type measurements have been performed in order to characterize the magnetic properties of the studied samples. Among the different possible studies that can be performed with DC measurements, the analysis of magnetization as a function of the temperature, M(T), is most common. In this case, two approaches are used for the analysis: Zero-field cooling (ZFC) and Field cooling (FC). In ZFC, the sample is cooled down without any applied field. Then, at low temperatures, a small magnetic field is applied, and finally, the temperature is incrementally increased while the magnetization is measured in each increment. On the other hand, in FC, the sample is cooled down in presence of a magnetic field, typically the same as the one used for the ZFC measurement, and the magnetization is stepwise measured during warming while the magnetic field is maintained. From the measurements one can extract the various magnetic transition temperatures, such as, Curie, Néel and blocking temperature.[2] From the shape of the curves, indirect qualitative information of interparticle dipolar interactions or the particle size distribution can be obtained.

In order to carry out the experiments, the superconducting quantum interference device (SQUID) magnetometry system has been used. This technique requires the sample to be placed inside the magnetometer. By measuring its total magnetic moment as a function of temperature and magnetic field, it provides information about the type of magnetic ordering, as well as the presence of any phase transition that occurs at a critical temperature or magnetic field.

2.2.1. Superconducting Quantum Interference Device (SQUID)

The Superconducting Quantum Interference Device (SQUID) magnetometer is very sensitive to extremely weak magnetic signals. This instrument allows measuring the magnetization and/or the DC-susceptibility of the sample. It is based on superconducting loops containing Josephson junctions.[3] Those junctions allow to measure small variations of the magnetic flux inside the coil. A DC current is applied to the SQUID coil, and the sample placed in the center of the detectors is moved perpendicularly to generate a magnetic flux that can create voltage changes in the junctions, which allows to measure the magnetization of the sample.

The detection coils, the connecting wires and the input coils form a closed superconductive circuit, as shown in Figure 10. The SQUID and detection coils are a concentric superconducting DC magnet, which allows to apply the external magnetic field to the studied sample. Thus, any change of the flux detected by the coils produces a change in the persistent current flowing within the detection circuit. This change produces a variation of the SQUID output voltage that is proportional to the magnetic moment of the sample.

In this thesis, magnetic measurements have been carried out with a commercial MPSM3 SQUID-VSM EverCool system from Quantum Design. The experiments have been carried out by measuring the magnetic moment of the sample and scaling it to the mass of the sample to obtain the magnetization. We studied the ZFC/FC curves of the as-prepared nanoparticles to identify the characteristic Verwey transition[4] of the magnetite structure associated with changes in its magnetic, electrical, and thermal properties. Further details of the characterized samples are provided in the corresponding chapter.

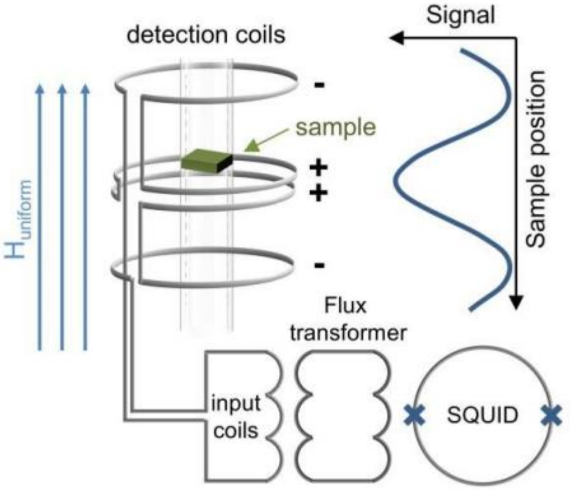

Figure 10. Schematic of the SQUID magnetometer detection system.

2.3. Electron Microscopy

The resolution of spectroscopic and microscopic techniques is limited by diffraction. However, changing the illumination source to smaller wavelengths is a commonly used strategy to overcome this limitation. Electron microscopy techniques are based on a beam of accelerated electrons that substitute light as illumination source. The wavelength of an electron beam is dependent on its acceleration, meaning that the higher the acceleration of electrons is, the shorter is the wavelength and therefore, the higher the resolution of the resulting image. Electron microscopy can span magnifications ranging from thousands to millions with resolutions ranging from nanometers to Ångstroms and even to the atomic scale. Thus, this technique is very useful for imaging nanomaterials with different sizes and geometries.

Figure 11 schematically shows the main interactions between the accelerated electron beam and the studied sample. Depending on how electrons are collected by the detector, electron microscopy can be referred to as scanning electron microscopy (SEM) or transmission electron microscopy (TEM).

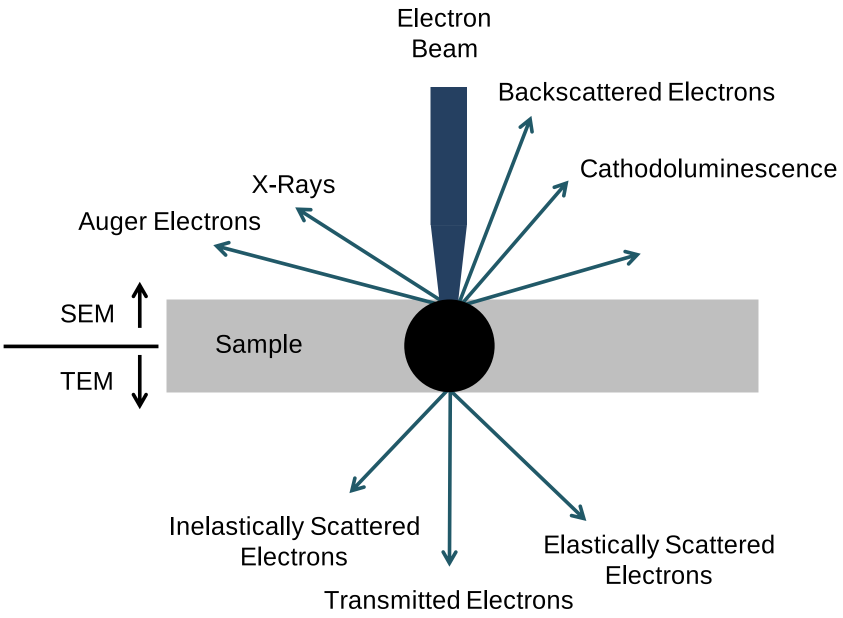

Figure 11. Illustration of the main types of interactions between an accelerated electron beam and a sample in an electron microscope.

2.3.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is very useful, especially in nanoscience, for analyzing micro and nanostructures of materials, including their shape, topography and morphology. In SEM, an electron beam scans across the sample surface and interacts with the sample. Secondary electrons or backscattered electrons, emitted from the sample surface, are collected by the detector. Those electrons result from the excitation of the sample by the electron beam. The amount of emitted secondary electrons depends on the topography of the surface of the sample, while the intensity of the backscattered electrons depends on the atomic number Z. Therefore, the detection of those electrons enables topological or compositional imaging of the sample. Moreover, as it is shown in Figure 11, further modes are available in SEM imaging, which involve detection of characteristic X-rays, auger electrons, cathodoluminescence or charge of the sample.

For the SEM experiments performed in this thesis, an ULTRA plus ZEISS field emission scanning electron microscope (FESEM), equipped with an Ammeter EDAX (Apollo model) accessory for the elemental analysis of the samples by energy dispersive spectroscopy (EDS), was used. The specific process conditions are explained in each corresponding chapter.

2.3.2. Transmission Electron Microscopy (TEM)

In transmission electron microscopy (TEM), the electron beam passes through the sample and the transmitted electrons are detected in order to generate an image of the studied sample. Only thin samples or powders can be analyzed with this technique, since the electrons have to pass through the sample. The transmission of the electron beam depends on the interaction of the beam with the sample and thus on the atomic number Z. The achievable resolution in TEM images is usually an order of magnitude higher than in SEM images. In a well-adjusted TEM, even crystalline lattices of materials and single atoms can be observed.

2.3.3. Energy-Dispersive X-ray Spectroscopy (EDS)

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis of a specific sample. In this case, a high-energy beam of charged particles, electrons or protons, excites an electron from an inner shell of an irradiated atom, expelling it from the shell and leaving an electron hole behind. This hole will be filled with an electron from an outer shell, and the difference in energy between the outer and the inner shell will be released as X-ray radiation. The energy emitted by the X-rays is specific of the emitting atom and is measured by an energy-dispersive spectrometer. In this way, EDS gives a precise analysis of the elemental composition of the sample. Usually, EDS measurements are carried out in parallel to TEM or SEM imaging, thus, resulting in a complete analysis of elemental composition and structural information of the sample.

For all the TEM-EDS experiments performed in this thesis, a FEI Titan microscope, operating at 300 kV in scanning mode with a coupled energy-dispersive X-ray spectrometer (STEM-EDS) and equipped with a Quantum GIF 965 electron energy loss spectrometer (EELS), was used. All the measured powder samples were prepared by ultrasound dispersion in ethanol and drop casting on holey carbon TEM grids. Further details of the analyzed samples are provided in the corresponding chapter.

2.4. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a very sensitive technique for the analysis of the inorganic composition of materials. For an analysis, inductively coupled plasma is used to atomize the sample and create atomic and small polyatomic ions, which are then detected in the mass spectrometer. This technique is applied for detecting very low concentrations of metals and non-metals in liquids with extreme precision. Moreover, it can detect different isotopes of the same element. The rapidity, accuracy and sensitivity of this technique make it highly valuable in micro and nanoscience.

In a typical ICP-MS analysis, samples are provided in liquid form. If samples are solid, they have to be pretreated in a process known as sample digestion, where they are dissolved and then diluted with dionized water and an acid, for example, nitric acid. For the measurement, the introduced liquid sample is transformed to a gas or aerosol by evaporation or nebulization. Liquid droplets are formed and become nebulized in the presence of a perpendicular argon gas flow. Later, in the torch where the plasma is generated, the argon gas with the nebulized sample is atomized. The formed atoms absorb energy from the plasma until they release electrons and become ionized. The newly formed ions pass to the mass analyzer. In order to analyze and determine the composition of the sample a mass spectrometer is coupled to the plasma system. The ions from the plasma are extracted into the mass spectrometer with a series of cones. Here, the ions are separated based on the mass of their mass-to-charge ratio. A detector receives a signal proportional to the concentration, and afterwards, the concentration of the sample is determined through calibration with a certified reference material, such as a single or multi-element reference standard.

There are many applications of ICP-MS, such as, metal speciation (determination of oxidation state) or quantification of proteins and biomolecules, but usually this technique is used for elemental analysis. ICP-MS has the capability to scan all the elements of a sample simultaneously, allowing a rapid sample processing. It allows the determination of elements with atomic mass ranges from 7 to 250 (from lithium to uranium), and with sophisticated instrumentation and methods, sometimes even higher.

In this thesis, the elemental analysis of the studied powder samples was done with an iCAP-Q, Thermo Fisher Scientific GmbH equipment, Germany. Further details of the sample preparation and processing are given in the corresponding chapter.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is an analytical technique, where a thermobalance is used to determine materials' thermal stability and its fraction of volatile components by monitoring the weight change that occurs when the sample is heated at a constant rate until temperatures of 1000 °C. This measurement provides information about physical phenomena (phase transitions, absorption, adsorption and desorption) and chemical phenomena (chemisorptions, thermal decompositions and solid-gas reactions) of a specific sample.[5]

In a TGA process, the sample is placed in a container with a precision balance inside a furnace with programmable temperature control. During the process a thermogravimetric analyzer continuously measures the sample mass, while the temperature of the sample is changed over time and the thermal reaction is taking place. In order to carry out the reaction, a gas passes through the chamber (furnace). The nature of this gas depends on the kind of reaction that is expected to occur and can be air, inert gas, oxidizing or reducing gases, among others.

The collected thermogravimetric data from the thermal reaction are compiled and a quantitative analysis is done by measuring the loss or gain in mass. The TGA curve typically shows horizontal and curved sections, indicating a change in mass upon heating or cooling of the sample. The obtained data is used for determining purity and composition of materials, sublimation, drying or ignition temperatures of materials and for evaluating the stability of the compounds as a function of the temperature.

In this thesis, TGA measurements were done with a Netsch STA, Germany, for identifying the fraction of sulfur in the cathodic materials of lithium-sulfur batteries. The specific variables for each case are detailed in the corresponding chapter.

2.6. Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) is an analytical technique for measuring the average size and size distribution of particles dispersed in a suspension and/or emulsion. Usually, micro- or nanoparticles and macromolecules are measured. The technique is based on the Brownian motion of the dispersed particles.[6] Since particles are constantly colliding with solvent molecules, those collisions cause energy transfer, which affects the particle mobility. Since the energy transfer is rather constant, it is possible to determine the speed of the particles. By means of Stokes-Einstein equation,[7] the speed of the particles and the particle size are correlated, therefore the average size of the particles can be determined based on the correlation function, which is determined from the acquisition of so-called speckle patterns.

Figure 12 explains the DLS technique. A single frequency laser is directed to a sample contained in a cuvette. The incident laser light is attenuated using some lens positioned between the sample and laser (generator and detector). When the incident laser light reaches the sample where particles are, it is scattered in all directions.

The scattered light is detected at a certain angle over time and this signal is used to determine the diffusion coefficient (speed of particles) and the particle size with the Stokes-Einstein equation.

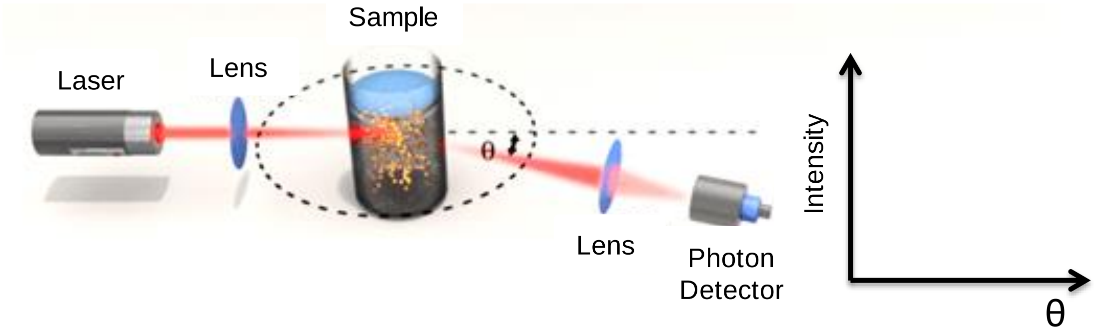

Figure 12. Schematic illustration of the procedure in the dynamic light scattering technique. Figure adapted from *https://lsinstruments.ch/en/technology/static-light-scattering-sls* taken on 13/12/2019.

Movements of the particles cause fluctuations in the generated pattern. The dynamic information of the particles is derived from an autocorrelation of the intensity trace recorded during experiments. From the intensity trace, a second order correlation function is obtained given by Equation 2.

$$g^2(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} \tag{2}$$

where $I(t)$ is the intensity of the scattered light at a time t, and the brackets indicate averaging over all t. The correlation function depends on the delay τ, the amount that a duplicate intensity trace is shifted from the original before the averaging is performed. Once the autocorrelation data is obtained, using some mathematical approaches and taking advantage of Stoke Einstein equation, the average particle size and the size distribution can be obtained.

In this thesis, the average particle size of the ALD-coated powders has been measured using a Nanosizer DLS equipment from Malvern. The powder samples were dispersed in a solvent before characterization. A more detailed description is given in the corresponding chapter.

2.7. Electrochemistry

Electrochemistry studies rely on the conversion of electrical energy to chemical energy and vice versa. The electrochemical characterization of batteries specifically investigates the chemical reactions that take place at the electrode interfaces, which often involves electrical discharge and charge transfer between the electrodes and the electrolyte of the cells. Measurements for evaluating the electrochemical performance on lithium-sulfur batteries can be carried out by cyclic voltammetry (CV),[8] galvanostatic charge-discharge testing[9] and electrochemical impedance spectroscopy (EIS).[10], [11] In this thesis, galvanostatic measurements were performed.

Galvanostatic cycling is used in order to determine the practical capacity of an electrode material. During those processes, electrons flow from one electrode to another and the electrodes are charged and discharged in each step. The term “specific capacity” is used in order to study the electrochemical behavior of a battery. The specific capacity, C, is the amount of charge that can be stored per unit of mass of a material in the electrode. It is often expressed in terms of $mAh \cdot g^{-1}$ and calculated as shown in Equation 3:

$$C_{electrode} = \frac{nF}{M} \times \frac{1000}{3600} \tag{3}$$

where n is the number of electrons transferred in the reaction, F is the Faraday’s constant ($96{,}485\ C \cdot mol^{-1}$) and M is the molar mass of the electrode material ($g \cdot mol^{-1}$). Given the specific capacities of the cathode and anode, the specific capacity of the battery can be calculated as follows (Equation 4):

$$\frac{1}{C_{battery}} = \frac{1}{C_{cathode}} + \frac{1}{C_{anode}} \tag{4}$$

A related parameter is the specific energy density of a battery ($W_{battery}$), which is the amount of energy that can be stored per unit of mass or volume. It can be calculated, as a function of the calculated specific capacity and the average voltage applied to the battery.

Moreover, there is an additional indicator that links the discharge and charge parameters of a rechargeable battery, known as Coulombic Efficiency (CE). This parameter is calculated as shown in Equation 5:

$$CE\ (\%) = \frac{Discharge\ capacity}{Charge\ capacity}\, x\ 100 \tag{5}$$

In lithium-sulfur batteries, a value of 100% of CE indicates a completely reversible reaction, in which the amount of dissolved sulfur ions and the ones regenerated to S_8 is the same. However, experimentally, CE is less than 100%, meaning that undesirable side reactions, due to the generation of polysulfides and reactions with electrolyte, are taking place.

Usually, the galvanostatic discharge-charge measurements for studying the performance of batteries are done by the analysis of the C-rates and the cycle-life of the battery.

C-rate experiments

When the behavior of a battery is described, the discharge current is often expressed as a C-rate in order to normalize it against the battery capacity. The term C-rate describes how fast a battery is charged or discharged. A battery is usually cycled at various discharge (or charge) rates, also known as C-rates. C/*n* is defined as the current needed to complete the discharge or charge of the battery in *n* hours, based on the theoretical capacity of the electrode material. For instance, C/5, C/2, 1C and 2C correspond to complete discharge or charge cycles of the battery in 5h, 2h, 1h and 0,5h, respectively. For low-power applications, such as in experimental cells, usually low C-rates are employed, like

C/5 or C/10. However, in high-power applications, often high current densities are used, for example 2C, 5C or even higher. Those high C-rates can drastically affect the performance and the lifetime of a battery. Consequently, ways to improve their use are being intensely investigated.

Cycling or cycle-life analysis

Another typical experiment for testing the batteries' long-term stability is cycling. Here, batteries are charged and discharged multiple times and their capacity is measured, maintaining the current density constant, until their failure. The operating life of the battery is affected by the applied C-rate and by other conditions, such as, the temperature. Cycle life is an important parameter for evaluating the battery performance. The capacity retention with respect to the first cycle is reported as $x\%$ over a specific number of cycles, and the decay rate per cycle can be calculated as (100-x)/number of cycles.

In this thesis, electrochemical measurements have been carried out by means of galvanostatic testing, in order to study the cell performance of the modified lithium-sulfur batteries. Coin cells were assembled with the modified ALD sulfur cathodes and then tested with a BaSyTec Cell Test System (Germany). The specific experimental conditions are described more in detail in the corresponding experimental sections of each chapter.

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Chapter 3

A Concerted Coating and Reduction Atomic Layer Deposition Process on TiO_2-coated Magnetite Nanoparticles

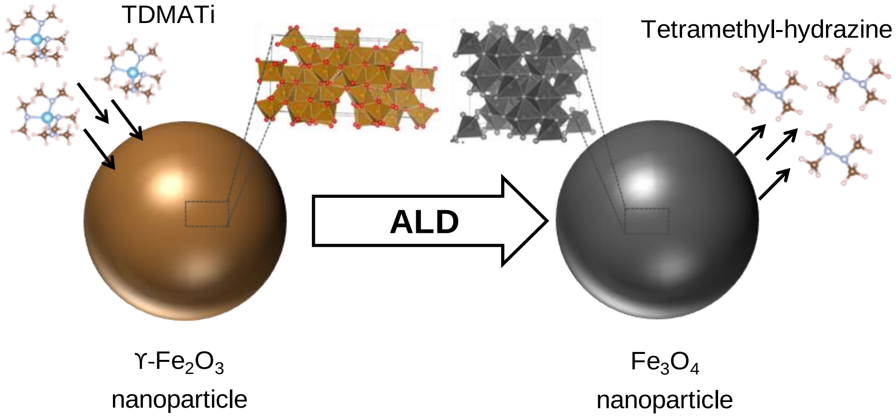
This chapter describes the initial experiments of the thesis in the area of ALD-coated particles. Iron oxide nanopowders have been coated by ALD in a chamber-type ALD reactor where particles were static and not fluidized. The work shows that the choice of a metal precursor with an appropriate ligand can unveil a novel approach to concertedly coat and reduce γ-Fe_2O_3 nanoparticles to form a final product composed of Fe_3O_4-TiO_2 core-shell nanoparticles. To this aim, an appropriate design of precursors and selection of substrates will pave the way for numerous new compositions, while the ALD process itself allows for easy up-scaling to large amounts of coated and reduced particles for industrial use.

This chapter describes the part of the thesis that was published in the journal *Chemical Science* from the Royal Society of Chemistry. The experimental work described in this chapter was performed at nanoGUNE, while the supporting modeling in form of density functional theory (DFT) calculations was performed by collaborators from the University of Texas in Dallas (USA). Graphs, figures and parts of the text of the publication are reused in this thesis with permission of the publisher.

Article:

Ligand-induced reduction concerted with coating by atomic layer deposition on the example of TiO_2-coated magnetite nanoparticles

Sarai García-García, Alberto López-Ortega, Yongping Zheng, Yifan Nie, Kyeongjae Cho, Andrey Chuvilin and Mato Knez. *Chemical Science*, **10**, 2171-2178 (2019).



3.1. Introduction

Atomic layer deposition (ALD)[1]–[3] is a coating technology that in recent years became indispensable in microelectronics,[4],[5] and it enjoys a rapidly growing interest for emerging applications in energy storage[6]–[9] and medicine[10]–[12] among others. One of the important aspects of ALD is that it is a chemical deposition technology and as such requires understanding and control of the chemical processes that occur during the coating.[13]–[15] Most considerations for the development of a process are directed to the precursor chemistry, which is usually thoughtfully designed to enable a rapid process with ideally no impurities in the growing film and no corrosion or any other kind of harm to the coated substrate. Typically, metalorganic, organometallic or halide compounds are utilized as metal source for coatings and the ligands of those compounds shall ideally be highly volatile.[16]–[19] However, in numerous cases those ligands corrode the substrate or compete for adsorption sites,[20],[21] which are side reactions of such processes. Typically, such side reactions are unwanted, and precursors are chosen which will not release reactive ligands or intermediates. The ability to control such side reactions might, however, be of great interest, since one could achieve synchronous coating and alteration of a substrate in one process, thus saving time and energy otherwise needed for post treatment of the sample. One such scenario refers to the oxidation state of a substrate material. Since most ALD processes operate with a counter precursor that contains oxygen, for example, water vapor, oxygen plasma or ozone, it becomes difficult to preserve or achieve a reduced state of a metal during the process, particularly in those cases where the metal is prone to easily oxidizing. The choice of a precursor which contains ligands that upon release can reduce the substrate can be beneficial as it would avoid the need of post-processing, for example in the form of reductive annealing.

In this work, the synthesis of Fe_3O_4-TiO_2 core-shell nanoparticles by ALD at moderate temperatures is carried out. An ALD process is applied, which involves two independent and concerted chemical reactions. As substrate, commercial iron oxide nanoparticles are used and as precursors, Ti-based precursors with different ligands and deionized water. The possibility of coating and reducing at the same time iron oxide particles depending on the existing ligand in the selected metal-based precursor is demonstrated. In other words, while the ALD process to coat the particles with TiO_2 takes place, the Fe^{3+} ions in the seed nanoparticles can be partially reduced to Fe^{2+}, enforcing the transformation of the γ-Fe_2O_3 to the well-known magnetite, Fe_3O_4, structure. The resulting core-shell particles have been systematically studied by X-ray diffraction, magnetometry, energy dispersive X-ray analysis and electron microscopy. The underlying mechanism for the reduction reaction was further modeled by density functional theory. Upon comparisons with various optional Ti-precursors, the study showed that the ligands of the titanium precursor tetrakis (dimethylamino) titanium (IV) (TDMATi) are responsible for the partial reduction of Fe^{3+} by forming tetramethylhydrazine as byproduct during the corresponding oxidation reaction. Both, simulation and experiments show that only this class of precursor enables the synchronous coating-reduction reaction, while the energy barriers for a reduction are too high in case of alternative choices of precursors. Those will only yield a coating of the particles.

This finding opens the possibility to design novel ALD precursors for a combined one-step capping and reduction process for the synthesis of further material combinations, while the ALD process itself allows for easy up-scaling to large amounts of coated and reduced particles for an industrial use.[22]–[26]

3.2. Experimental section

3.2.1. Sample preparation

All the samples were prepared following the same procedure. Commercial maghemite (γ-Fe_2O_3) nanoparticles with a particle size less than 50 nm, (CAS: 1309-37-1) from Sigma Aldrich, were dispersed in ethanol and sonicated for 15 minutes for better dispersion. Thereafter, the nanoparticles were spread over fused quartz substrates and dried for 24 hours. Prior to loading, the fused quartz substrates were cleaned in an ultrasonicator using acetone and ethanol and blown dry using nitrogen gas.[27]

3.2.2. ALD process

The coating of the nanoparticles was performed in a commercial pump-type ALD reactor (Savannah S100, Cambridge NanoTech Inc), where particles were coated being static inside the reactor chamber. The processes were carried out under a constant nitrogen gas flow of 20 standard cubic centimeters per minute (sccm) and under vacuum at a base pressure of 1 mbar.

Various metal-containing ALD precursors were used for the coating of the nanoparticles, including tetrakis (dimethylamino) titanium (IV) (TDMATi, $[(CH_3)_2N]_4Ti$), titanium chloride ($TiCl_4$), tetrakis (dimethylamino) tin (IV) (TDMASn, $[(CH_3)_2N]_4Sn$) and tetrakis (dimethylamino) hafnium (IV) (TDMAHf, $[(CH_3)_2N]_4Hf$), all of which were obtained from Sigma Aldrich. Demineralized water was used as oxygen source. The coated nanoparticles were prepared following a typical ALD timing sequence expressed as t_1-t_2-t_3-t_4, where t_1 is the exposure time to the first precursor, t_2 is the purge time following the first exposure, t_3 is the exposure time to the second precursor, t_4 is the purge time following the exposure to the second precursor. The times corresponding to t_1-t_2-t_3-t_4 were 20-25-20-25, all given in seconds (s). The pulsing times were a function of the vapor pressure of the precursor. For TDMA-based precursors (titanium, tin and hafnium) 0,5 s at 150 °C process temperature were used and 0,2 s was the pulsing time only for the comparative case, at 250 °C process temperature. For the chloride precursor 0,05 s were used, and for demineralized water in all the cases 0,05 s was the pulsing time. The process temperature in all cases was 150 °C. One further process was carried out at 250 °C with TDMASn in order to evaluate the thermal impact of the ALD process on the substrate. For all coatings, a thickness of approximately 30 nm was targeted. In order to obtain this thickness, 440 ALD cycles were performed for TiO_2 deposition with TDMATi, calculated from the obtained growth rate of 0,73 $Å \cdot cycle^{-1}$. For the $TiCl_4$ process, 500 ALD cycles were applied, resulting from the growth rate of 0,66 $Å \cdot cycle^{-1}$. For the SnO_2 and HfO_2 processes, 380 ALD cycles (growth rate: 0,79 $Å \cdot cycle^{-1}$) and 400 ALD cycles (growth rate: 0,82 $Å \cdot cycle^{-1}$) were applied, respectively.

After the ALD coating process, TiO_2-coated Fe_2O_3 nanoparticles with TDMATi and demineralized water, were subjected to *ex situ* annealing in order to crystallize the deposited film. The thermal treatment was carried out in air at atmospheric pressure and at 470 ^{o}C for 3 hours.[28]

3.2.3. Structural characterization

Scanning transmission electron microscopy (STEM) images were acquired with a FEI Titan operating at 300 kV in scanning mode with a coupled energy-dispersive x-ray spectrometer (STEM-EDX). The samples were dissolved in ethanol and drop casted onto carbon coated copper grids.

Powder x-ray diffraction (XRD) patterns were recorded with a PANalytical XPert Pro x-ray diffractometer using Cu Kα radiation (λ=1,5405980 Å) operating at 45 kV/40 mA in the 25^{o} – 65^{o} 2θ range with a scan speed of $0{,}00144^{o} \cdot s^{-1}$. Quantitative analysis of the XRD data was performed with a full pattern fitting procedure based on the fundamental parameter approach (Rietveld method) using the MAUD software (http://maud.radiographema.eu/).

The magnetic properties of the nanoparticles were measured from tightly packed powder samples using a vibrating sample mode magnetometer (Quantum Design SQUID-VSM overcool) with 70 kOe maximum field. Magnetization versus temperature measurements were performed in zero-field cooled (ZFC) and field cooled (FC) conditions with 50 Oe probe fields.

3.2.4. Computational methods

All the calculations in this work were performed using the density functional theory (DFT) method implemented in the Vienna *ab initio* simulation package (VASP)[29], [30] with the projector-augmented wave (PAW) method.[31] The generalized gradient approximation (GGA) with semilocal Perdew-Burke-Ernzerhof (PBE)[32] function was adopted to describe the exchange correlation interactions. The cutoff energy was set to be 450 eV. The structures were optimized with criteria of convergence for energy and force as 10^{-4} eV and 10^{-2}

$eV \cdot Å^{-1}$, respectively. On-site Coulomb repulsion of Fe 3*d* electrons was corrected by GGA+*U* method[33] with U_{eff}=4 eV according to previous theoretical reports.[34], [35]

The minimum activation barriers of reducing Fe_2O_3 to Fe_3O_4 by different ALD precursors were determined as the reaction energy of the Reaction 9:

$$6Fe_2O_3 + M\text{-}L_4(ad) \rightarrow 4Fe_3O_4 + MO_2 + 2L_2(ad) \qquad (9)$$

, where $M\text{-}L_4(ad)$ and $L_2(ad)$ denote the adsorbed ALD precursors and adsorbed oxidation products, respectively. Although the reaction energies are typically positive, this reduction reaction will be driven by the entropy change as L_2 desorbs and becomes gas phase.

3.3. Results and discussion

Commercial γ-Fe_2O_3 nanoparticles (sample FeO_x) have been coated with TiO_2 by ALD using at a first stage, TDMATi and water as precursors (sample TDMATi-FeO_x). Figure 13(a) shows x-ray diffraction (XRD) patterns obtained from the samples before and after ALD coating. Both diffraction patterns are very similar showing characteristic peaks of the cubic spinel structure stemming from the iron oxide. It should be noted that no characteristic peaks from titanium oxide are seen, which is due to the amorphous character of the TiO_2 deposited in the applied processing conditions.

However, the transmission electron micrographs show the formation of a core-shell structure. In Figure 14 the core-shell construction of the nanoparticles is very obvious both from the contrast in scanning transmission electron microscopy (STEM) as well as the energy-dispersive x-ray spectroscopy (EDX) images, which show the involved elements in different colors. A more detailed analysis of the x-ray diffraction (XRD) patterns of samples FeO_x and TDMATi-FeO_x shows a clear alteration of the pristine iron oxide structure after the ALD process. While both patterns reveal the presence of a cubic spinel structure, the shift in their diffraction peaks and the concomitant variation of their cell parameter, points towards the presence of two different iron oxide phases in the two samples.

The commercial particles have a cell parameter of 8,347(5) Å (see Table 1) which is characteristic for completely oxidized maghemite, γ-Fe_2O_3 (JCPDS Card No. 39-1346), where Fe^{3+} cations occupy the octahedral and tetrahedral sites of the structure. In contrast, sample TDMATi-FeO_x shows an increase of the cell parameter to values of 8,390(5) Å (see Table 1), which is characteristic for a partial $Fe^{3+} \rightarrow Fe^{2+}$ reduction of the octahedral cations to form the well-known magnetite, Fe_3O_4 structure (JCPDS Card No. 19-629). Note that the crystal size of both samples is very similar with values of roughly 30 nm. The expected change of the volume of about 6% after ALD process is not notable from Rietveld-based XRD measurements, since the resolution is not high enough for clearly confirming such small changes.

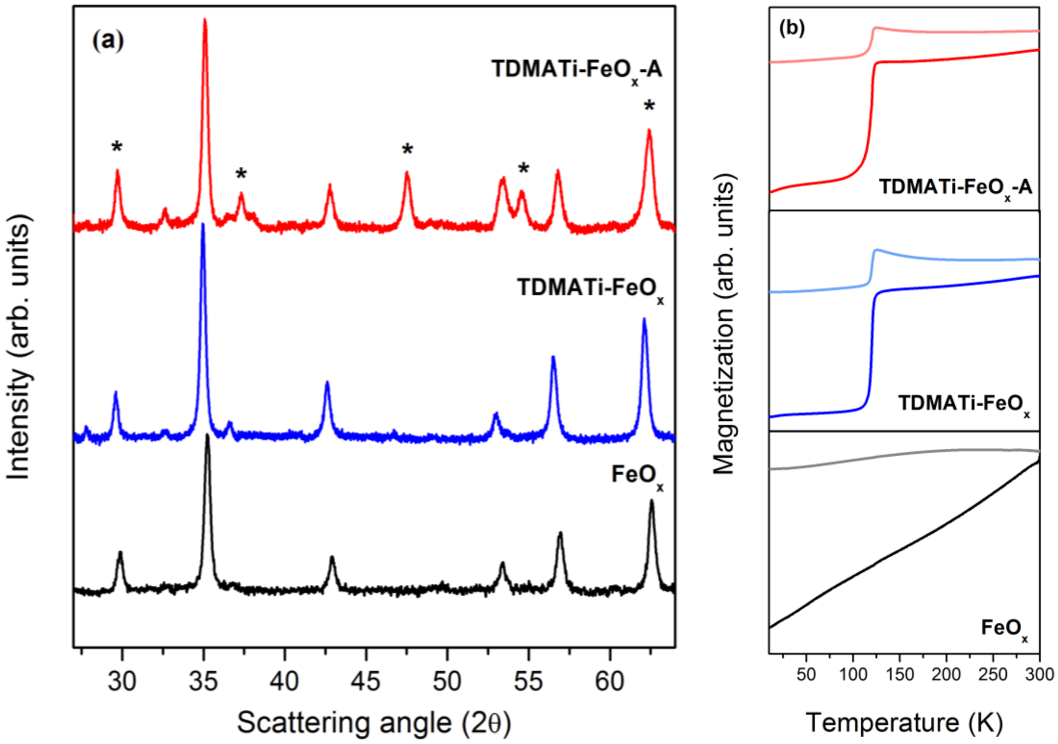


Figure 13. (a) XRD patterns of uncoated γ-Fe_2O_3 particles (FeO_x), TiO_2-coated γ-Fe_2O_3 nanoparticles with TDMATi and H_2O precursors, before annealing (TDMATi-FeO_x) and after annealing at 470 °C (TDMATi-FeO_x-A). (b) Magnetization curves vs. temperature for the samples in (a). * denotes diffraction peaks originating from TiO_2.

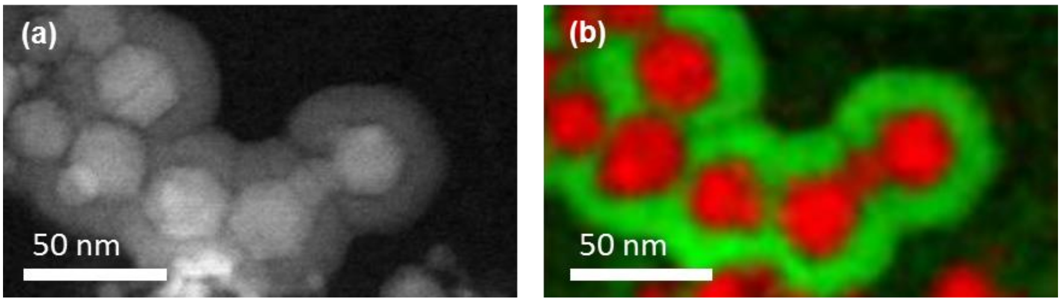


Figure 14. (a) STEM micrograph and (b) STEM-EDX map of Fe_3O_4 (red)-TiO_2 (green) core-shell nanoparticles.

In order to gain more insight into the phase transformation observed after the ALD process the magnetic properties of both samples are compared by measuring their magnetization temperature curves in both field cooling (FC) and zero field cooling (ZFC) conditions (see Figure 13(b), in bold ZFC). Both samples depict the expected behavior for nanostructured magnetic nanoparticles, where the FC and ZFC curves are distinct at low temperatures and tend to converge at the so-called blocking temperature (T_B).[36] Indeed, for such large iron oxide particles (i.e., 30 nm) this transition was observed at temperatures above RT.[37] Sample TDMATi-FeO_x shows a similar trend as the untreated sample, but with an extrapolated T_B at higher temperatures. More interesting is, however, another magnetic transition that can be clearly observed at 120 K and can be ascribed to the Verwey temperature (T_V) of Fe_3O_4. This transition is characteristic of Fe_3O_4 which undergoes a transformation from cubic ($T > T_V$) to monoclinic ($T < T_V$) symmetry.[38] Such transformation is related to modifications in the crystal symmetry and the cation ordering and is accompanied by dramatic changes in electrical conductivity and heat capacity. Given the results of the magnetic characterization, it can be stated that the iron in the commercial particles (FeO_x) suffered a transformation from a completely oxidized state as typical in maghemite (γ-Fe_2O_3) to a partially reduced state as it is typical of magnetite (Fe_3O_4) during the ALD process.

Table 1. Structural properties and Verwey transition of nanoparticles.

Sample	Composition	ALD process	Phase	Lattice parameter (Å)	Crystal size (nm)	Verwey transition
FeO_x	Commercial FeO_x	---	γ -Fe_2O_3	8,347(5)	32,5(5)	NO
TDMATi-FeO_x	TiO_2-FeO_x	TDMATi+H_2O (150 °C)	Fe_3O_4	8,390(5)	31(5)	YES
TDMATi-FeO_x-A	TiO_2-FeO_x	TDMATi+H_2O (150 °C)	Fe_3O_4	8,388(5)	32(5)	YES
		Annealing (470 °C)	TiO_2	3,782(5)/9,483(5)	23(5)	
$TiCl_4$-FeO_x	TiO_2-FeO_x	$TiCl_4$+H_2O (150 °C)	$\gamma - Fe_2O_3$	8,339(5)	28(5)	NO
TDMASn-FeO_x	SnO_2-FeO_x	TDMASn+H_2O (150 °C)	γ -Fe_2O_3	8,351(5)	23(5)	NO
TDMASn-FeO_x-250	SnO_2-FeO_x	TDMASn+H_2O (250 °C)	Fe_3O_4	8,380(5)	30(5)	YES
TDMAHf-FeO_x	HfO_2-FeO_x	TDMAHf+H_2O (150 °C)	Fe_3O_4	8,382(5)	44(5)	YES

For crystallographic confirmation of the deposition of titanium oxide over the iron oxide, the particles have been annealed at 470 °C (sample TDMATi-FeO_x-A). Figure 13(a) shows the evolution of anatase-type TiO_2 (JCPDS Card No. 21-1272) after annealing, which resulted from the crystallization of the deposited film. Moreover, the peaks of the cubic spinel structure of Fe_3O_4 are not affected by the heat treatment, preserving the structure obtained after the ALD process. The magnetization measurement of the particles after annealing further confirms the presence of magnetite showing its characteristic Verwey transition (see Figure 13(b)). It is interesting to note that no traces of any further iron oxide crystal structure can be found, and the crystal size of the phase is very similar to the untreated sample (i.e., 30 nm). Both effects demonstrate that the TiO_2 coating avoids intimate contact between the particles and thus their agglomeration and phase transformation to more stable iron oxide phases (i.e., α-Fe_2O_3), even if the temperature is increased to 470 °C.[39]

The TiO_2 coating of iron oxide particles by ALD using TDMATi as precursor not only protects the nanostructures from oxidation and agglomeration, but also induces a partial reduction of the pristine γ-Fe_2O_3 and a concomitant phase transformation. Such transformation may be triggered by either the metal or by the ligand present in the ALD precursor. Therefore, a series of experiments has been performed in order to identify the source. Firstly, the growth of TiO_2 has been carried out using an alternative titanium precursor (titanium chloride, $TiCl_4$) in order to identify a potential effect of the titanium ion. In the second stage, the effect of the $(CH_3)_2N^-$ ligand has been evaluated by performing ALD coatings with another TDMA-based metal precursor, tetrakis (dimethylamino) tin (IV) (TDMASn).

Sample $TiCl_4$-FeO_x has been obtained after an ALD process of the same commercial iron oxide particles using $TiCl_4$ and demineralized water as precursors at 150 °C. From the Rietveld analysis of the x-ray diffraction data in Figure 15, it can be observed that after the TiO_2 deposition the cell parameter of the iron oxide core remains similar to the pristine sample (γ-Fe_2O_3) (see Table 1). The magnetometric curves, Figure 16, show no signs of Verwey transition. Therefore, the titanium cation appears not to be responsible for the partial reduction of the

γ-Fe_2O_3 particles, which is reasonable from the chemical perspective as it is already present in the oxidation state +4 and further oxidation would not be possible in the given conditions.

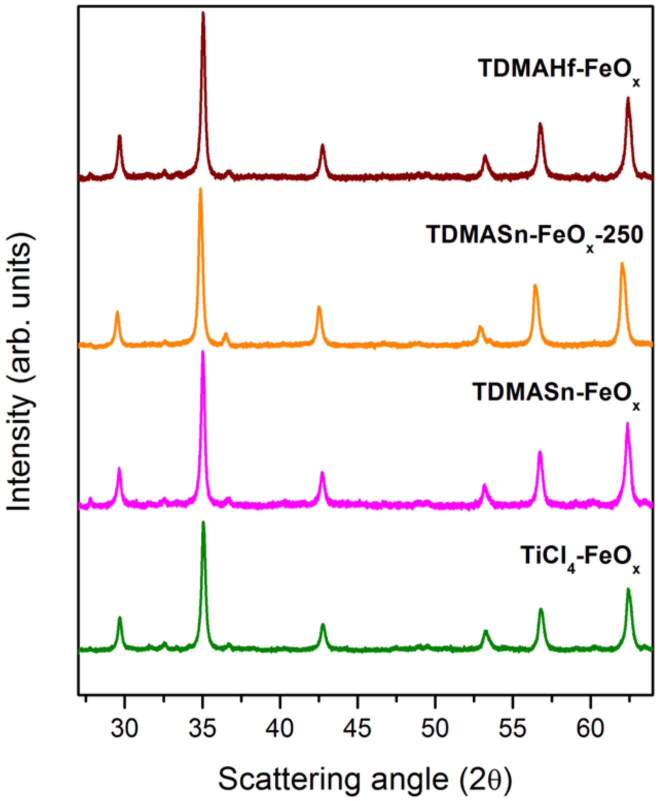


Figure 15. XRD patterns of TiO_2-coated γ-Fe_2O_3 nanoparticles with $TiCl_4$ and H_2O ALD precursors ($TiCl_4$-FeO_x), SnO_2-coated γ-Fe_2O_3 nanoparticles with TDMASn and H_2O ALD precursors, at processing temperatures of 150 °C (TDMASn-FeO_x) and 250 °C (TDMASn-FeO_x-250), and HfO_2-coated γ-Fe_2O_3 nanoparticles with TDMAHf and H_2O ALD precursors (TDMAHf-FeO_x).

For investigating the ligand ($(CH_3)_2N^-$) as potential reducing agent, TDMASn and demineralized water were used as precursors in an ALD process at 150 °C (sample TDMASn-FeO_x). Similar to the $TiCl_4$ ALD process, the crystal structure of the iron oxide particles after using TDMASn seem not to be affected. The particles largely maintain their cell parameters (Table 1) and no presence of Verwey transition is observed, Figure 16. However, considering the different Pauling electronegativities of Ti and Sn (i.e., 1.3 and 1.8 for Ti and Sn, respectively), the reactivity of the ligand may be strongly affected by the metal cation present in the precursor. Assuming that the energy required for the ligand dissociation from the coordination sphere of the metal in the TDMASn is higher than in the case of the TDMATi, the ALD process with the tin precursor has been repeated at higher temperatures, namely, at 250 °C (sample TDMASn-FeO_x-250).

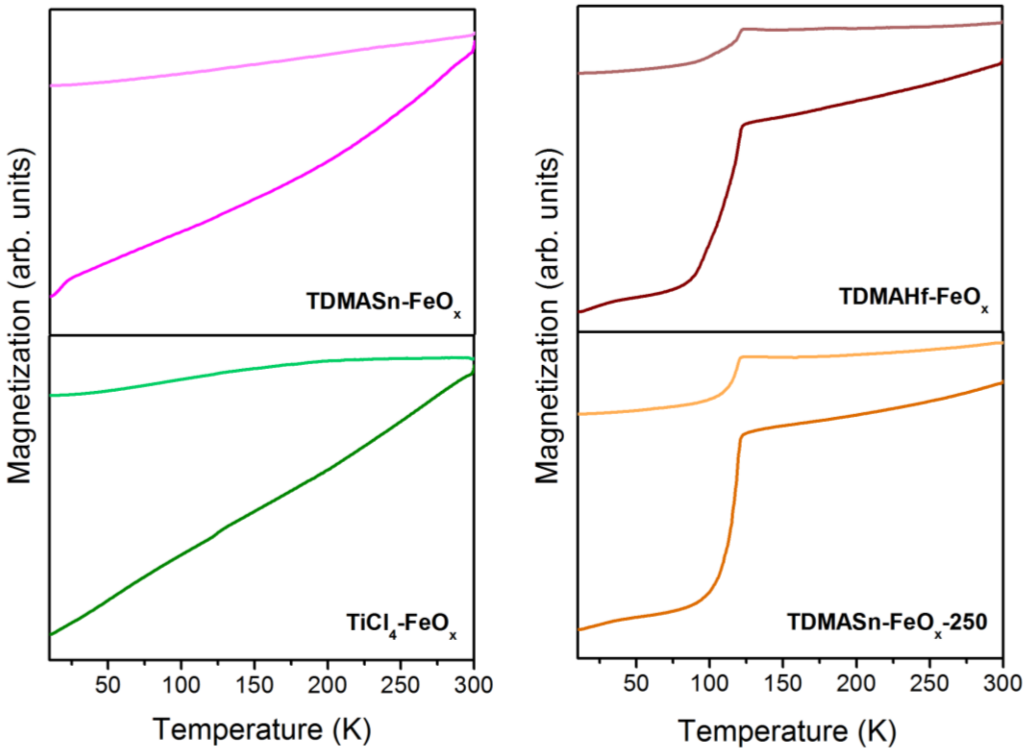


Figure 16. Magnetization vs. temperature curves of TiO_2-coated γ-Fe_2O_3 nanoparticles applying $TiCl_4$ and H_2O as ALD precursors ($TiCl_4$-FeO_x), SnO_2-coated γ-Fe_2O_3 nanoparticles with TDMASn and H_2O as ALD precursors, at 150 °C (TDMASn-FeO_x) and at 250 °C (TDMASn-FeO_x-250) process temperatures, and HfO_2-coated γ-Fe_2O_3 nanoparticles with TDMAHf and H_2O ALD precursors (TDMAHf-FeO_x).

As a result, the iron oxide nanostructure is affected in a similar manner as with TDMATi. The cell parameter is increased (Table 1) and the Verwey transition appears in the magnetization curves, Figure 16, confirming the Fe^{3+} → Fe^{2+} partial reduction and, thus, the Fe_3O_4 formation.

Finally, in order to further confirm that the TDMA ligand is responsible for the reduction, a further ALD process with tetrakis (dimethylamino) hafnium (IV) (TDMAHf) as precursor has been performed (sample TDMAHf-FeO_x). Hf has an electronegativity similar to Ti (i.e., 1.2), which implies that upon correct assumption of the mechanism, similar results as with TDMATi can be obtained. A partial reduction of the γ-Fe_2O_3 may take place already at lower temperatures. Indeed, the Rietveld analysis of the sample TDMAHf-FeO_x shows that the cell parameter is increased after the TDMAHf process to permit the formation of the Fe_3O_4 structure. In the magnetization curves, Figure 16, the Verwey temperature is clearly observed.

The results show that the anion of the precursor, ($(CH_3)_2N^-$), is responsible for the partial reduction of iron oxide and the concomitant structural modification of the initial seed nanoparticles. In the first step of the ALD process, the TDMATi precursor loses the amino groups while anchoring to the surface of the nanoparticles. Those ligands can lose one electron each and recombine to form gas phase tetramethylhydrazine ($(CH_3)_2NN(CH_3)_2$), which is the oxidation product as the γ-Fe_2O_3 substrate is being reduced.

A DFT modeling of the reaction activation energies was performed for such a case and it was compared to the model of reactions with different precursors varying the central metal ion and the ligands (Figure 17). Indeed, the calculations show that the TDMATi energetically favors the reduction of γ-Fe_2O_3 to Fe_3O_4 with an estimated activation barrier of 0,85 eV, and the TDMAHf has a reduction capability similar to TDMATi (a lower barrier of 0,73 eV). However, the TDMASn is energetically less favorable for such a reduction reaction with a larger activation barrier of 1,12 eV, indicating that a higher reaction temperature is needed to trigger the reduction, which is in full agreement with the experimental observations. For Ti precursors with different ligands such as $Ti(OiPr)_4$ (titanium isopropoxide) or $TiCl_4$, DFT calculations show significantly higher values of 4,08 eV and 4,45 eV, respectively, meaning that no reduction is expected. These theoretical results well explain the phenomena observed experimentally and support the importance of precursor ligands for such concerted reduction-coating processes. When an ALD process is carried out, the electrons originating from the amino ligands of the TDMATi create a chemical potential gradient at the nanoparticle surface triggering the reduction process along the whole iron oxide structure.

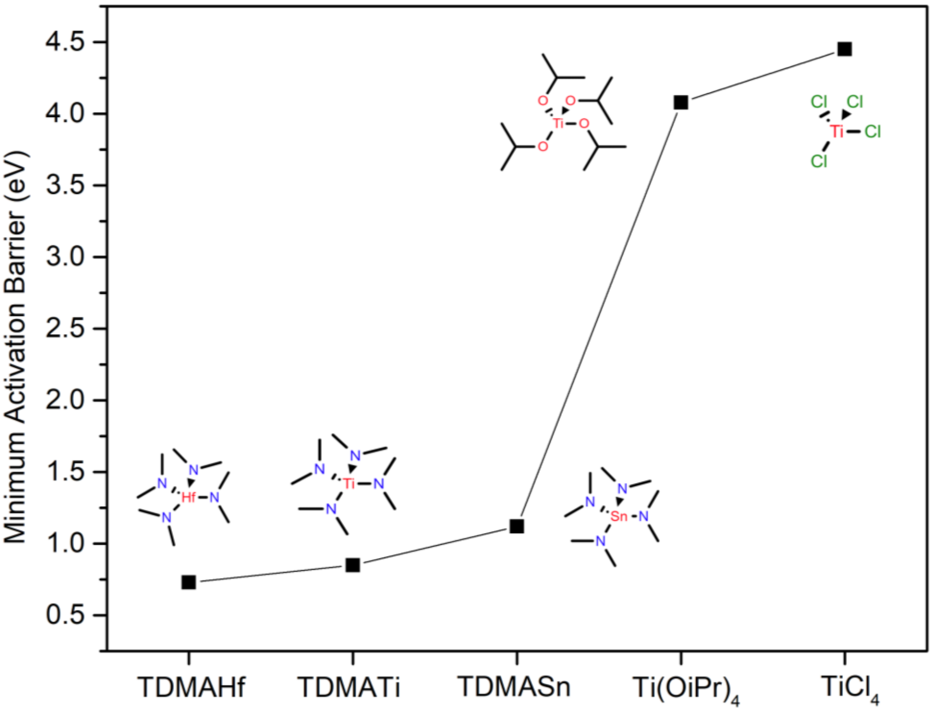


Figure 17. Comparison of DFT calculated minimum activation barriers for reducing Fe_2O_3 to Fe_3O_4 by using various ALD precursors as sketched in the graph.

This hypothesis is supported by the magnetometric curves measured after different ALD cycle numbers and the visual color change of the particles after ALD process (Figure 18). The characteristic T_V for the Fe_3O_4 structure appears already after the first ALD cycles and becomes more pronounced as the number of cycles increases, which is very likely related to a mediated diffusion and growth mechanism.[40] Besides, it is possible to appreciate visually, the color change from orange, in commercial γ-Fe_2O_3, to black, after the reduction to Fe_3O_4.

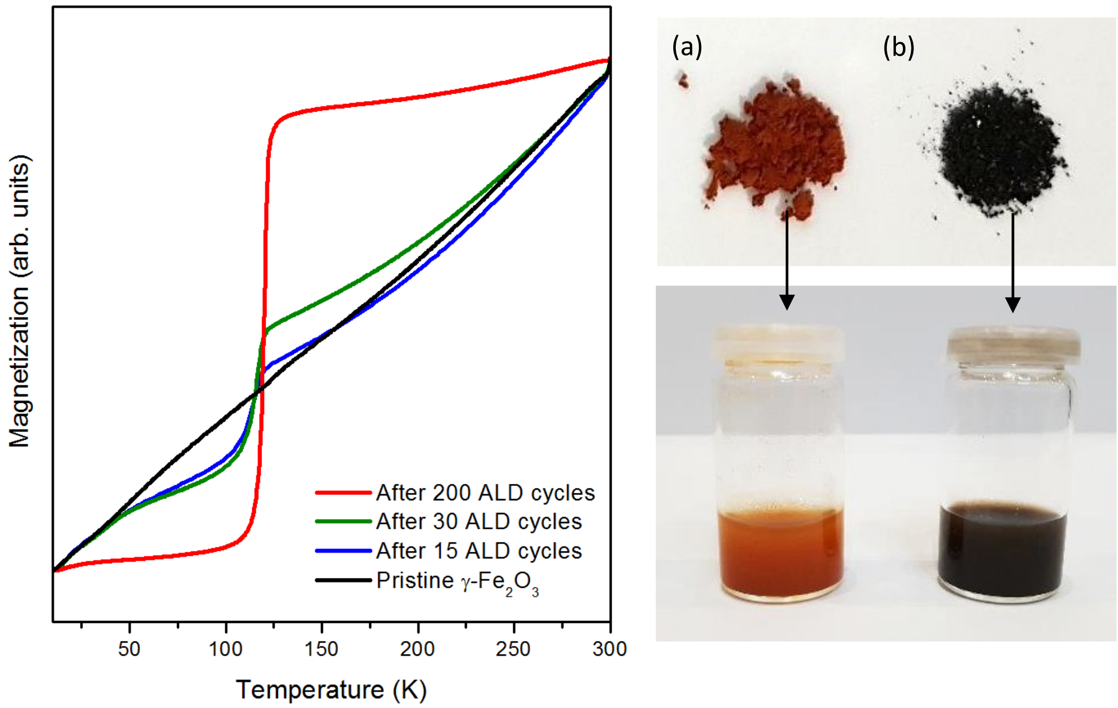


Figure 18. Left panel: Magnetization vs. temperature curves of Fe_3O_4-TiO_2 core-shell nanoparticles after various numbers of ALD coating cycles and a concerted reduction of the γ-Fe_2O_3 nanoparticles to Fe_3O_4. Right panel: Visual color change of the particles in powder form (top) and dispersed in water (bottom); (a) untreated commercial γ-Fe_2O_3 nanoparticles, (b) the same particles after applying various ALD cycles, forming Fe_3O_4-TiO_2 core-shell nanoparticles. The color change from orange to black is indicative of a transformation from γ-Fe_2O_3 to magnetite.

3.4. Conclusions

In this work, it is demonstrated that the ALD process not only coats nanoparticles in a controlled way, but also depending on the ligand of the metallic precursor, the substrate material is modified on its final chemical and/or structural properties. γ-Fe_2O_3 nanoparticles have been coated with TiO_2 and concertedly reduced to magnetite. As a result, Fe_3O_4-TiO_2 core-shell nanoparticles have been generated by atomic layer deposition at moderate temperatures. The deposited coatings prevent agglomeration of the nanoparticles and re-oxidation to γ-Fe_2O_3 even at high temperatures, allowing for the use of post-process annealing and thus crystallization of the amorphous TiO_2 to anatase; a beneficial characteristic which has an important role in many industrial and bio-related applications.

The reduction of γ-Fe_2O_3 to Fe_3O_4 is a function of the applied precursor and the processing temperature. The ligand of the precursor $(CH_3)_2N^-$ can become oxidized and recombine to form tetramethylhydrazine, while acting as reducing agent for the Fe^{3+}. The cation of the precursor also plays an important role. The more electronegative the cation is, the more energy is necessary to release the ligands, which is important for the recombination. Therefore, the temperature required for ALD processes to reduce the sample is higher for TDMASn than for TDMATi and TDMAHf.

The use of an ALD process to concertedly coat and reduce nanomaterials simplifies numerous attempts to generate multifunctional materials for emerging applications, such as energy storage or medicine. The appropriate design of precursors and selection of substrates will pave the way for numerous new compositions, while the ALD process itself allows for easy up-scaling to large amounts of coated and reduced particles for an industrial use.

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CAPITULO 5

El contenido del capítulo está sujeto a confidencialidad

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El contenido del capítulo está sujeto a confidencialidad

Chapter 4

Controlled Atomic Layer Deposition of Aluminum Oxide on Sulfur-based Cathodes of Lithium-Sulfur Batteries

This chapter presents the modification of cathode materials of lithium-sulfur batteries by atomic layer deposition (ALD) using a conventional static ALD reactor. For this aim, the cathode of lithium-sulfur batteries was coated with alumina. The study is focused on low-temperature ALD coatings and the effect of the deposited material on the final cathode, after applying various numbers of deposition cycles. The alumina deposition results in an improved capacity of the system, especially at high current densities. Besides, the process temperature plays an important role, in particular for few-cycle ALD processes, aiding a better performance of the cell. It is also demonstrated that higher numbers of ALD cycles, especially at elevated process temperatures, lead to a considerable loss of sulfur, which in turn significantly lowers the cell performance. This work reports the optimal parameters for application of ALD to sulfur-based electrodes. Cathodes modified with alumina at low process temperatures and with low numbers of ALD cycles are proposed as alternative to conventional lithium-sulfur cathodes, since they have a higher specific capacity and Coulombic efficiency.

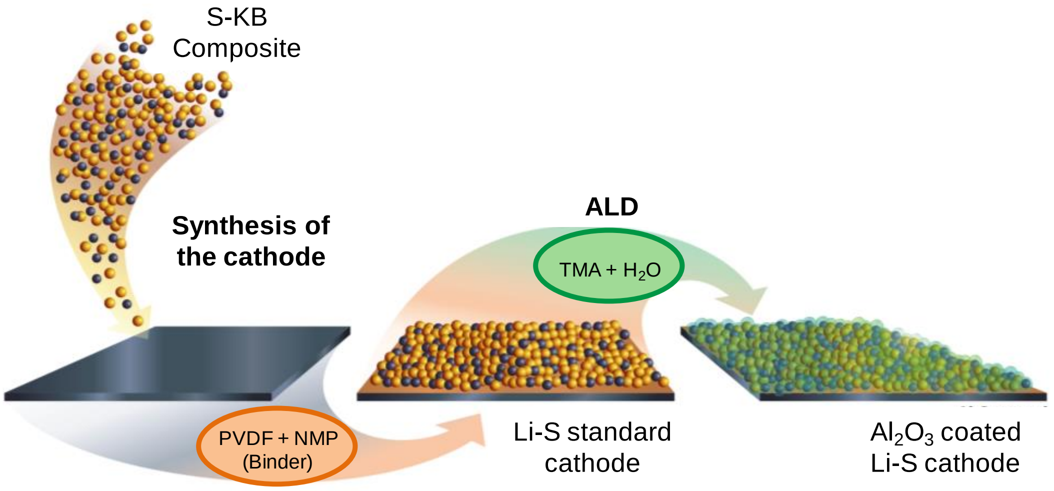
This chapter describes the part of the thesis that was under revision in the journal *Energy Technology* from Wiley-VCH at the time of submission of the thesis. The

ALD processes carried out in this chapter were performed at nanoGUNE, while the physicochemical and electrochemical characterizations of the samples were performed at Cidetec.

Article:

Controlled Atomic Layer Deposition of Aluminum Oxide to Improve the Performance of Lithium-Sulfur Batteries

Sarai García, Olatz Leonet, Eneko Azaceta, Iñaki Gómez, Antonio Reifs, J. Alberto Blazquez, Mato Knez, submitted to *Energy Technology*. Manuscript number: ente.201901432.



4.1. Introduction

Lithium-sulfur (Li-S) batteries are recognized as most promising next generation energy storage devices due to their overwhelming advantages in specific capacity and energy density. Thanks to the extraordinary properties of sulfur as cathodic material,[1]–[3] Li-S batteries are proposed as alternative to the conventional lithium-ion batteries (LIBs). However, Li-S batteries suffer from several issues that affect their commercial application. One of the most challenging issue to be solved is known as the “shuttle effect”, resulting in high overcharge and poor Coulombic efficiency (CE) of the battery.[4],[5] In an effort to address the shuttle effect, various immobilizers and physically confining structures have been developed. In spite of their benefits, those strategies potentially affect the volume and weight of the cells, consequently reducing the Li-S energy density.[6]–[9]

A promising pathway to overcome the mentioned shuttle effect could be the use of atomic layer deposition (ALD).[10]–[13] In recent years, ALD enjoys a rapidly growing interest for emerging applications in energy storage devices [14]–[17] among other applications.[18]–[21] ALD provides ultimate control over the conformality of films and their thickness,[22]–[24] being more suitable for its application in batteries comparing with other deposition technologies.

In LIBs, the conformal deposited coatings and thickness control by means of ALD led to many improvements in the stability of this systems.[25] A protective layer, deposited by ALD, improves the stability of the LIBs by suppressing side reactions between the electrolyte and electrodes, thereby preventing the decomposition of the electrolyte.[26],[27] More recently, ALD has been evaluated for improving Li-S batteries. The application of a protective layer on the electrodes of this kind of batteries has proven to enhance the Li-S batteries´ performance, especially through reducing the polysulfide dissolution by absorbing or bonding them to the deposited material.[16]

Alumina (Al_2O_3) is the most popular metal oxide for ALD-type of deposition, being economic and facile.[28],[29] Already few cycles of alumina deposition can greatly increase the reversible capacity and long-term durability of the cathodes in conventional lithium-ion [15] and lithium-sulfur batteries.[6] However, Al_2O_3 is electrochemically inactive and insulating, and it does not make any contribution to the capacity of a battery. Thus, a thick alumina coating can serve as a barrier for the Li-ion mobility and in this way decrease the total capacity of the battery.[1] On the other hand, if the number of alumina cycles is not sufficient to generate a coating, dispersed clusters or islands will be generated on the cathode that might act as a chemical absorber for binding polysulfides, thereby reducing the shuttling to the anode and improving the capacity retention of S cathodes.[30]

In this work, it is demonstrated that applying a specific number of ALD cycles of Al_2O_3 on prefabricated sulfur cathodes for Li-S batteries can reduce the shuttle effect and thereby greatly improve the cyclability and capacity retention of fabricated Li-S batteries. A range of process temperatures and various ALD cycles numbers are tested in order to minimize sublimation of sulfur and thereby, the loss of this active material during the ALD process. In addition to the process temperature, purge times of ALD precursors are also modified to avoid parasitic CVD, which might occur due to the applied low process temperatures. In this case, longer purging times are needed to remove the excess of precursors and by-products and in this way avoid the mentioned parasitic CVD. Inductively coupled plasma with mass spectroscopy (ICP-MS) and thermogravimetric analysis (TGA) were used to study the deposition of alumina on the cathodes and sulfur sublimation during the ALD process. Thanks to the electrochemical analysis, it is found that a deposition of alumina with as few as 2 ALD cycles at 85 °C results in an insignificant sulfur loss (<1%) and greatly improves the specific capacity and Coulombic efficiency (CE) of the lithium-sulfur batteries, especially at high current densities.

4.2. Experimental section

4.2.1. Fabrication of cathodes

Cathodes were produced using 60 wt% commercial sulfur powder (<40 μm Merck) in the final formulation. A mixture of 80 wt% sulfur (S) and 20 wt% Ketjen Black (KB) 600JD (AkzoNobel) was homogeneously mixed by ball-milling in ethanol for 3h. The mixed carbon-sulfur powder was heated at 300 °C for 2h in order to properly impregnate the sulfur on the high-area carbon powder matrix. Afterwards, the dried powder was added to a solution of polyvinylidene fluoride (PVDF) 5130 (SOLVAY) in N-methylpyrrolidone (NMP) to form the cathodic slurry (see Figure 19). An additive conductor was added (carbon black, TIMCAL C-NERGY^{TM} SUPER C45), capable of forming micellar structures. The whole mixture was sonicated for 30 minutes and stirred overnight by using a mechanical mixer (RW 20 digital, IKA) for ensuring a homogeneous slurry. These slurries were then blade cast onto a carbon-coated aluminum foil (MTI Corp.) and dried at 60 °C under dynamic vacuum during 12 h before the cell assembly.

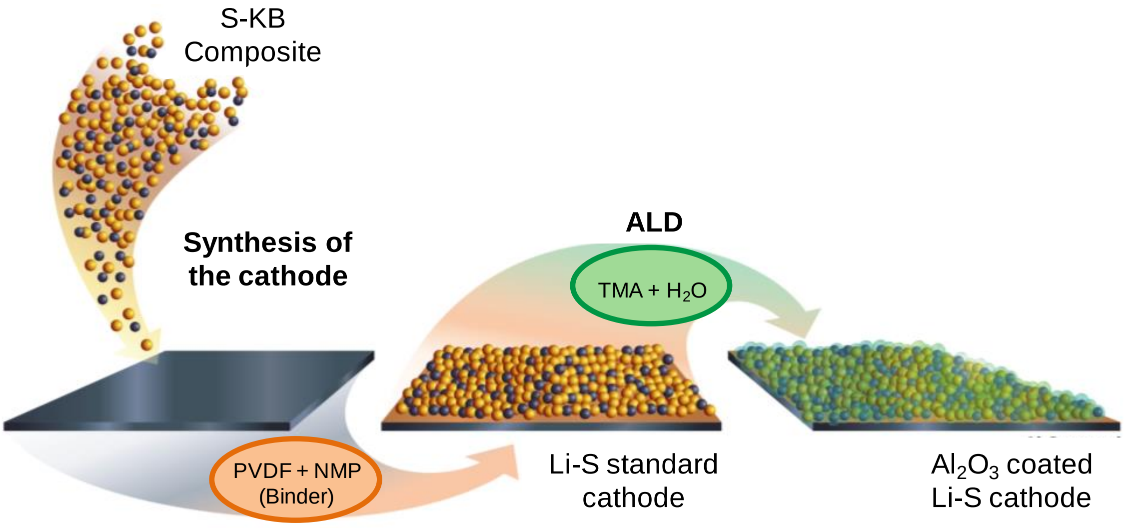


Figure 19. Schematic illustration of electrode assembly and alumina coating by ALD for lithium-sulfur batteries.

4.2.2. ALD process

The fabricated cathodes for Li-S coin cell batteries were used as a substrate in ALD experiments (see Figure 19). The coating of each cathode was performed in a commercial ALD reactor (Savannah S100, Cambridge NanoTech Inc). The processes were carried out under a constant nitrogen gas flow of 20 standard cubic centimeters per minute (sccm) at various process temperatures, 85 °C, 80 °C, 75 °C and 60 °C. Trimethyl aluminum (TMA), obtained from Sigma Aldrich, and demineralized water (oxygen source), were used as ALD precursors. Coating processes were run with 2, 5, 10 and 20 ALD cycles. The coated cathodes were prepared following a typical ALD timing sequence expressed as t_1-t_2-t_3-t_4, where t_1 is the exposure time of the first precursor, t_2 is the purge time following the first exposure, t_3 is the exposure time of the second precursor, t_4 is the purge time following the exposure to the second precursor. The times corresponding to t_1-t_2-t_3-t_4 were 10-x-10-x, where x was varied as follows: for 85-80 °C x= 60, for 75 °C x=90 and for 60 °C x=120. All values are given in seconds (s). The pulsing times were a function of the vapor pressure of each precursor, being 0,1 s for TMA and 0,05 s for water vapor. The processes were performed under vacuum at a base pressure of 1 mbar.

4.2.3. Physicochemical characterization

The physicochemical properties of the produced electrodes were characterized to confirm alumina deposition and determine the sulfur loss during the ALD process. Elemental analysis of alumina was carried out using ICP-MS (Induced Couple Plasma with Mass Spectroscopy, performed with an iCAP-Q, Thermo Fisher Scientific GmbH, Germany), which provides the mass fraction of aluminum in the coated samples, Al wt%. To determine Al wt% in the samples, a small amount of the electrode material (dried slurry), without aluminum foil, was dissolved in a pre-prepared solution of 0,5 $mg \cdot mL^{-1}$ of nitric acid in water. After dissolution, the samples were aged for 72 hours and diluted in MQ (milli-Q) water in a ratio of 1:25 to obtain 2,7 % HNO_3, 20 $\mu g \cdot mL^{-1}$. The samples were then analyzed with ICP-MS to determine the mass fraction of aluminum in the samples. The elemental sulfur content of the cathodes was determined via thermogravimetric analysis (TGA) using a Netsch STA. A small amount of powder from the electrode material (dried slurry without aluminum foil) was thermally ramped from 25 °C (room temperature) to 400 °C with a heating rate of 10 $°C \cdot min^{-1}$ under N_2 atmosphere.

4.2.4. Li-S cell electrochemical characterization

The fabricated cathodes were assembled into lithium-sulfur (Li-S) coin cells. The cathodes were prepared with a sulfur loading of 1,8 $mg_S \cdot cm^{-2}$ and a theoretical capacity of 2,7 $mA \cdot h \cdot cm^{-2}$, derived from the theoretical capacity of elemental sulfur (1672 $mA \cdot h \cdot g^{-1}$). One layer of a commercial polyolefin separator, Celgard 2501, soaked with 50 µL of 0,38 M solution of Bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) (Sigma-Aldrich) and 0,32 M of lithium nitrate ($LiNO_3$) (Sigma-Aldrich) as additive in a 1/1(v/v) mixture of dimethoxyethane (DME) (BASF) and dioxolane (DOL) (BASF), was placed between the electrodes. Lithium foil (0,05 mm, Rockwood Lithium) was used as the anode in coin half cells (2025, Hohsen). Vacuum drying of electrodes and cell crimping has been performed in a dry room with a dew point below -50 °C. Thereafter, the assembled cells were aged for 20 hours and then cycled in a BaSyTec Cell Test System (Germany) at 25±1 °C controlled by air conditioning.

The electrochemical behavior of the obtained ALD coated sulfur electrodes was evaluated at different C-rates (C/10, C/5, C/2,5, 1C and 2C) considering the theoretical capacity of elemental sulfur (1672 $mA \cdot h \cdot g^{-1}$). The cycle life of the coin cells was investigated within a 1,7-2,6 V interval at C/5 charge-discharge current rates.

4.3. Results and discussion

Standard sulfur electrodes have been coated with alumina (Al_2O_3) using ALD at various process temperatures (60 °C, 75 °C, 80 °C and 85 °C) and under vacuum. The characterization of the samples by ICP-MS, as shown in Table 2, confirms successful alumina deposition after each of the processes.

Theoretically, in ALD the amount of deposited alumina increases almost linearly with the number of cycles. If ALD processes are performed within a material-specific temperature window (ALD window), the cycle-dependent linear growth behavior is largely independent of the process temperature. There is an exception for our samples coated at 60 °C. In this case, the tendency of the deposited alumina varies independently on the temperature and cycle number. This is attributed to the process being outside of the ALD window of alumina.[12],[31] The deposition process results in non-linear and scattered amounts of Al among the samples. Most likely the water precursor is not completely evaporated during purging, but rather some amount is remaining bound to the surface of the samples, reacting with the subsequent delivery of TMA and thus inducing some level of parasitic CVD coating in addition or instead of ALD. Furthermore, the activation energy that needs to be overcome for an ALD reaction, is higher at those temperatures. Consequently, the results are not consistent with the cases where the process is largely within the ALD window.

Table 2. ICP-MS derived aluminum amounts in ALD-coated sulfur cathodes for various process temperatures as a function of the number of processing cycles.

% Al (w/w)				
Temperature (°C)	2 ALD	5 ALD	10 ALD	20 ALD
60	0,46	10,78	10,46	7,88
75	0,55	1,39	5,64	13,17
80	0,44	1,71	4,03	10,59
85	1,97	1,75	5,80	13,10

Sulfur is the active cathodic material in Li-S batteries. Therefore, a reduction of the sulfur to carbon ratio in the electrode formulation leads to a lower capacity of the system. In the course of an ALD deposition, with the surface reaction being of chemical nature, a loss of the initial sulfur amount can be expected. To quantify the sulfur loss during the ALD processes, thermogravimetric analyses have been done for each sample after the ALD treatment. Figure 20 shows the percentual sulfur loss after various ALD cycle numbers for the studied process temperatures. The general trend is obvious: The higher the temperature is, the higher is the loss of sulfur. With respect to the cycle numbers, the same trend can be observed, namely the amount of sulfur decreases considerably with an increasing number of ALD cycles.

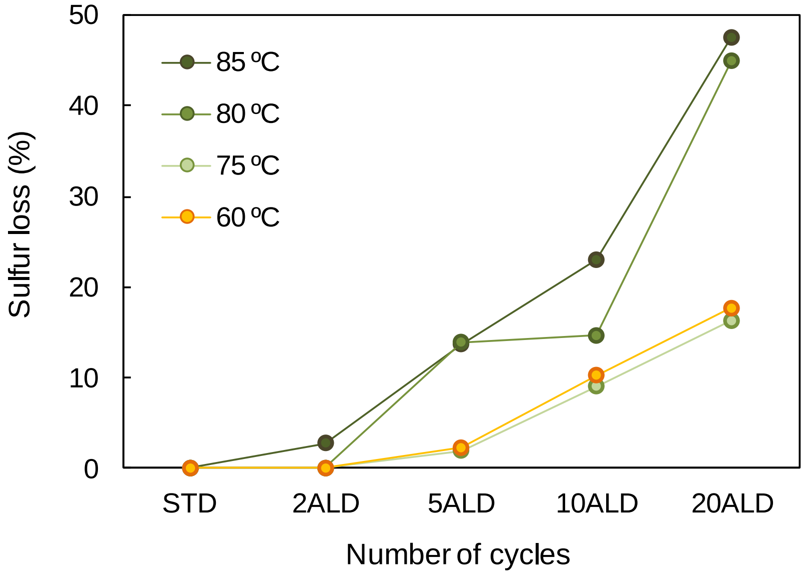


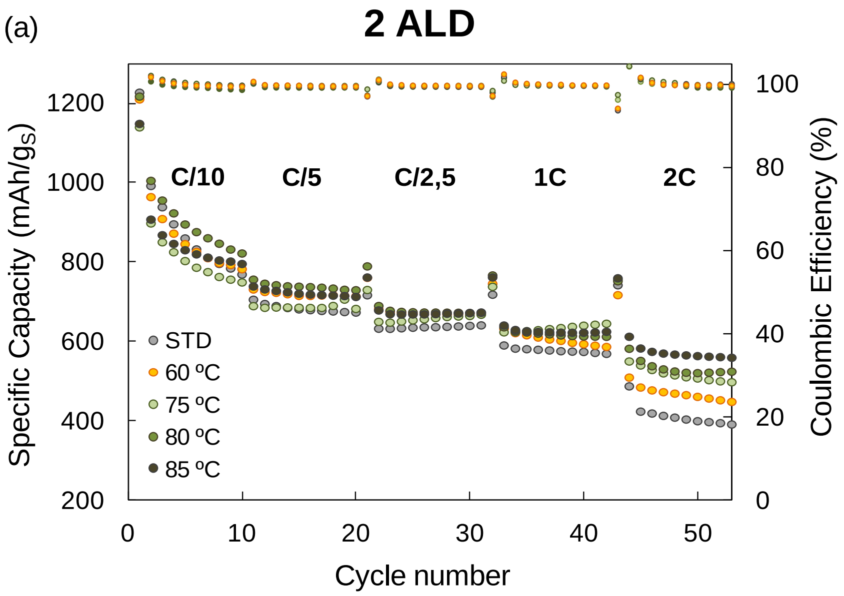
Figure 20. Loss of sulfur in the cathodes resulting from ALD processing at the indicated process temperatures as a function of the number of applied ALD cycles.

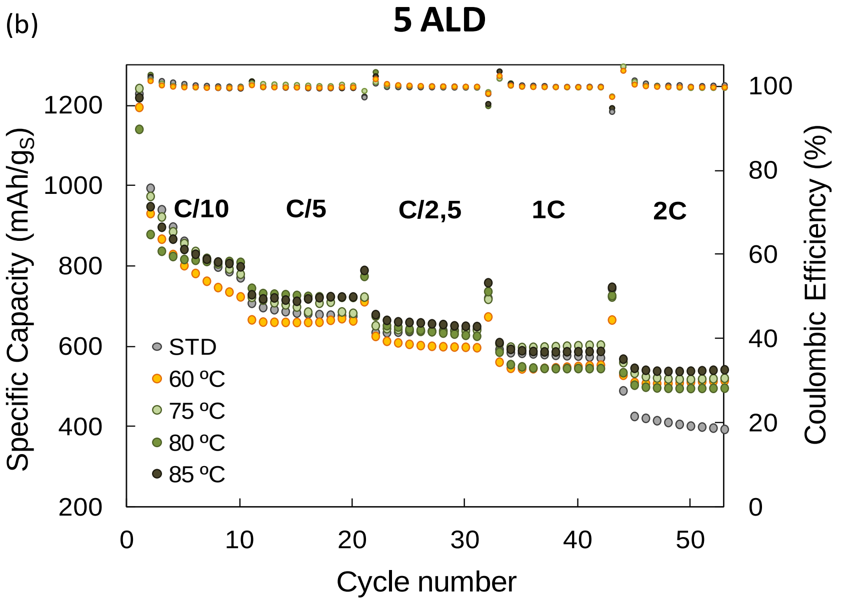
Two observable tendencies allow dividing the samples into two groups; samples done at 60-75 ºC and at 80-85 ºC. In the first case, processes at 2 and 5 ALD cycles have an acceptable sulfur loss of less than 5 %. In the second group (80-85 ºC), only the samples coated with 2 ALD cycles are showing a comparable and acceptable loss of sulfur. On the other extreme of applied cycle numbers, namely 20 ALD cycles, the significant loss of sulfur of more than 15 % for all applied temperatures, which resulted in discarding those samples from further electrochemical testing.

After physicochemical characterization, the samples were tested electrochemically. The most promising electrodes from previous characterizations (containing around 40-60 wt% of sulfur in the final cathode formulation) were selected for testing. 2025 type coin cells, assembled with those electrodes, were tested at C/10, C/5, C/2,5, 1C and 2C C-rates and their cyclability was analyzed at C/5.

Figure 21 shows the electrochemical performance of 2 ALD, 5 ALD and 10 ALD-coated alumina electrodes, processed at different ALD process temperatures

(60 °C, 75 °C, 80 °C and 85 °C), in Li-S batteries at different C-rates. If compared to the standard sample (cathode without ALD coating), only the assembly with the cathode after with 2 ALD cycles showed an improved performance of the battery, especially at elevated C-rates (1C, 2C), as depicted in Figure 21a; the higher the current density is, the better is the cell performance regarding the standard cathode. The reason could be the volume changes resulting from the different sulfur species generated during the redox reaction, which happens on a rather short time scale. Thanks to ALD, those volume changes could be largely suppressed and in this way the electron conductivity in fast kinetic reactions (high C-rates processes) improved. Those results are even more evident with higher processing temperatures, meaning that the obtained enhancement is dependent on the process temperature. Particularly at 85 °C, the capacity of the system increases from 400 mAh · g_S^{-1} in the standard sample to 600 mAh · g_S^{-1} in the 2 ALD-coated sample for high current densities (2C). After increasing the number of ALD cycles to 5 and 10 (Figure 21b and Figure 21c, respectively), a tendency similar to the previous case (2 ALD) can be observed, however, with some slight differences: At low C-rates an improvement of ALD-treated samples with respect to the standard sample is not very obvious in neither case.





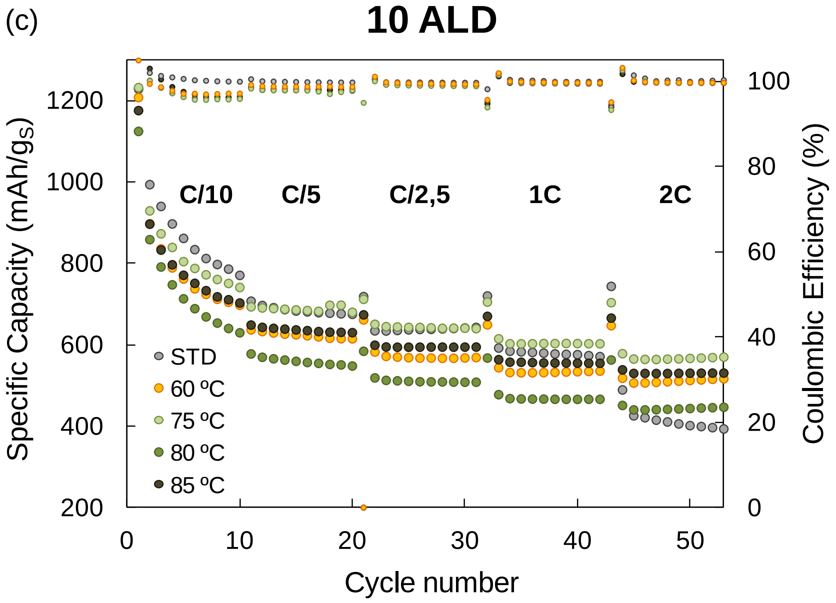
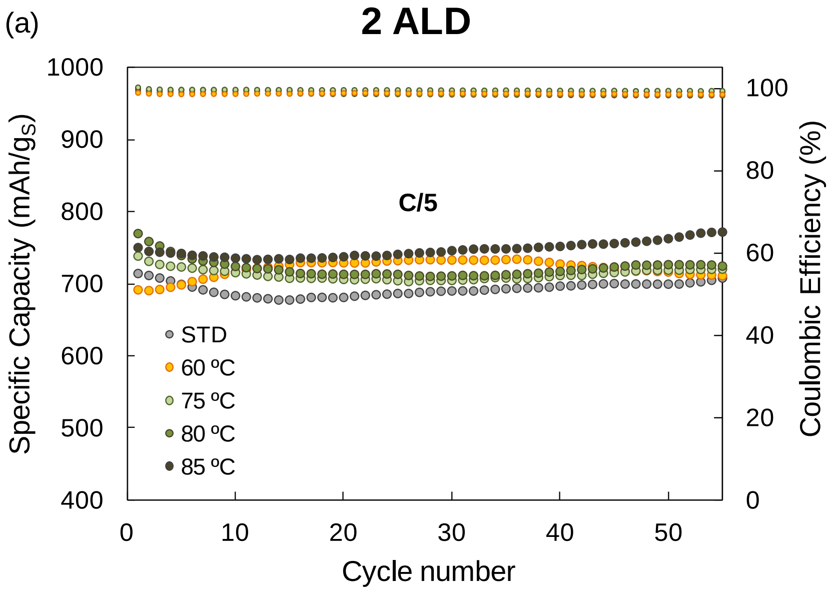


Figure 21. Electrochemical performance of 2025 type Li-S coin cells at different C-rates for (a) 2-ALD, (b) 5-ALD and (c) 10-ALD coated sulfur electrodes (sulfur loading of 1,8 mg · cm^{-2}) at ALD process temperatures of 60 ºC, 75 ºC, 80 ºC and 85 ºC.

However, at high current densities (2C) the cell performance is considerably better with ALD-processed cathodes than in the case of standard cathodes, with the capacity retention being improved for all the samples. While with 5 ALD-coated samples the performance of the battery enhances significantly from 400 mAh · g_S^{-1} to around 600 mAh · g_S^{-1} for all process temperatures, with 10 ALD-coated electrodes this distribution is wider, and the enhancement is not as good. The capacity is increased to almost 600 mAh · g_S^{-1} in the best case, the 10 ALD-coated electrode at 75 °C.

Looking at the cycle life of the cells, Figure 22a shows enhanced capacity retention during cycling at C/5 with 2-ALD samples processed at different process temperatures. This is most strongly expressed with samples processed at 85 °C. Here, the specific capacity of the cell increases from 700 mAh · g_S^{-1} to almost 800 mAh · g_S^{-1}, even after 50 charge-discharge cycles. However, with higher numbers of ALD cycles, that is, samples 5-ALD and 10-ALD, the cycle life and capacity retention of the cathodes do not improve at all. For 5-ALD, only the sample coated at 85 °C is better than the reference sample, increasing the capacity up to 800 mAh · g_S^{-1} even after 50 charge-discharge cycles (Figure 22b), while for the 10-ALD samples, none of the modified samples shows improvement (Figure 22c).



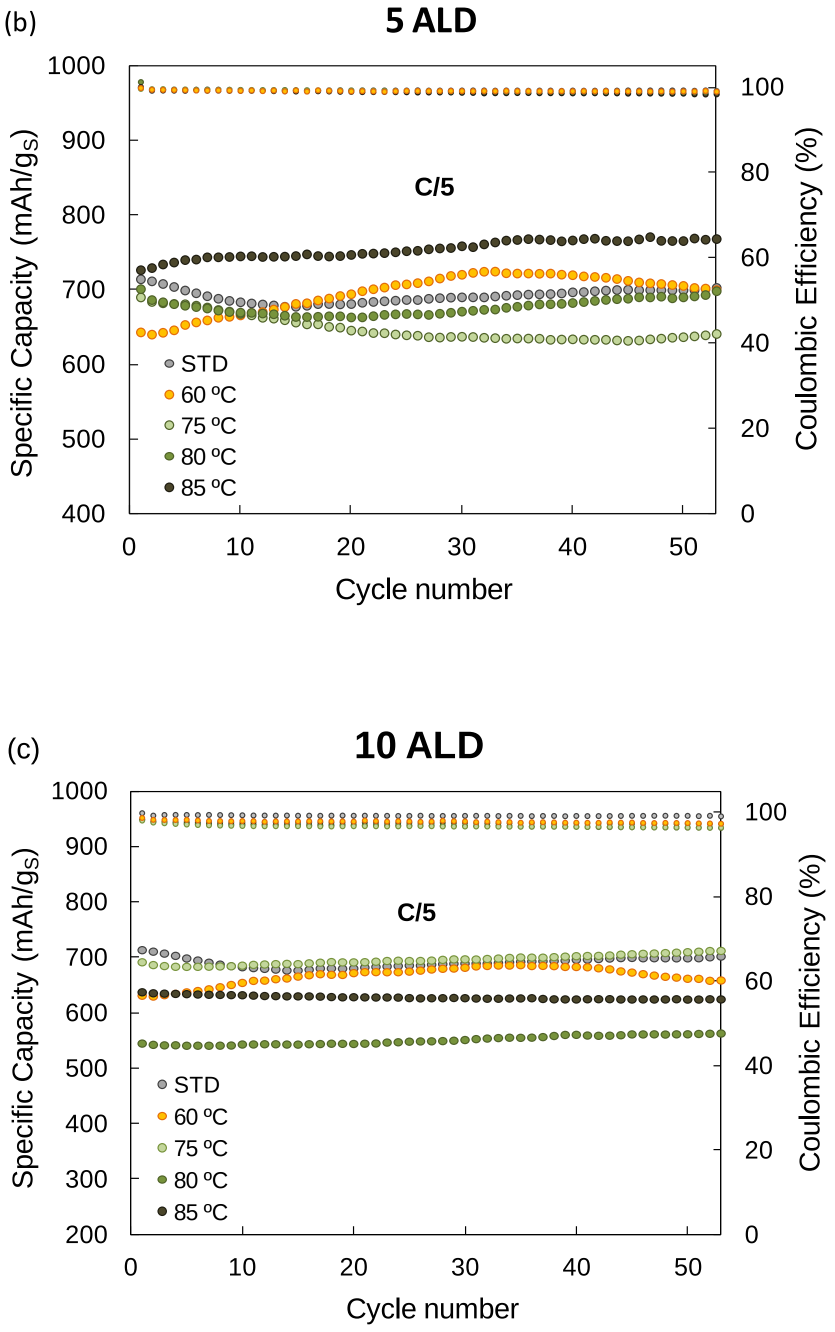


Figure 22. Cycling performance at C/5 of (a) 2-ALD, (b) 5-ALD and (c) 10-ALD sulfur electrodes (with a sulfur loading of 1,8 mg · cm^{-2}) at ALD process temperatures of 60 ºC, 75 ºC, 80 ºC and 85 ºC.

It is worth mentioning that for the 10-ALD samples the sulfur loss is ≥10 % for all processing temperatures (see Figure 20). Consequently, the results are not comparable with the standard sample. The sulfur amount in 10-ALD samples is deviating much more than the other ALD modified samples regarding the standard cathode, while the applied electrochemical conditions are the same. For this reason, the 10-ALD sulfur cathodes are not a suitable alternative for standard sulfur cathodes.

The electrochemical results further show that ALD processing does not induce significant differences to the performance of the lithium-sulfur batteries at low current densities (from C/10 to 1C). However, for high C-rates (2C) the performance is enhanced for all ALD processed samples, at any processing temperature. This may be attributed to trapping of polysulfides by alumina, which can bind polysulfides from the cathode, thus suppressing their dissolution and a resulting generation of extra resistance to the electronic conductivity of the cell. At high current densities this improvement is more evident, since the kinetic of the reaction is faster.

Apart from the trapping of polysulfides by Al_2O_3, another reason for the capacity improvement in ALD-modified cathodes could be the cohesion of the particles at the surface electrode with the particles in the subsurface, enhanced by the deposited alumina. This will enhance both the electronic conductivity and the electrolyte absorption by the electrode, resulting from the cohesions generated by deposited alumina which can bind electrode particles improving the contact with each other. However, since alumina is an insulator, the higher amount of deposited material on the surface of the cathode in the case of 5-ALD and 10-ALD samples can worsen the performance of the cathode by increasing its resistance. The mentioned sulfur loss during ALD processing for those samples adds another issue to the described drawbacks.

Given the physicochemical and electrochemical analysis, the 2-ALD electrode processed at 85 °C shows most promise as alternative to the standard sulfur cathode. It is the only sample that shows an improvement of the cell capacity both for different C-rates and cycle life. Moreover, the deposition of only 2 ALD cycles saves time and precursors during the ALD process.

The charge-discharge voltage profiles of 2-ALD, processed at 85 °C, and the standard sample for different C-rates are compared. Figure 23 shows that at low C-rates there is no significant difference in the profiles of the samples with the standard cathode and the 2-ALD cathode. Moreover, at low C-rates (C/10), ALD worsens the cell performance. However, with increasing the C-rate the discharge capacity of the ALD-coated cathode improves, as also shown previously in the current densities and cycle life analyses. For instance, at C/5 the discharge capacity is increased, namely from 680 $mAh \cdot g_S^{-1}$ in the standard cathode to around 750 $mAh \cdot g_S^{-1}$ in the 2-ALD sample. Furthermore, for the highest C-rate (2C) the discharge capacity increases considerably from 400 $mAh \cdot g_S^{-1}$ in the standard cathode, to around 600 $mAh \cdot g_S^{-1}$ in 2-ALD sample.

On the other hand, one can see two discharge plateaus, one between 2,4 and 2,3 V and another at 2,1 V for all C-rates except of 2C. In the latter case, the first plateau is reduced from the standard cell, while the 2-ALD modified cell still maintains it. This shows a moderate improvement of the specific capacity of the test cell, but this increased potential could significantly raise the energy density in a real battery prototype.

Regarding polarization, ALD is decreasing the resistance of the electrochemical process especially at high C-rates. As stated above, ALD enhances the current density, meaning that electrolyte penetration and its absorption is enhanced with the presence of small amounts of alumina, improving the wettability of the cathode as well as the cohesion of sulfur particles and reducing the shuttle effect due to the blocking of polysulfides.

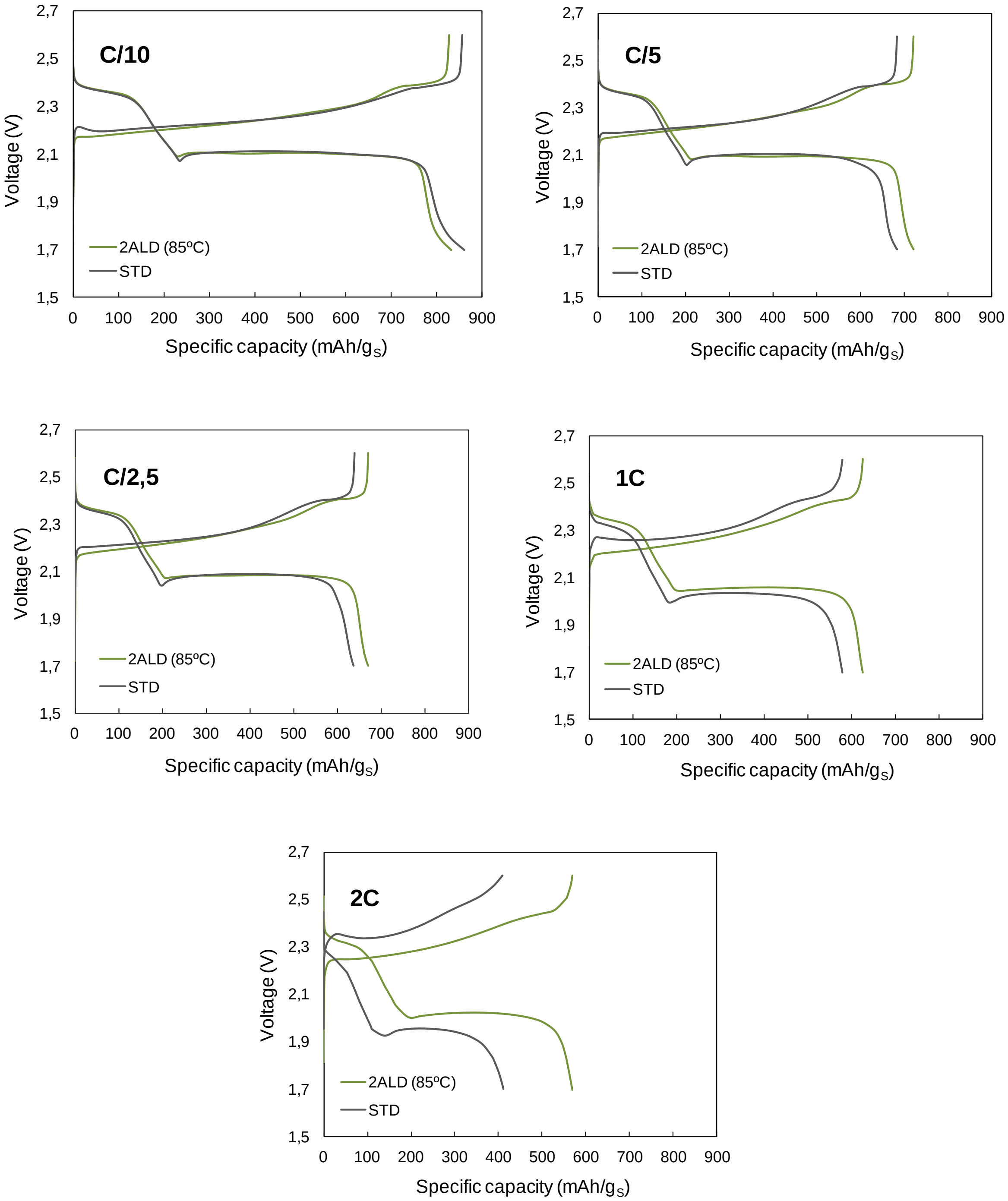


Figure 23. Voltage profiles of the standard electrode (STD) in comparison to 2-ALD coated electrodes processed at 85 ºC at different C-rates.

4.4. Conclusions

In this chapter, it is demonstrated that applying ALD directly to the produced cathodes improves the performance of Li-S batteries. The optimal parameters for the ALD processes involve deposition of alumina with few ALD cycles at low temperatures. Besides the improved performance of the batteries, this way of processing is more cost-effective and time efficient.

The physicochemical characterization of the materials confirmed deposition of alumina on the sulfur cathodes by ALD, which improves the cohesion of the particles between the electrode surface and subsurface area, thus improving the electronic conductivity and increasing the absorption of the electrolyte by the cathode. Furthermore, alumina may bind polysulfides, thereby blocking their transport to the anode and their dissolution in the electrolyte.

The loss of sulfur during the ALD process, which results from elevated process temperatures and long exposure times of the substrate to the precursors, has negative consequences for the performance of the batteries. For this reason, samples processed with larger numbers of ALD cycles, which resulted in less than 40 wt% of sulfur in the cathode formulation, were discarded from electrochemical performance testing.

Among the tested samples, the cell performance showed that at low C-rates (C/10-1C) ALD did not improve the efficiency of the cells considerably. However, at high C-rates (2C), the capacity of the system was significantly increased for ALD-coated samples with 2, 5 and 10 applied ALD cycles. The best performance was observed from 2-ALD samples processed at 85 ºC. Compared to the standard cathode, this sample showed better capacity retention for low and high current densities, meaning that only 2 ALD cycles are sufficient to improve the cell performance.

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List of publications

[1] *Ligand-Induced Reduction Concerted with Coating by Atomic Layer Deposition on the Example of TiO_2-coated Magnetite Nanoparticles*
Sarai García, Alberto López-Ortega, Yongping Zheng, Yifan Nie, Kyeongjae Cho, Andrey Chuvilin and Mato Knez, *Chemical Science*, **10**, 7, 2171–2178 (2019).
(Chapter 3)

[2] *Controlled Atomic Layer Deposition of Aluminum Oxide to Improve the Performance of Lithium-Sulfur Batteries*
Sarai García, Olatz Leonet, Eneko Azaceta, Iñaki Gómez, Antonio Reifs, J. Alberto Blázquez and Mato Knez, submitted to *Energy Technology*, manuscript number: ente.201901432.
(Chapter 4)

Patents

[1] *High Energy Density Sulfur Cathode for Lithium-Sulfur Batteries*
Sarai García, Olatz Leonet, Eneko Azaceta, Iñaki Gómez, Mikel Beltrán, J. Alberto Blázquez and Mato Knez, submitted as *European Patent* (2020). Patent number: EP20382003
(Chapter 5)

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