IMPORTANCE & APPLICATIONS OF NANOTECHNOLOGY

Introducing the Application of Nanotechnology in Lithium-Ion Battery

***Ehsan Kianfar*[1,2]**; Hassani Joshaghani A*[1]*; Seyyed Ali Razavikia*[3]

[1]*Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran.*

[2]*Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran.*

[3]*Department of Chemical Engineering, Yasuj Branch, Islamic Azad University, Yasuj, Iran.*

Corresponding Author: Ehsan Kianfar

Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran.

Email: e-kianfar94@iau-arak.ac.ir & ehsan_kianfar2010@yahoo.com

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Abstract

This chapter discusses the application of nanotechnology in lithium-ion batteries, but it can also be generalized to other batteries such as sodium ion and magnesium ion. This chapter describes the applications of nanotechnology in a categorized manner, and the applications of nanotechnology in battery components will be discussed in other researches. In this chapter, the advantages of nano processing in increasing the power and capacity and its disadvantages such as reducing the volumetric energy density are stated. Defect solutions are referred to by nanotechnology such as nano coatings and engineered nanostructures.

Keywords: Nanotechnology; Lithium-ion batteries; Sodium ion; Magnesium ion.

Introduction

The application of nanotechnology, as we will see later in this series, does not make a surprising difference compared to other areas in which nanotechnology is present, such as the semiconductor industry and the pharmaceutical industry; Rather, what makes the use of nanotechnology in batteries important is the need to use batteries, which forces us to turn to nanotechnology to solve its problems. The purpose of this section is to titrate nanotechnology applications in the field of lithium batteries [1-4]. By nanoscale, the contact area between the electrode and the electrolyte increases. This is a good thing because the electrolyte, which prevents ions from conducting ions, ions, but because nanomaterials have a higher surface-to-volume ratio, they are more reactive; therefore, the possibility of unwanted reactions between the electrolyte and the electrode increases. To solve this problem of nanoscale, with nanotechnology itself, there are solutions that are mentioned. But the positive thing that must be created by nano imaging the active materials is the reduction of the required penetration length, which increases the battery power. The relationship between time, length and diffusion coefficient is $D = L_2/t$ where L is the characteristic length (here the particle length) and t is the characteristic time and D is the penetration length. Because D is almost constant, as the dimensions decrease, the penetration time decreases a second time, which is a significant effect. For example, for a lithium battery cathode called $LiFePO_4$, the typical time is 83 hours when the particle length is 2 microns, while for a 40-nanometer particle the same time is reduced to 13 seconds. This shows how much battery power can be increased by nano [4-8].

Advantages of nano sizing of the active substance

When we reduce the penetration length with nanotechnology, we can use active materials that normally have good capacity, stability or but cannot be used due to low power; For example, vanadium oxide or lithium iron phosphate cathodes are normally low in strength but show good capacity and stability, respectively. By nanoscale we can improve the low power of these cathodes and thus make it possible to use them. Some active ingredients, such as lithium iron oxide, do not have good electronic conductivity; to improve battery power, we must use additional conductive materials with the active ingredient. These materials increase weight but do not participate in capacity. Thus the electrode capacity decreases; but with nanotechnology, a smaller amount of conductive material (even with higher conductivity such as carbon nanotubes and graphene) can be used more effectively, reducing the necessary penetration for the electron and increasing the power without reducing the capacity. Even nanotechnology directly improves capacity by reducing ion and electron penetration distances. Because most active materials do not have good electron and ion conduction, electrons and ions **(Figure 1)** do not reach the center well, especially at higher currents, and the center capacity remains unused; but when we reduce the penetration length, the total percentage of active substance in the company's capacity. In many active materials, the entry and exit of lithium, due to its volume, leads to stress in the material, stress also leads to the failure of the active material and disconnects it from the current collector and other components, so the capacity is reduced. Nano sizing can provide the necessary space for deformation and solve the problem of mechanical stress. In addition, nanomaterials are more resistant to failure. For example, silicon is considered as a high-capacity anode, but a high volume change of about 400% is caused by the entry and exit of lithium, which is crushed, but by nano sizing, the volume change process can be done without crushing. Provide regarding the fifth advantage, for example, we can mention the $LiFeO_2$ cathode, which shows low activity in the micron state and is not considered as the active substance of the cathode, because it shows only 8 mAh/g capacity, which is due to the difficulty of changing the oxidation number of iron in this compound. But with nano, a capacity of about 100 mAh/g is created, and due to the low price of iron can be an option. Other materials in this category include (TiO_2 (B) and (MnO2 (β). The goal in the battery is to reach the theoretical capacity of the active substance. It was said that the capacity of the battery depends on the capacity of the anode and cathode. The capacity of each electrode depends on the amount of active substance in the electrode. It was previously stated that in each electrode, there are other components such as binder and current collector, etc. Therefore, the higher the amount of active substance in the electrode, the greater the capacity of the electrode. Conventional electrodes use micron powders of the active ingredient with a binder and a carbon-conductive conductor placed on a current collector. Binder is used to bond and maintain the integrity of these powders, and carbon is used to maintain electrical bonding. With the sixth advantage of nanotechnology, we can grow the active material directly in the form of nanowires on the current collector and reduce the need to maintain the connection through the binder and conductor, or with this advantage provide an electrode that eliminates the need for a current collector (so-called free standing) or reduce the weight of the collector. Nanotechnology also affects the capacity of the active substance. The maximum capacity of an active substance is the same as its theoretical capacity, which is obtained through the calculations stated in previous articles. But in practice, due to stability problems, poor conductivity of electrons and ions, etc., the capacity of the active substance is rarely equal to the theoretical value, but with nanotechnology with advantages 1 and 2, the capacity can be approached closer to the theory. But nanoscale has a disadvantage (instability) that causes instability. To solve it, we have to go to nanocoatings and nano additives, which are described below. An interesting thing happens in relation to the capacity of the active substance, and that is the storage of lithium ions on the surface, which creates a capacity in addition to the theoretical capacity of the active substance. This capacity is added to the theoretical value. This phenomenon can be considered as part of advantage 5. This property of nanotechnology is relatively new and very attractive. Case 4 is more than an advantage, it is a property and shows that nano not only reduces the over-potentials (which have synthetic causes), but also changes the chemical potential and consequently the thermodynamic voltage of the battery. For example, nano sizing increases the potential from 1 to 100 millivolts. Because the material on this topic requires background, it is not discussed here, nor is it of practical importance in contrast to the synthetic effects of nano. If we want to mention the advantages that come with the nano sizing of the active substance, we include the following [9-14]:

1. Less time required for the penetration of lithium ions and electrons and as a result higher power and even better capacity.
2. Increasing the interface between the electrode and the electrolyte and thus better ion transfer.
3. Easier volume change of the active substance due to the entry and exit of lithium ions without causing mechanical failure.
4. Changes in thermodynamics and solubility and voltage.
5. Introduction of new active ingredients and new reactions that were not introduced in the micro state.
6. Reduce the use of inactive electrode materials and thus improve electrode capacity.

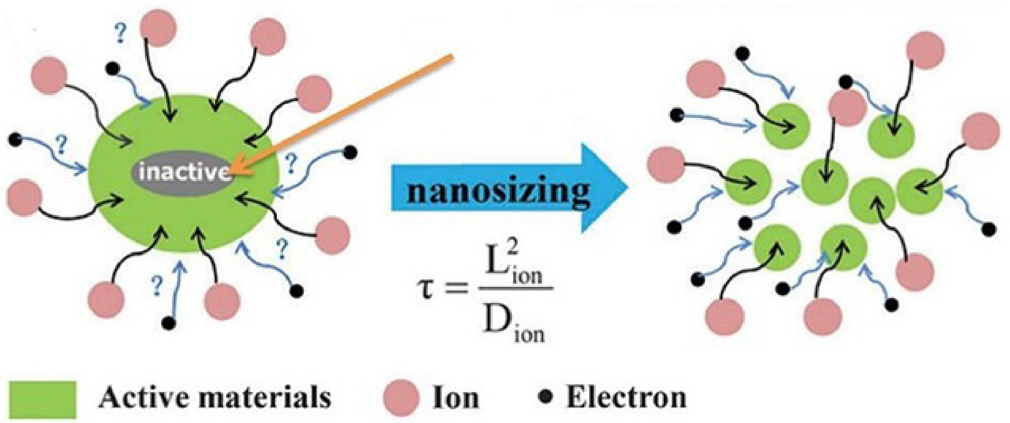

Figure 1: Demonstration of high capacity utilization by nano sizing the active material.

Disadvantages of nano sizing active materials

It was said that nanotechnology, despite its advantages, has disadvantages such as low volumetric energy, the possibility of unwanted reactions (due to higher levels), etc., but we have to go to nanotechnology to improve problems such as low capacity and power. Interestingly, many of these problems are solved by nanotechnology itself. For example, to solve the problem of the reaction between the electrolyte and the active substance, nanocoatings of materials that are resistant to the electrolyte can be used to prevent direct contact between the electrolyte and the active substance, or for low volumetric densities of mesoporous and mesocrystalline materials, which in Those large secondary particles were micron-sized, but had porosity in the former and nanometer-sized primary particles, respectively, or used hierarchical structures. The following figures show two examples of hierarchical structure. With these structures, the problem of agglomeration can be eliminated, low bulk density can be solved, and as the contact between the electrode and the electrolyte decreases, stability can be increased. This field is actually nano sizing and is one of the fields that has good quality articles. **Figure 2** shows a hierarchical nanostructure. Figure A shows the MnO_2 nanotubes acting as an active ingredient. Figure B shows the same nanotubes with high magnification, and it is determined that these nanotubes have micron dimensions but an inner radius of nanometers, and the nanotubes themselves are composed of small initial MnO_2 nano sheets. **Figure 3** shows a mesoporous structure of cobalt oxide with a cyclic performance diagram. Cyclic diagram corresponds to a mesoporous structure and diagram b corresponds to nanoparticles. As can be seen, and for the reasons stated above, the battery capacity during work cycles is better for mesoporous than nanoparticles. **Figure 4** shows section A of the agglomerate nanoparticles compared to section B, where the nanowires self-assemble to form a nanosphere. The image obtained from the self-assembly of the nanowires shows that the structure is porous. The morphological differences are quite clear, electrochemical differences are discussed in the relevant articles. **Figure 5** shows two mesocrystalline samples consisting of nanosheets in (a) and nanowires in (b). In these nanostructures and other forms, due to the lack of agglomeration, the available capacity increases.

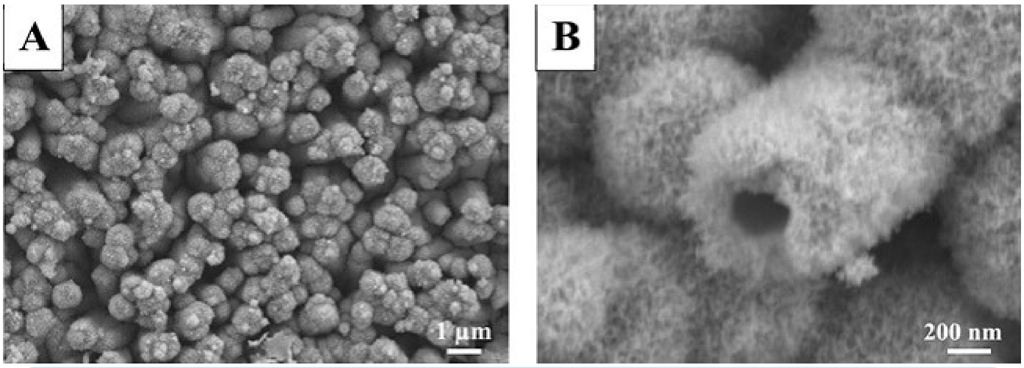

Figure 2: A hierarchical structure of MnO_2 **(A)** low magnification and **(B)** high magnification.

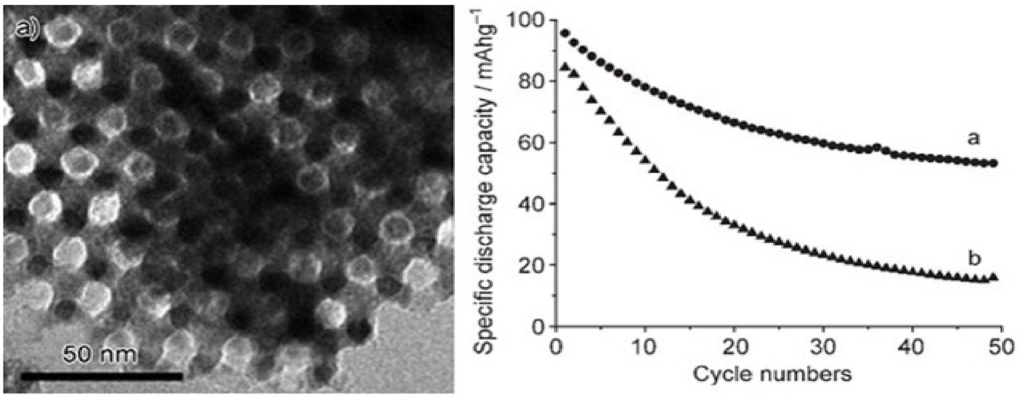

Figure 3: A hierarchical structure of MnO_2 **(a)** low magnification **(b)** high magnification.

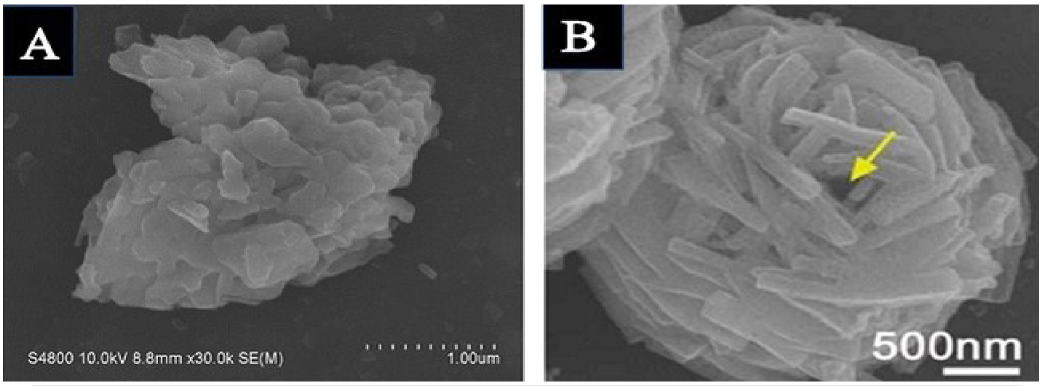

Figure 4: Two samples of mesocrystals, **(a)** made of nanosheets, **(b)** made of nanowires.

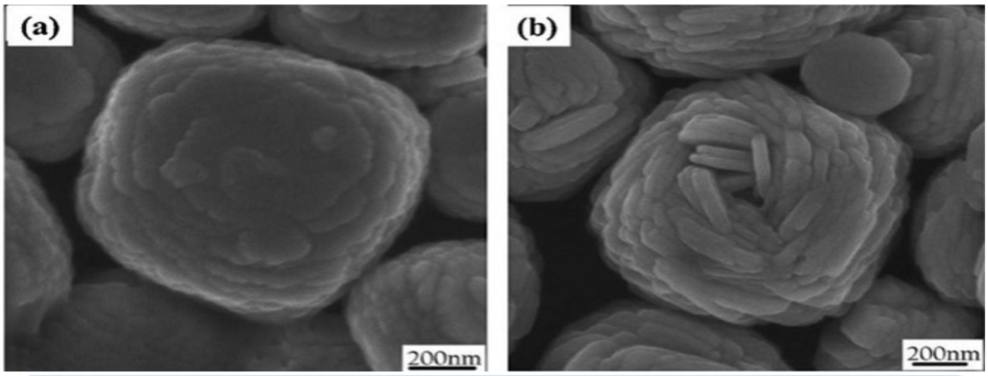

Figure 5: Two samples of mesocrystals, (a) made of nanosheets, (b) made of nanowires.

These architectural structures and the electrochemical effects will be discussed in future articles. One of the drawbacks of nanotechnology, as mentioned, is the more difficult and costly synthesis due to surface activity. Investing in production reduces costs to some extent, but solving this problem by providing and optimizing synthesis and building structures with higher properties with easier methods is an important area of research. For example, it has been proven that nanometer silicon materials offer better properties for the anode than microns (explained in anode articles), but there are still many articles published in this field that are less costly and It is more scalable. For example, one-dimensional silicon nanostructures can be produced by both chemical vapor deposition and electro spinning, but the latter method is much cheaper and can be industrialized. In addition, each method presents different results in the dimensions of nanomaterial's, purity, crystallinity, etc. Also, in each synthesis method, different results are obtained by changing the synthesis parameters such as temperature, pressure, concentrations, etc. In almost all areas in which nanotechnology is involved, including batteries, there is a constant connection between properties and synthesis, and the two are largely inseparable, and very good articles on the proper synthesis method with excellent properties. Disadvantages of nano sizing active materials include [15-20]:

1. Harder and more expensive synthesis.
2. Existence of a large interface between the active substance and the electrolyte that the high activity of nanomaterials causes unwanted reactions and instability.
3. The bulk energy density of nanomaterials is lower due to lower compaction and is a problem in cases where volume reduction is desired.
4. The possibility of agglomeration during synthesis or during battery operation.

Nano partition in battery

If we want to have a division for the use of nanotechnology in lithium batteries, we can consider two general groups: 1) The use of nanomaterials in improving the performance of battery components such as anodes, cathodes, etc., 2) The use of nanotechnology to make different batteries such as batteries Flexible, nano-batteries and 3D batteries and The topics of the second group are much less and more scattered than the first group. Of course, it is continuously related to the first group, but compared to the first group, which affects one component of the battery and thus changes the overall performance of the entire battery, it is considered as a separate division in the relevant collection of articles. Making new batteries in various forms, such as making nano-batteries or making flexible batteries or making batteries with viruses, etc., which is a newer and more innovative field compared to the first group. Our discussion here focuses on the first group. The application of nanotechnology in electrolyte is also discussed separately in the relevant chapter, as it is very different from the topics related to electrodes (anode and cathode) [21-23].

Inactive nanomaterials in the battery

The first group of applications of nanotechnology in batteries is itself divided into two categories: The first group of nanosizing the active substance in the electrode discussed in the previous articles, the second group of using nanotechnology to improve the performance of electrodes (cathode or anode) by adding other nanomaterials Other than the active ingredient, or the use of nanocoatings. For example, nanoscale additives such as nanocarbons, graphene, carbon nanotubes, etc. have better electron conduction, or the use of nano-thick coatings on the active material to prevent unwanted reactions with the electrolyte, modulate stress, and provide stability and for it. For example, for a $LiFePO_4$ cathode, the amount of electron conductivity is poor. Conductivity is improved by using a conductive carbon coating on its particles or by using a conductive carbon material as an additive. A nano-thick coating of oxide is used. If we want to illustrate the field of nano research in this category by mentioning an example, in the same $LiFePO_4$ cathode, it has been determined that carbon coating increases conductivity and consequently power, capacity, etc., but one of the research areas is how to create this coating. Be cheap, effective, etc. .; therefore, research in the field of synthesis methods is very important. On the other hand, how to add the same coating and additives to be more effective, so the engineering and architecture of nanostructures is one of the important areas of research and the preparation of these engineered structures is also an interesting issue. Consider **Figure 6** to clarify the matter. This figure shows two types of nano-engineered structures for the $LiFePO_4$ cathode that use carbon nanotubes to improve conductivity. In addition to differences in performance, each of these structures has a different synthesis method, which indicates the importance of synthesis [24-29].

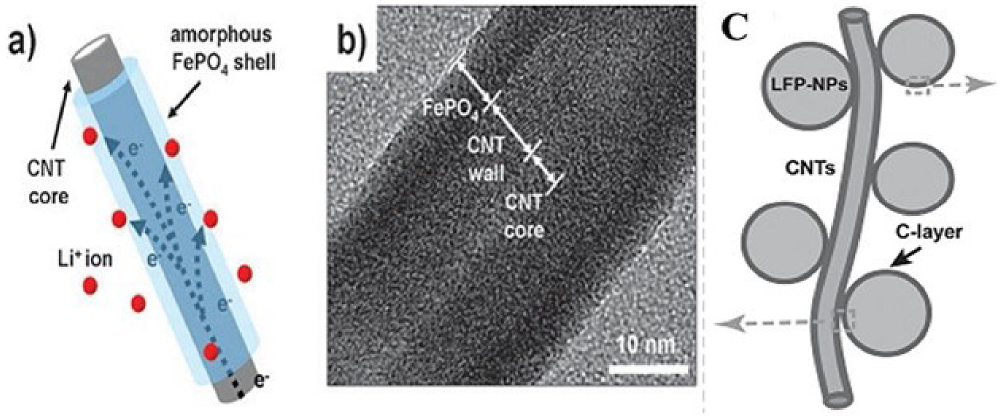

Figure 6: **(a)** And **(b)** with carbon nanotube core and $LiFePO_4$ wall, and **(c)** $LiFePO_4$ nanoparticles attached to carbon nanotube.

Conclusion

In this chapter, the benefits of nano sizing of the active substance were stated. It was found that nanotechnology by providing penetration length, stress modulation and other benefits can provide high capacity and power or indirectly with the mentioned advantages can use active materials that are safe, stable and low cost. It turned out that nanotechnology also has disadvantages that can be eliminated with engineered nanocoatings and nanostructures. There was talk of inactive nanomaterials that are present to improve conductivity and so on. In general, the importance of nanomaterial synthesis and engineering of electrodes in nanoscale was emphasized.

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