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NANOMATERIALS FOR BATTERIES

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Batteries are a well-known technology to store energy. If the first batteries were made at the end of the nineteenth century, major technological issues prevented their development for decades. Today, batteries are regarded as a promising way to store energy from sustainable sources, but their performance still has to be improved. In this article, the use of nanomaterials for batteries is explored and the advantages as well as the current limits of such material is exposed.

1. INTRODUCTION TO BATTERIES

Contrary to what people may think, batteries are quite an old technology. At the end of the nineteenth century, batteries were already used in cars such as *La jamais contente*, a Belgian car able to reach a speed of 30 m·s^{-1}.[1] To give another example, the first wireless communication – relying on batteries – happened in the US in 1920.[2] Still, the development of batteries was slow as finding suitable electrode materials and electrolytes is challenging. For years, the difficulty to master the interface between the electrode and the electrolyte has been reponsible for the low development of batteries, as it has a huge impact on the efficiency of the battery[1]

In parallel with the battery technology, combustion reactions took the lead in the automotive field as well as in most industrial areas producing energy. Fossil fuel combustion had met such a success that the emission of carbon dioxide arising from this combustion started to be troublesome. Indeed, CO_2 emission accelerates global warming. Due to the urgent need to find green alternatives to fossil fuels, batteries have been seen as a potential solution to store and restore when needed the energy from sustainable sources (*e.g* wind and solar energies) whose intermittent nature is a huge drawback.

A battery is composed of two electrodes – the anode and the cathode – connected by an electrolyte. When a current exists between the two electrodes, the electrolyte allows the transport of charged species between the electrodes and thus maintains the charge balance. If the electrodes are connected, electrons spontaneously travel from the most negative to the most positive potential. In rechargeable batteries, one can apply a larger voltage in the opposite direction compared to the voltage in the discharge mode to recharge the battery.[1] An example of battery is presented in figure 1. Batteries are characterized among other things by their theoretical voltage *i.e.* the difference in the electrochemical potential between the two electrodes, and their charge storage capacity, *i.e.* the capability of the material to uptake a certain amount of charge.[3]

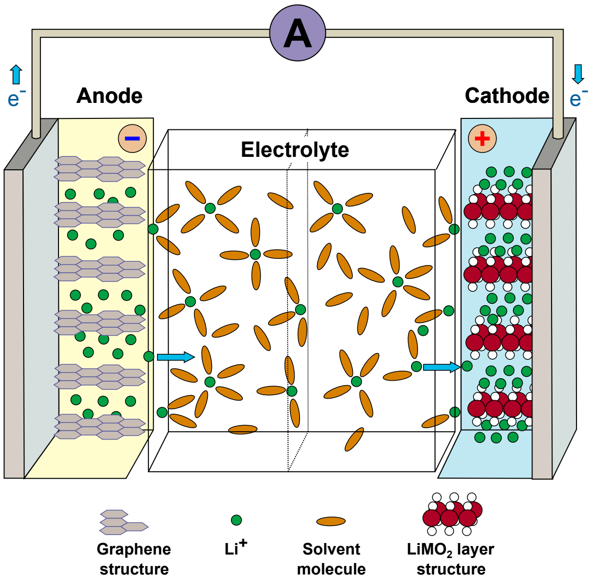

Fig. 1 Example of a lithium-ion battery in the discharge mode. Adapted with permission from [4]. Copyright 2004 American Chemical Society.

In the past few decades, a particular battery has attracted attention : the lithium-ion battery. Commercialized in 1991, this battery represented in figure 1 consists in an anode made of graphite and a cathode made of a layered lithium metal-oxide exchanging lithium cations, separated by a lithium-ion conducting electrolyte such as a solution of $LiPF_6$ in ethylene carbonate-diethylcarbonate.[5] This technology relies on the reversible insertion of lithium within both electrode structures. Even if lithium-ion batteries are commercially successful, their carbon footprint is high (70 kg CO_2 per kWh[6]) and their storage capacity is only a few times higher than the old lead-acid batteries. The carbon footprint could be reduced by recycling old lithium-ion batteries, or using the incredible amount of lithium available in the seas[7,8] to make the lithium-ion battery instead of extracting the terrestrial resources : lithium could be easily extracted by concentrating brines thanks to solar energy. Besides, other promising metal-ion batteries such as sodium-ion batteries are being developed as an alternative to Li-ion batteries.[3] As the performances of the metal-ion batteries seem to reach their limit with the current electrode and electrolyte materials, nanomaterials are increasingly seen as a solution to further improve those batteries.

2. NANOMATERIALS FOR LITHIUM-ION BATTERIES

Nanomaterials are known to have interesting and tunable optical, electrical and mechanical properties that can be used for electrochemical energy storage.[5,9] They can be used in nanoelectrodes as well as in solid polymer electrolytes.

Nanomaterials have proved their value in the design of anodes. While an alternative to the conventional graphite anode is to use semi-conductors able to store lithium by forming alloys in a partially reversible way, those metallic electrodes are quickly cracked and crumbled due to the alloying/dealloying process.[10] Therefore, even if the theoretical specific capacity of aluminium, tin and silicon anodes is estimated to be 10 times higher than graphite, they cannot be used as is in lithium-ion batteries.[5] This is where nanomaterials come in : to limit cracking and crumbling of the electrode, the active/inactive nanocomposite concept seems to be an interesting solution. The idea is to mix two materials, an active one reacting with lithium and an inactive one used as a confining buffer. This gives rise to nanometallic clusters able to capture lithium and significantly reduces the strains previously responsible for the cracking of the metallic electrode.[11-13] In particular, the Si-C nanocomposites[14-16] are worthy of interest as their specific capacity can reach $1000\,\mathrm{mA\cdot h\cdot g^{-1}}$ for more than 100 cycles,[16] while the theoretical capacity of graphene is only $372\,\mathrm{mA\cdot h\cdot g^{-1}}$.[5]

However, if primary nanomaterials (*i.e.* nanomaterials containing particles of nanometer dimensions) did lead to significant progress in the design of electrodes, they still have a huge drawback : the possibility of side-reactions with the electrolyte. Because of the high surface area of the electrode, undesirable reactions between the electrode and the electrolyte can occur, leading to poor lifespan and even safety concerns. Such reactions can be avoided or at least limited if the materials fall within the stability window of the electrolyte. Another solution is to resort to secondary nanomaterials *i.e.* nanomaterials containing micrometer-sized particles but internally consisting in nanometer-sized regions or domains. If those materials are more complex and harder to make, they also reduce the reactions with the electrolyte and provide higher volumetric energy densities.

Although less developed, cathodes can also be improved using nanomaterials.[5] However, adapting the classical cathode materials at the nanoscale raises important issues : as previously observed, it leads to greater reaction with the electrolyte, but also to the dissolution of the cathode. In cathodes made of $LiMn_2O_4$ for example, using nanoparticles causes higher dissolution of Mn. A way to use primary nanomaterials without having such problems lies in coating the nanoparticles with a stabilizing surface layer, but the rate of insertion/removal of lithium is also reduced and therefore the advantage of using small particles is less important. Another alternative is to use porous alumina[17] or porous polymer[18-20] as a template for the growth of nanopillars such as $LiMn_2O_4$[17,18] or V_2O_5.[19,20] Indeed, those electrode structures can accommodate their volume and support high rates.[21]

To further increase the electrode capacity, one can increase the surface-area of the electrode by using aerogel : those disordered mesoporous materials have the advantage of presenting a high pore volume. As the intercalation rate of Li^+ is limited by diffusion in the solid, aerogel are of interest in lithium-ion batteries due to the small diffusion distance that has to be travelled by the ions into this material.[22] V_2O_5 aerogels have been shown to support high rates and to have greater electroactive capacities than non-porous V_2O_5 powders.[23]

So far only primary nanomaterials for cathodes has been discussed in this report. But secondary nanomaterials are also studied for their ability to be less easily dissolve. An interesting example of cathode made of secondary nanomaterials is the layered $LiMnO_2$ intercalation cathode.[24] Indeed, despite the fact that this layered $LiMnO_2$ with the $\alpha{-}NaFeO_2$ structure undergoes a phase transition into spinel on cycling, it is still cycled with more than 99.9% capacity retention.[5] This surprisingly high capacity retention can be explained by the fact that the spinel phase is nanostructured, and each crystallite is composed of nanodomains. Those nanodomains switch between cubic and tetragonal structures, and the relief of strain at the domain wall boundaries accompanying the cubic tetragonal phase transition is probably responsible for the easy cycling of the material. Those examples highlight the wide diversity of research studies on the nanomaterials for cathodes.

Finally, the electrolyte in lithium-ion batteries can benefit from nanomaterials as well. The most concerning problem with commonly used lithium-ion batteries is the safety issue related to the liquid electrolyte. That is why solid polymer electrolytes formed by solvent-free membranes are more and more developed : they are non-corrosive, non-explosive and cannot leak out. However, due to the poor ionic conductivity, these electrolytes usually require a high working temperature. For example, electrolytes made of polyethylene oxide (PEO) work at a temperature of $60\,^\circ\mathrm{C} - 80\,^\circ\mathrm{C}$.[25] To reduce this temperature, nanosize ceramic powders can be dispersed in PEO : the conductivity of the electrolyte at room temperature is then increased several-folds.[25-27]

It has been thought for 30 years that an amorphous phase was required for the ionic conductivity to occur in polymer electrolytes, and the use of nanosize ceramic powders to reduce the crystallinity of the polymeric phase (which indeed results in an increased conductivity) reflects this view. But it has been shown in the 2000s that conductivity in the crystalline phase of solid polymer electrolytes can be greater than conductivity in the equivalent amorphous material : this is the case for crystalline 6 : 1 complexes $PEO_6 : LiXF_6$ (X = P, As or Sb).[28-30]

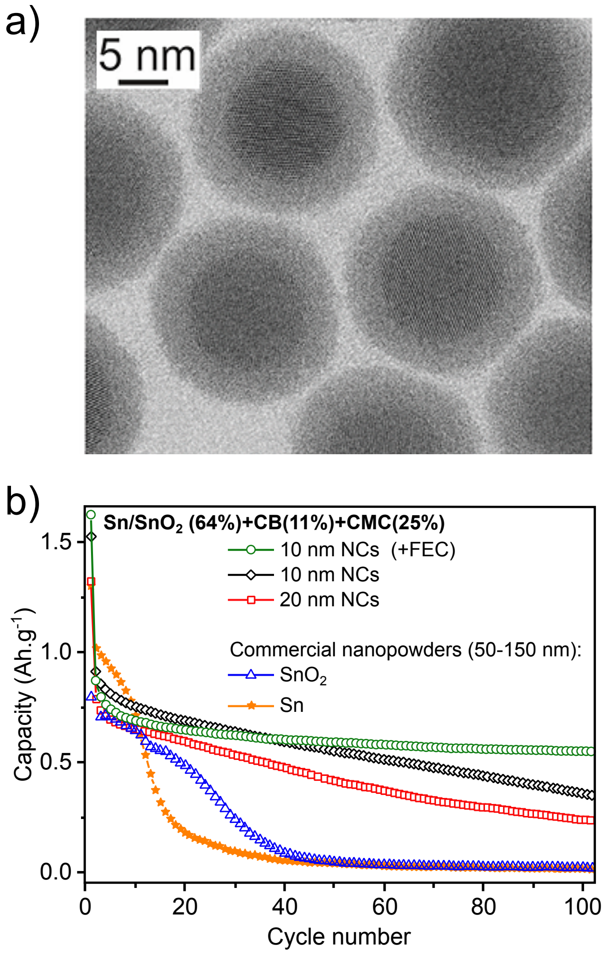

Fig. 2 (a) BF-STEM image of colloidal Sn/SnO$_2$ nanocrystals and (b) reversible discharge capacities of anodes made of colloidal Sn/SnO$_2$ nanocrystals compared to commercial Sn and SnO$_2$ nanopowders with current density being $1\,\mathrm{A \cdot g^{-1}}$. Reprinted with permission from [31]. Copyright 2013 American Chemical Society.

Nanomaterials have proved to be useful to improve properties of anodes, cathodes and electrolytes for lithium-ion batteries. Recent breakthroughs in the use of secondary nanomaterials for electrodes and crystalline solid polymer electrolytes offer new promising scientific directions. Still a lot of research remains to be done to make the best of nanomaterials for batteries. A precise area in nanomaterials could be very useful in that respect : colloidal nanocrystals and nanoparticles. Indeed, due to their well-defined and controlled composition, surface chemistry, shape and size, those nanomaterials could help to better understand the effects of those characteristics on the electrochemical properties of electrode materials.

3. Colloidal nanoparticles for batteries

Colloidal nanoparticles are of great interest in research into batteries due to their well defined structure, size, shape and composition. Indeed, the better defined the nanomaterial, the more accurate the interpretation of the results : structure-property relationships can be determined from those uniform nanomaterials unambiguously. Downsizing has interesting effects on the electrochemical properties of electrode materials : it reduces damages due to the insertion and removal of the alkali ions, increases surface-to-volume ratio and thus the kinetics of insertion/removal, and poor ionic and electronic conductors can even become usable in the form of nanocomposite in a conductive matrix.[3] Those three effects of downsizing can be directly related to the size and the morphology of particles. But for now, because of the high manufacturing costs (syntheses require organic solvents, surfactants, and molecular precursors), these nanomaterials are far too expensive to be industrially applicable. Still, colloidal nanoparticles can provide useful model systems for research purposes.[3]

As previously mentioned, one of the issues that materials for anodes have to deal with is the volumetric changes due to insertion and removal of the alkali ions. As it is cheap, nontoxic, and naturally very abundant, tin would be an interesting material for anodes, but even small nanocrystals suffer from mechanical damages during the insertion/removal of Li^+. However, colloidal core-shell nanoparticles of Sn/SnO$_2$ used with fluoroethylenecarbonate (FEC) as an electrolyte additive have shown better cycling stability compared to commercial nanopowders[31] (figure 2). This example shows how helpful well-defined monodispersed nanoparticles can be to understand the effects of the size and core-shell structure on the nanoparticles properties.

Another advantage of studying colloidal nanoparticles is the easy tunability of the nanocrystals composition. While tin presents an interesting electronic conductivity, germanium has a good specific capacity : colloidal Sn−Ge nanodimers used as anodes have been reported to have a high charge storage capacity ($>1000\,\mathrm{mA{\cdot}h{\cdot}g^{-1}}$) at a quite high current density ($1\,\mathrm{A{\cdot}g^{-1}}$) and an improved cycling stability compared to Sn nanocrystals.[32] Such well-defined nanodimers would be hard to obtain through top-down methods.

Precisely engineered colloidal nanomaterials can give rise to complex structures such as hollowed structures which provide extra free space, thus reducing the volume changes during insertion and removal of Li^+, and allowing stable cycling. For example, galvanic replacement reaction on Mn_3O_4 nanocubes through the reduction of Mn(III) by Fe(II), led to $Mn_{3-x}Fe_xO_4$ nanocages. Tuning the $x =$Mn/Fe ratio can easily be done on colloidal nanoparticles, and it allowed to find out that the best electrochemical properties were obtained for $x \in [1, 2]$.[33]

Nanomaterials for cathodes are less developed and there are not many colloidal nanocrystals as cathode materials reported in the literature. However, some interesting iron oxide nanocrystals as cathodes for lithium and sodium-ion batteries were formed through the oxidation of iron nanocrystals using the Kirkendall effect : high cycling stability at elevated current density and high capacities were observed.[34,35] Kirkendall effect happens at the interface between two metals having different diffusion rates. It leads to the displacement of the interface.[36] Those examples show how useful colloidal nanoparticles are to precisely study the effect of composition, size and structure on the electrochemical properties of an electrode material.

4. Conclusions and perspectives

Batteries are a technology that is more than a century old and is continuously improving. Lithium-ion batteries marked a turning point in 1991, and nowadays new metal-ion batteries such as sodium-ion batteries are emerging. To further improve the characteristics of Li and Na-ion batteries, nanomaterials are a promising area of research : studied as electrodes, they reduce the damages related to insertion and removal of ions, increase surface-to-volume ratio and thus improve the kinetics of insertion/removal, and allow to use poor ionic and electronic conductors once included in a conductive matrix. They can also be useful as electrolyte. However, the effect of the size, the shape and the composition of nanomaterials on electrochemical properties is not fully understood and studying colloidal nanoparticles allows to precisely relate electrochemical properties to those characteristics. Therefore, studying them is still of importance even if colloidal nanoparticles are too expensive to be industrially used in the near-future.

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