



A Brief Review on the Influence of Nanomaterials on Supercapacitor Configurations and Performance

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ABSTRACT

Energy storage devices have been made and developed over hundreds of years in order to power many real-life applications and store energy for when it is not easily accessible. Recently, due to advancements in nanotechnology, supercapacitors, which differ from traditional capacitors and batteries, have become an excellent middle-ground device. These nanomaterials impact how the supercapacitor performs in various metrics, including capacitance, energy density, and power density, which are essential when considering the context in which they will be used. It follows that the specific groups of nanomaterials used in these experiments, including metal oxides, carbon and graphene, and even a mix of the two groups, impact these properties even more than just the existence of nanomaterials. The chemistry behind how energy is stored and how electric fields are created differs between different types of supercapacitors, including electrostatic storage, electrochemical reactions, and a combination of both between the two plates, which has different effects on the aforementioned metrics. While many efforts have successfully improved performances over time, cycle stability and the cost of the materials continue to be pertinent problems that are still being tackled.

INTRODUCTION

The ability to store energy has been an important point of consideration for a long time, and we have tried to find ways to make this process as efficient as possible. Many examples of such devices include capacitors, fuel cells, and batteries. However, with recent advancements through nanotechnology, a new type of energy storage device has become more widespread.

Supercapacitors are essentially a subset of capacitors, which use oppositely charged plates that create an electric field. However, what sets supercapacitors apart is their use of nanomaterials. Nanomaterials are defined as materials with at least one dimension between 1 and 100 nm. Because of these very thin dimensions, nanomaterials tend to have very high surface area to volume ratios, resulting in increased strength and differences in properties (physical, electrical, optical, etc.) compared to their bulk materials. This means that they can be extremely useful when trying to optimize different metrics in their applications.

Capacitors, like supercapacitors, are meant to store energy. The two plates of a capacitor, when hooked up to an electrical circuit, store opposite charges on each of the plates over time. Because of this potential difference between the plates, energy can be stored within the electric field created.

Nanomaterials that are attached to the plates of capacitors modify two properties that significantly increase their capacitance. Firstly, the small surfaces along the capacitor increase their surface area perpendicularly to the plates of the capacitors, increasing capacitance. Also, the nanomaterials that extend from both plates reduce the gap between them. By “bringing the plates” closer together, the electric field becomes stronger inside the capacitor, making energy easier to store [1]. The formula $C = (\epsilon_0 * A) / d$ takes both of these variables into account, with the epsilon representing the ability of free space, or perhaps a dielectric if it's in between, to create an electric field.

Additionally, there are many ways to quantify the performance and effectiveness of any capacitor. Note that since all metrics have a direct correlation with the size of the supercapacitor, we will normalize our measurements per unit mass or unit volume.

Perhaps the simplest metric is **capacitance** (C), which measures the ability to keep charge. Traditionally, capacitance is measured in farads (F), but we will be measuring our capacitances in farads per gram (F/g) in order to normalize the effectiveness of each material.

However, when energy storage is the main concern, **energy and power density** are just as, if not more, important to consider. Energy density, as the name suggests, is how much energy can be stored by a material per mass or volume. Since power is the rate that energy is transferred, the power density of a supercapacitor represents how quickly energy can be sent to another system for its use. Since power is measured in watts (W), power density will often be measured in W/kg or W/m³. While the SI unit for energy is the joule (J), this paper will report its energy values using watt-hours (1 Wh = 3600 J) and energy density values with units Wh/kg.

Finally, current density represents the current that flows through any cross section, given by the formula $J = I/A$ and measured with units A/m².

Most of our sources mainly focused on measuring the capacitance of specific supercapacitors, so while energy and power density are important to consider, they might not be

the most “consistent” metrics examined in the following paragraphs. In the context of comparing supercapacitor performance to other energy storage devices, though, energy and power density are the two main factors considered. Compared to batteries and fuel cells, supercapacitors have higher power densities but lower energy densities. Despite being able to store less energy, supercapacitors’ advantage lies in power density: they are much more efficient at transferring energy to other devices, meaning charging and discharging is faster. This is a significant advantage when great amounts of energy are not needed, but speed is. On the other hand, capacitors have extraordinary charge and discharge rates due to electrostatic interactions, but these same interactions fail to store lots of energy.

These relations between energy storage devices can be displayed in a Ragone plot, as shown in Figure 1, with power density graphed against energy density. Notice how the supercapacitors act as a “bridge” in between the powerful capacitors and the energy-holding batteries (and fuel cells), leading to their effectiveness in situations where neither metric needs to be extremely large.

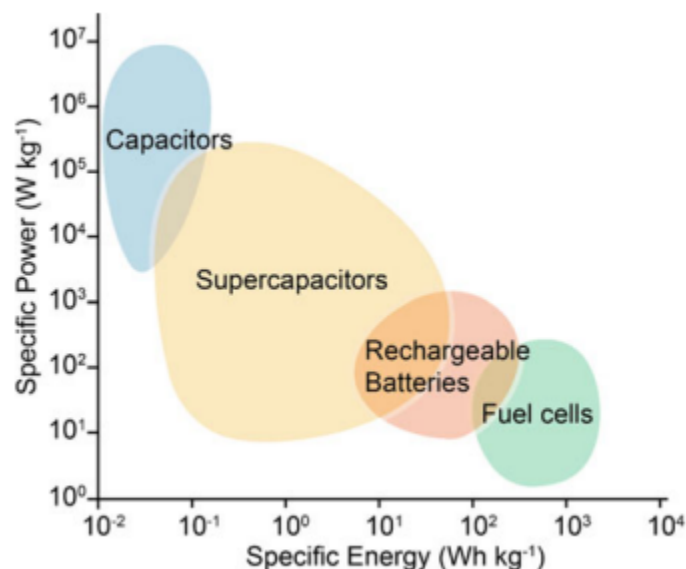


Figure 1: A Ragone plot of the main types of energy storage devices. [2]

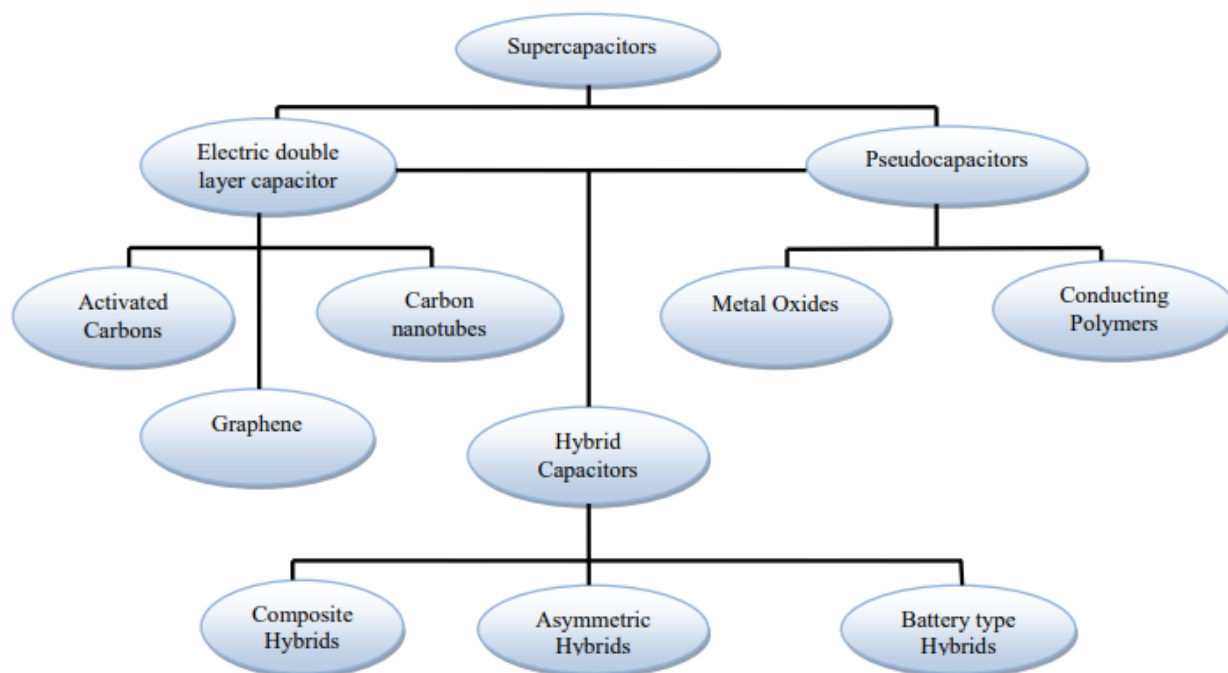


Figure 2: The different classifications of supercapacitors. [3]

Not every supercapacitor has the exact same properties, though, and performance is ultimately dependent on the material that is actually used. This paper will explore the use of nanomaterials and how their chemical identities and structure within the supercapacitor impact various performance metrics and their practicality for real-world applications. The main types and subtypes, as illustrated in figure 2 below, are clarified and discussed in each of the sections below, which will change the results of select experiments using these nanomaterials.

CARBON NANOMATERIALS AND ELECTRIC DOUBLE-LAYER CAPACITORS

Out of the three main types of supercapacitors, electric double-layer capacitors (EDLCs) are the most heavily reliant on pure carbon nanomaterials. While regular capacitors rely on dielectrics between the plates to store energy, EDLCs use electrodes, which are charged materials that lie on the plates, to store energy. Since the plates are oppositely charged, ions from both sides go to opposite plates, creating two positive-negative layers. When the mechanism is discharged, the ions return to the electrolyte and release all of the energy. Because no chemical reaction takes place, EDLCs are generally more reliable and sustainable than other types of supercapacitors, including pseudocapacitors. [1]

EDLCs also tend to have lower capacitances and energy densities than other types, but their higher power densities ensure that energy transfer happens quicker. These properties make EDLCs functionally closer to normal capacitors as opposed to fuel cells or batteries. They also have very high cycle rates and cycle stabilities, which supports their usability for real-life applications.

Activated carbon is the most often used form of carbon nanomaterials used in supercapacitors because of enhanced properties at a lower cost. While these notably have an abundance of micropores, which are gaps smaller than 2 nm, it is these same micropores that make the ions in the electrolyte unable to pass through the electrode, meaning the electric double layer is not very well supported.

However, they tend to be cheaper than alternative carbon nanomaterials and exhibit larger surface areas despite their limitations, making them a surprisingly popular choice for supercapacitors.

An alternative to activated carbon would be the use of **graphene**, which is often in the form of **graphene nanoplatelets**. Graphene nanoplatelets take plates of graphene, which are only an atom thick, and allow the carbon atoms to form π -bonds between the sheets, making the carbon layers between atoms very strong. Because of these bonds, more electrons are able to move the graphene sheets, causing a very high electrical conductivity. [4]

When considering the use of graphene in supercapacitors, the results have proven to be promising. The theoretical capacitance of an EDLC that uses graphene layers is 550 F/g. However, real-life performances are limited by the π bonding that occurs between layers of graphene, and measured capacitance values have fallen very short compared to 550 F/g. Also, due to the lack of micropores, supercapacitors that utilize GNPs tend to have lower specific capacitances than those of activated carbons and other materials. [4]

Another possible carbon nanomaterial forms when graphene sheets are rolled into cylinder-like tubes, creating **carbon nanotubes (CNTs)**. Despite graphene being classified as 2D, carbon nanotubes are classified as 1D because their diameter is essentially negligible compared to their length. (2) These nanotubes also have high electrical conductivity and other properties because they are made up of graphene like GNPs are.

In addition, CNTs can also be enclosed by other larger CNTs to form multi-walled nanotubes, or MWNTs. A singular nanotube is thus abbreviated as SWNT, and there are also double-walled and triple-walled nanotubes (DWNT and TWNT, respectively). These differences in structure cause different specific capacitance values. For instance, there have been reported values of 102 F/g for MWNTs, but only 180 F/g for SWNT. [4]

While the traditional hexagonal structure of CNTs is the most common, a new structure of nanotubes has emerged in the last few years. Vertically aligned CNTs, or VA-CNTs, have each unit cell aligned with the unit cells above and below it instead of traditional graphene, making the entire structure sturdier. In 1 M H_2SO_4 , a VA-CNT supercapacitor has been measured to have a capacitance of 365 F/g. [4]

METAL OXIDES AND PSEUDOCAPACITORS

Instead of storing energy electrostatically, pseudocapacitors take advantage of chemical reactions to store energy electrochemically. The electrodes of pseudocapacitors undergo Faradaic chemical reactions in order to store energy. They rely on redox reactions that occur at the surface, and electrodes are normally made of either metals or polymers that can oxidize or be oxidized. Their capacitance values and energy densities tend to be higher than those of EDLCs because of the redox reactions that take place, but cycle rates are weaker. Due to the

repeated redox reactions that occur, the materials of the electrodes and electrolyte will change, causing material fatigue damage to the pseudocapacitor. This prolonged damage over time leads to a limited cycle life and lifespan, making them less stable than EDLCs but still more stable than batteries.

Despite the use of many different metal oxides in supercapacitors, there are a few that are most commonly used due to high specific capacitance and energy density values. Other favorable properties, such as cost, also play a role in the usability of these materials for supercapacitors.

For instance, nickel oxides, and especially nickel hydroxide, are a commonly used material because of their efficient energy storage capabilities. Zhu et al. measured the possible capacitances of $\text{Ni}(\text{OH})_2$ by stretching them out into ultrathin nanosheets. In these nanosheets, the anions are inserted, or intercalated, into the $\text{Ni}(\text{OH})_2$ structure, making a layer gap between the layers and a greater electrochemical effect. [5] Due to the presence of these ions, the nanosheets used in this experiment can be classified as $\alpha\text{-Ni}(\text{OH})_2$ nanosheets. These ultrathin $\alpha\text{-Ni}(\text{OH})_2$ pseudocapacitors have resulted in an extremely high capacitance of 4172.5 F/g. In fact, this specific capacitance is one of the highest reported ones ever, and it was the highest as of 2014 (when the value was reported). [6]

It is also worth noting that this value of 4172.5 F/g was obtained with a current density of 1 A/g. When the discharge current density is doubled to 2 A/g, the specific capacitance was measured to be only 3650 F/g. Doubling the density to 4 A/g lowered it once again to 3270 F/g, and, to show the other extreme case, a current density of 16 A/g resulted in a capacitance of 2680 F/g. It may seem counterintuitive for capacitance to decrease with respect to current density since current and capacitance are proportional. However, when these Faradaic reactions are involved, a surplus of charge flow can prevent the ions from diffusing into the electrodes and reacting with them. Nevertheless, all four of these values are still very high, making them significantly superior at storing energy compared to EDLCs and carbon-based supercapacitors. [6]

Another prominent metal that is utilized for pseudocapacitors is ruthenium, and more specifically, ruthenium (IV) oxide (RuO_2). As a pseudocapacitor material, RuO_2 exhibits a higher specific capacitance and power density than many other materials [2] and has been studied for these favorable properties. The two main drawbacks to using ruthenium, however, are its extremely high cost and toxic effects on the environment. RuO_2 supercapacitors have still been studied and tested, but their practicality in the real world remains uncertain. [2]

Although ruthenium is commonly combined with carbon to make more effective supercapacitors, some have been made without carbon. More specifically, using the sol-gel process, which involves turning solutions into gels and taking out the nanomaterials, pure ruthenium oxide samples have shown incredible results on their own.

For instance, values of specific capacitance of crystalline RuO_2 have been determined as around 350 F/g. This is a decent value, but when compared to hydrous ruthenium oxide with

760 F/g and a specific energy of 27 Wh/kg, it becomes apparent that the sol-gel process is only beneficial. [7]

HYBRID SUPERCAPACITORS

Instead of having two identical electrodes, hybrid supercapacitors use asymmetric electrodes, where one side is made of a metal oxide and the other is made of some carbon material. As we have already discovered, the metal oxide's redox reactions result in higher specific capacitance and energy density, while the carbon nanomaterial's ability to create ionic movement results in a higher power density. By having one electrostatic side and one electrochemical side, hybrid supercapacitors are able to combine the aforementioned properties, making them the best choice for many applications. Unfortunately, cycling stability is still an issue that limits the practicality of these hybrid capacitors because of the metal oxide electrode (which is a problem present in pseudocapacitors). [8]

The type of hybrid supercapacitor described thus far can also be called asymmetric since the two plates are different. When both metal oxides and carbon nanomaterials are combined on each of the two plates, both Faradaic and electrostatic processes occur on each plate. [9]

Lots of previously discussed materials that have stood on their own as individual supercapacitors have been combined in hybrids, yielding a variety of results. By combining GNPs and manganese cobalt oxide (MnCo_2O_4 , known as MCO) nanoflakes (extremely thin 2D nanomaterials), as Al-Rubaye et al. observed in their experiment, extra benefits are created from the two substances working together. These supercapacitors also implemented the use of ammonium fluoride (NH_4F) being synthesized into the electrodes, with experimental masses ranging from 0 g to 1 g.

With only 0.4-MCO, or MCO with 0.4 g NH_4F , the specific capacitance reached 1064 F/g, staying relatively constant even after 10,000 cycles, which is surprising to see for a metal oxide material. However, with the addition of GNPs, the specific capacitance rose to 1323 F/g, once again retaining all of the specific capacitance. This extremely high capacitance and cycle stability seems to come from the nanoflake structure, as it is able to expand and contract to distribute stresses along the entire plate. [10]

Another combination involves an asymmetric hybrid, with nickel hydroxide on one plate and graphite foam the other plate. In this experiment, ultrathin-graphite foam (UGF) was chosen due to its pairing of low density and high electrical conductivity. This asymmetric composite was able to reach 166 F/g when the current density was 0.5 A/g, which is unfortunately not as high of a value as others covered earlier in the paper. Additionally, the reduction of this capacitance to 111 F/g at current density 10 A/g may make the $\text{Ni}(\text{OH})_2/\text{UGF}$ inefficient in some scenarios, but generally, the low manufacturing cost, maximum power density of 44.0 kW/kg, and efficient diffusion of ions to the electrode, gives significant advantages over others. [11]

CONCLUSION

As discussed in this review paper, the use of nanomaterials between the electrodes of supercapacitors decreases the interplanar distance and increases the surface area to make the electric field more effective at storing energy compared to regular capacitors.

Carbon-based nanomaterials, such as 2D graphene nanoplatelets, activated carbons, and 1D carbon nanotubes, help to store electrostatic energy on both electrodes, while metal oxide electrodes, including those made of nanostructured nickel, ruthenium, and manganese, store electrochemical energy through Faradaic reactions within the system. Hybrids then combine both of these storage methods, either with both methods on both plates or separating the two.

While metal oxide pseudocapacitors have exhibited the highest levels of capacitance, their stability raises the main concern for use in real-life applications. On the other hand, EDLCs tend to have higher cycling stabilities and power densities yet lower energy densities. Hybrid supercapacitors were invented later in order to combine the strengths and mitigate the drawbacks of both types, especially by increasing specific capacitance, although some experiments have still demonstrated low cycle lives and stabilities comparable to those of pseudocapacitors.

For supercapacitors to become more suitable as energy sources in electric and hybrid vehicles, researchers should ensure that their cycle life can support repeated use in high capacitance and energy density devices. Especially for hybrid and metal oxide supercapacitors, which have higher capacitance and energy density values, improving cycling stability should be the major goal for future scientists.

REFERENCES

- [1] M. S. Halper and J. C. Ellenbogen, "Supercapacitors: A Brief Overview," MITRE Nanosystems Group., 2006.
- [2] Y. Liu, P. R. Shearing, G. He and D. J. L. Brett, "Supercapacitors: History, Theory, Emerging Technologies, and Applications," in *Advances in Sustainable Energy*, Springer, Cham, 2021, pp. 419-449.
- [3] Z. S. Iro, C. Subramani and S. S. Dash, "A Brief Review on Electrode Materials for Supercapacitor," *International Journal of Electrochemical Science*, vol. 11, pp. 10628-10643, 2016.
- [4] L. Dai, D. W. Chang, J.-B. Baek and W. Lu, "Carbon Nanomaterials for Advanced Energy Conversion and Storage," *Small*, vol. 8, no. 8, pp. 1130-1166, 2012.
- [5] S. Sharma, P. Kaydan, R. K. Sharma, N. Kumar and S. Grover, "Progressive updates on nickel hydroxide and its nanocomposite for electrochemical electrode material in asymmetric supercapacitor device," *Journal of Energy Storage*, vol. 87, 2024.
- [6] Y. Zhu, C. Cao, S. Tao, W. Chu, Z. Wu and Y. Li, "Ultrathin Nickel Hydroxide and Oxide Nanosheets: Synthesis, Characterizations and Excellent Supercapacitor Performances," *Scientific Reports*, vol. 4, no. 5787, 2014.
- [7] M. Ramani, B. S. Haran, R. E. White and B. N. Popov, "Synthesis and Characterization of Hydrous Ruthenium Oxide-Carbon Supercapacitors," *Journal of The Electrochemical Society*, vol. 148, no. 4, pp. A374-A380, 2001.
- [8] J. M. Lim, Y. S. Jang, H. V. T. Nguyen, J. S. Kim, Y. Yoon, B. J. Park, D. H. Seo, K.-K. Lee, Z. Han, K. Ostrikov and S. G. Doo, "Advances in high-voltage supercapacitors for energy storage systems: materials and electrolyte tailoring to implementation," *Royal Society of Chemistry*, vol. 5, pp. 615-626, 2023.
- [9] M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, "Nanostructured carbon–metal oxide composite electrodes for supercapacitors: a review," *Nanoscale*, vol. 5, pp. 72-88, 2013.

- [10] S. Al-Rubaye, R. Rajagopalan, C. M. Subramaniam, Z. Yu, S. X. Dou and Z. Cheng, "Electrochemical performance enhancement in MnCo₂O₄ nanoflake/graphene nanoplatelets composite," *Journal of Power Sources*, vol. 324, pp. 179-187, 2016.
- [11] J. Ji, L. L. Zhang, H. Ji, Y. Li, X. Zhao, X. Bai, X. Fan, F. Zhang and R. S. Ruoff, "Nanoporous Ni(OH)₂ Thin Film on 3D Ultrathin-Graphite Foam for Asymmetric Supercapacitor," *ACS Nano*, vol. 7, no. 7, p. 6237–6243, 2013.