

# Transition Metal Oxide and Carbide Pseudocapacitors

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## Introduction

Energy storage and delivery is shaping up to be one of the biggest challenges in our future. Our modern lifestyle is surrounded by constant interaction with electronic devices, many of which are portable and require electricity be generated on the go. However the use of technologies such as lithium-ion cells in these devices leads to long charging times as well as low specific power, which is required in contemporary applications like electric vehicles. Furthermore, renewable energy generation needs to be paired with a sufficient energy storage technology for it to be a feasible way of harnessing electricity. With shorter charge times and higher specific power, supercapacitors are one energy storage device that could ease our transition to a renewable energy future.

As opposed to lithium ion batteries which rely on relatively slow chemical reactions to function, capacitors store static electricity and can be discharged much more quickly. In the past, the major downside of using capacitors has been their poor power and energy density statistics as compared to other energy storage methods such as lithium-ion batteries. The two research papers juxtaposed in this paper predominantly use a form of charge storage called pseudocapacitance, which paired with electrical double layer capacitance form supercapacitors. Both these research papers use pseudocapacitance in their own ways, which has led to vast improvements in the reported power and energy densities of their respective devices.

Citing low intrinsic electronic and ionic conductivity of pseudocapacitive transition metal oxides, Lukatskaya et al. have focused instead on using two-dimensional transition metal carbides (MXenes) electrodes. On the other hand Ling et al. have shown that a tailored metal oxide electrode can overcome these barriers. Both groups have shown significantly improved performance, but MXene electrodes are a more accessible contemporary technology.

## EDLC

An electrical double layer is a structure that forms on surface of an electrode when it is exposed to a electrolyte. A capacitor is any device that stores electric charge, and an electrical double layer capacitor (EDLC) is no different.

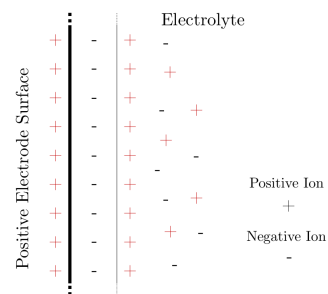


Figure 1: Electrical Double Layer Formation

For example as shown in Figure 1. when a negative electrode has electricity flowing through it, there is a rearrangement of electrolyte ions on the electrode-electrolyte interface [Winter and Brodd, 2004]. We may model this rearrangement similar to a capacitor, where there is a separation of two plates of charges by some distance. A device that uses this form of charge storage is called an EDLC, and the capacitance of it is directly proportional to the surface area of the electrode plates that can be used.

The aforementioned physical arrangement of electrolyte ions is usually considered a faster mechanism than chemical reactions. EDLCs have been the prevalent form of electrochemical capacitance, and pseudocapacitance is a newer technology with the potential of storing orders of magnitude more charge than its accompanying electrical double layer.

## Pseudocapacitance

Pseudocapacitance is an emerging technology that uses chemical reactions to function, but these reactions by their nature are faster than the ones taking place in lithium-ion cells or EDLCs for comparison. Pseudocapacitors use a charge storage mechanism that is different that of the aforementioned EDLCs. Rather than aligning ions at an electrode surface, they use chemical reactions at the surface to store charge, and as a result can also store more energy than electrical double layer capacitors (EDLCs).

## MXene Electrodes

An MXene is a two dimensional transition metal carbide with the general formula  $M_{n+1}X_nT_x$  with:

- transition metal M
- $n \in \mathbb{Z}^+$  such that  $1 \leq n \leq 3$
- Carbon or Nitrogen as X
- surface functional group  $T_x$

The structure of MXenes in this paper is what is what allows them to overcome issues of electrical conductivity and ion transport.

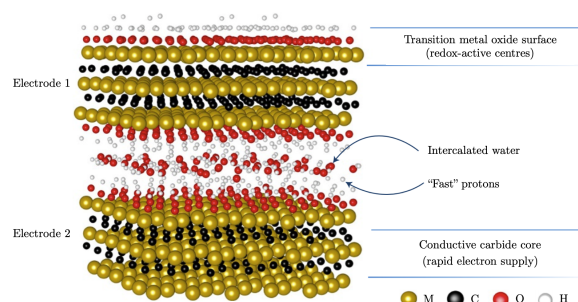


Figure 2: MXene Molecular Structure  
[Lukatskaya et al., 2017]

When the electrodes in Figure 2 are connected to a power source and a potential difference is created between them, and so one becomes an anode and the other a cathode. At the anode, a surge of electrons from the power source travel through the conductive carbide core and thus become a rapid electron supply. They meet the intercalated water protons at the electrode-electrolyte interface which then become the redox active sites, where the vast majority of charge is stored in this device. What occurs in the transition metal oxide surface of electrode 1 is beyond the scope of this paper.

Lukatskaya et al. manipulated the design their MXene electrode in two main ways, for maximizing

volumetric performance (power density) and for maximising rate performance (specific power).

## Volumetric Performance

For maximizing volumetric performance, Lukatskaya et al. investigated the effect of the thickness of the conductive carbide layer. The increase in volumetric performance is in reference to the volume of the electrode itself, which with decreased width has increased capacitance.

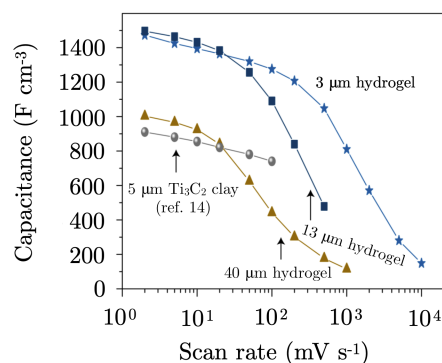


Figure 3: MXene Core Layer Thickness  
[Lukatskaya et al., 2017]

In Figure 3. it can be seen that reducing the MXene layer thickness dramatically increases the performance of the device. To do this the authors created hydrogel MXene electrodes of varying thickness through a relatively simple procedure outlined in their supplementary material. It's surprising to see that a difference on the scale of micrometres makes a huge impact in the volumetric capacitance as well as increased ability to withstand higher scan rates. The maximum volumetric capacitance recorded was a truly impressive  $1500 \text{ F g}^{-3}$  at a scan rate of  $2 \text{ mV s}^{-1}$ , which matched performance to a more expensive  $\text{RuO}_2$  electrode.

An explanation for why thicker electrodes lead to ion transport issues arise because ions, and thus electrons, in an electrolyte have to travel longer distances to interact with a material if its thickness is too large. This leads to an overall decrease in ion access to electrochemically active sites and poorer overall storage performance.

## Scan Rate Performance

For maximizing rate performance, Lukatskaya et al. increased the macroporosity of the MXene electrodes. Previously, pseudocapacitors were known to have weak charging rate handling and the authors proclaim that most were only tested at relatively low scan rates.

Lukatskaya et al. essentially went one step further in tackling the same ion transport problem in planar MXene sheets. Macropores are another solution that increase the surface area of the electrode, but their structure also promotes high-rate charge transfer as well as lower impedance of ion transport to redox active sites. Since the macropores were still in contact with surrounding pores it did not limit electronic conductivity.

In doing this the group altered some parameters in the charge storage kinetics of the system and generated a specific capacitance of  $210 \text{ F g}^{-1}$  at a scan rate of  $10 \text{ V s}^{-1}$ , a rate orders of magnitude higher than what is usually expected out of pseudocapacitors.

## Metal Oxide Electrodes

In previous research, metal oxide electrodes have shown to have high resistance - which leads to low power density - due to the low electronic conductivity of pseudocapacitive metal oxides [Lukatskaya et al., 2017]. Ling et al. have overcome the intrinsic barriers of transition metal oxides by designing a system that has its major charge storage mechanism not in surface redox reactions like MXenes, but in ion intercalation in the electrode material.

They achieved this by altering the larger physical structure of the electrodes, similar to what Lukatskaya et al. did. Further, the group created their transition metal oxide electrodes through a process they called atomic level structure engineering.

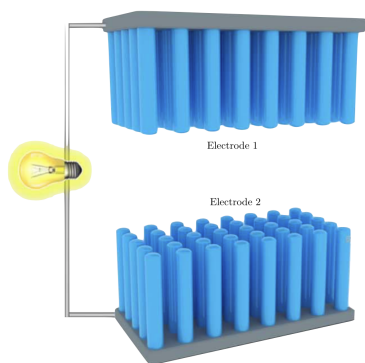


Figure 4: Transition Metal Oxide Cell Structure [Ling et al., 2018]

Figure 4 shows that instead of going with a traditional parallel plate design, Lin et al. chose to create transition metal oxide nanorods that protrude out from a conductive flat core. These nanorods were created on their desired location on top of the conductive core and that they are all monocrystalline to ensure less resistance in charge transportation. The overall effect of

these rods is primarily, again, to increase surface area and thus interactions between ions in the electrodes and electrolytes.

## Atomic Level Structure Engineering

The main technique this Lin et al. investigated was the use of zinc doped cobalt oxide as an electrode material that interacted with electrolyte to store charge. Substitutional doping was used to switch out  $\text{Co}^{2+}$  ions with  $\text{Zn}^{2+}$  at a rate which can be controlled by the temperature of the reaction. Since zinc has a complete d-shell whereas cobalt only has 8 electrons in its d-shell, doping cobalt oxide with zinc changes the resultant compound's electrical properties to make them more conducive to charge transport. It was found through manipulating the concentrations of  $\text{Zn}^{2+}$  ions in  $\text{Zn}_x\text{Co}_{1-x}\text{O}$ , where  $x$  is the concentration of zinc and cobalt ions, that  $\text{Zn}_{0.04}\text{Co}_{0.96}\text{O}$  (or four  $\text{Zn}^{2+}$  ions for every 96  $\text{Co}^{2+}$ ) yielded the best capacitance and energy density performance.

The cation exchange method Lin et al. used to create  $\text{Zn}_x\text{Co}_{1-x}\text{O}$  had side effect of creating nanofacets near the surface of the bulk material which allowed for large amounts of oxygen vacancies. Low energy barrier oxygen vacancies are important because now the hydroxide electrolyte had somewhere intercalate between the electrode and oxidize the  $\text{Co}^{2+}$  ions, thus form a charge storage mechanism. Between the  $\text{Zn}_{0.04}\text{Co}_{0.96}\text{O}$  and  $\text{Zn}_{0.06}\text{Co}_{0.94}\text{O}$  tested, it was found that  $\text{Zn}_{0.04}\text{Co}_{0.96}\text{O}$  had more oxygen vacancies, and this could explain its better performance.

The dominant form of charge storage does change from surface redox reactions, but from an electron energy-loss spectroscopy it can be seen that the oxygen vacancies are only 2 nm to 3 nm from the surface of the electrodes. So the charge storage location isn't as far away from the surface as one might be lead to believe.

The best results from Lin et al.'s work were truly impressive. For one, they extended the usually small voltage window of transition metal oxide pseudocapacitors to a very useable 1.5 V, up from the 1 V window of Lukatskaya et al.'s device. This device can achieve specific capacitance of  $450 \text{ F g}^{-1}$  at a scan rate of  $1 \text{ V s}^{-1}$ , and a peak specific capacitance of around  $1000 \text{ F g}^{-1}$  at a scan rate of  $2 \text{ mV s}^{-1}$ . These are figures that are directly comparable to the best MXene electrodes.

## Discussion

Lukatskaya et al. have demonstrated a fairly straightforward method of creating a pseudocapacitive MXene electrodes, which can be tuned for either high volumetric or rate performance. This is an added benefit because we can set up processes to create base MXene electrodes, and then slightly modify their structure so that they perform differently for different use cases. Their final results push the boundaries of MXene electrode pseudocapacitors a little further, while still grounding themselves on relatively simple processes to create these devices. For example, for testing against a 90 nm MXene film they created thicker hydrogel ranging from 3  $\mu\text{m}$  to 40  $\mu\text{m}$ . The latter are surely easier to manufacture and handle and so lend themselves naturally to being produced at large scale. It's also worthy to note that the thicker 3  $\mu\text{m}$  planar hydrogel electrodes, with no macropores, still showed good performance with a capacity around 200  $\text{F g}^{-1}$  at scan rate of 1  $\text{V s}^{-1}$ .

On the other hand, Lin et al. have tweaked the structure of a transition metal oxide electrode such that it massively overcomes previously observed limitations of similar devices. With more theoretical calculations provided in their supplementary work, Lin et al. mention future routes of multi-element doping as well as decreasing crystal size for further improving capacity. Perhaps the most interesting statistic from this research is that they achieved an energy density of 67.3  $\text{Wh kg}^{-1}$  which is not too far off from the low end of lithium-ion energy density. This technique opens up more exciting avenues of research and higher performance devices.

It seems then, for getting high quality pseudocapacitors off the ground and into the market MXene electrodes would be the way to go. The  $\text{Ti}_3\text{C}_2\text{T}_x$  MXene used in the paper uses comparatively abundant materials than the  $\text{Zn}_x\text{Co}_{1-x}\text{O}$  metal oxide electrode. Thus MXene electrodes could soon help in high power situations where physical device space needs to be small, for example in a regenerative braking system for long haul trucks.

For a more long-term outlook, atomic level structure engineering of metal oxide electrodes would be the way to go as these devices do outperform MXene electrodes but at high costs and barriers to access. To develop this type of technology would require very fine instrumentation that is currently restricted to few people. In the future, when this technique becomes more prevalent and mature in our society, these pseudocapacitive metal oxide electrodes would be immensely useful devices that close the gap between what we now call a battery and a capaci-

tor. Large scale problems that require sizeable power density as well as energy storage like grid balancing would be a good and much needed application. In regions that have adopted solar energy generation like Southern California, the duck curve is a good, but difficult, problem to have as it requires ramping up and down of thermal plants that are much more rigid than what a Lin et al.'s pseudocapacitor could do. In the same region, energy storage is a problem as there are times during the year when the state is forced to sell its generated electricity to Arizona at negative rates because it has nowhere to store it [Penn, 2017]. Atomically engineered metal oxide pseudocapacitors would be a fit solution to this problem.

## Conclusion

With any technology it is important to understand its place in society. Lukatskaya et al.'s MXene electrodes are a great improvement to pseudocapacitive technology that is within reach of being implemented for consumer purposes in the near future. Atomic level structure engineering, or simply put rearranging atoms for a desired purpose, is a very 21st century process and seems like a dream for materials scientists. It is a relatively unexplored and intriguing path because of our short experience with the technology. Thus, Lin et al.'s pseudocapacitive electrodes may not be accessible soon, but investing in the technology to manufacture devices like it will likely pay off in the long run and allow for more exploration of atomically engineered energy storage devices.

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