

Nickel-rich T-Nb₂O₅ Electrodes for Optimal Pseudocapacitive Charge Storage

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Abstract. Nowadays pseudocapacitors are gaining more attention because its ultra-high charging speed. However, the capacitance and conductivity of traditional pseudocapacitors remains relatively low. In this research, the method of doping NiO into Nb₂O₅ to improve the performance of hybrid pseudocapacitor with T-Nb₂O₅ cathode is studied more, which is to optimize the performance in certain doping level, voltage range, and temperature. The target improvements is to both preserve the high energy density of Nb₂O₅ pseudocapacitor and increase the power density by increasing its conductivity.

Keywords: Hybrid Pseudocapacitor, T-Nb₂O₅, Doping Method, NiO, Energy-Storage Chemistry.

1. Introduction

Nowadays as the energy issues are becoming more severe, new types of energy storage equipment are needed. In this case, Nb₂O₅ asymmetric hybrid supercapacitors are studied widely because of its high energy density, excellent power density and long cycle life. Using porous T-Nb₂O₅ materials as cathode and for pseudocapacitor can give relatively large theoretical energy density (40.5Wh/kg) [1] compared to using MnO₂ as cathode (6.4Wh/kg) [2], also comparable to a traditional lithium-ion battery (100-265Wh/kg) [3]. T-Nb₂O₅, which is orthorhombic, features one directional intercalation channel. The characteristic tetrahedral holes promise fast lithium-ion diffusion and ample space for ion storage. T-Nb₂O₅ pseudocapacitor also has a high-power density of 7.5kW/kg, about 30 times compared to lithium-ion batteries (260Wh/kg) and near EDLC range (5-10kW/kg). Other than Nb₂O₅; MnO₂, V₂O₅ and NiO are also experimented to be a cathode material. Although a large capacitance (1000-1200F/g) is detected, they have a common issue that their electrical conductivity is relatively low. By doping these metal oxides with exotic transitional metals with close ionic sizes and electronegativities, the doped oxide cathodes may improve the capacitance of the pseudocapacitor and preserve the high conductivity. One of the productive dopants is NiO. Two possible benefits adding NiO to the cell are hypothesized and tested. Firstly, adding a second oxide and makes the electrode featuring a more chaotic crystal structure, this will add the paths of electron flow, while increase its conductivity, leading to a higher Coulombic efficiency; another reason is the difference in ionic sizes increases the size of crystallographic voids, and fastens Li ions diffusion, facilitates the redox reactions on the surface of electrode. The doping method has been applied in many areas making electrodes to increase their Coulombic efficiency. However, too much doping may collapse the

orthorhombic structure of the electrode and cause the energy and power density decrease a lot. I will also study how the doping level of NiO affects the performance of the electrode. Herein we improved the crystal structure of the Nb₂O₅ cathode of the hybrid pseudocapacitor by adding NiO with a hydrothermal procedure from 850 to 1000 degree Celsius. The cell capacitance and Coulombic efficiency can be improved, and the power density advantage is retained well.

2. Experiment

To synthesis the mixture metal oxides and preserve the good performance of T-Nb₂O₅, the crystal structure needs to be preserved as Orthorhombic crystal system. T-Nb₂O₅ is synthesized by hydrothermal synthesis procedure, which is more efficient in producing nanostructures. Use a similar procedure and exchange the pure ammonium niobate solution to a mixture of ammonium nickel and ammonium niobate.[4] Consist of the cathode with pre-made T-Nb₂O₅-NiO, acetylene black for electric conductivity and PVDF (poly (vinylidene fluoride)) as a binder together using a mass ratio as 8:1:1. Disperse the three materials in NMP (N-Methyl pyrrolidone) to a gel, coat the gel onto a nickel foam. For the anode, carbon materials like graphene is favored because of its high theoretical capacitance (550F/g) and high conductivity. No redox reactions happen on the graphene anode and this half works as traditional EDLC advantaged from graphene's excellent flexibility and large surface area. There are many ways to synthesis ultra-thin graphene, the relative economic and easy method is to perform a cleavage/exfoliation of graphite to graphene. Graphene sheets is mechanically exfoliated using a scotch tape and then dissolve the tape using acetone. To make the capacitance fully occupied, make the anode and cathode have same capacitance that is make the mass of graphene anode approximately twice the mass as T-Nb₂O₅-NiO mixture cathode. (1100F/g of the cathode material and 550F/g of the anode material). Use XRD to test if the mixture's crystal structure also an orthorhombic system and use HR-TEM to test where are the Lithium ions located in the crystal lattice cell. (For a good result, after charge, that is when Lithium ions immerse into the mixture structure the lattice size should not be enlarged by a big number, where the ions are located at the plane of one lattice. After discharge when Lithium ions are removed from the space of the lattice, no phase change and large lattice size change.) The cathode and anode were pre-lithiated in half cells before binding the whole cathode, anode and electrolyte. While good conductivity nickel foam is used as a current collector and a basis for the cathode and anode 2D-structure materials, an aqueous based *LiClO4* solution can be used as the electrolyte due to the high performance of Lithium ions suiting into the porous cathode surface and perform redox reactions. Nippon Kodoshi Corporation's high ion permeable separator is placed in the electrolyte between the electrodes. After the full cell is assembled, a cyclic voltammetry (CV) is measured at scan rates of 5,20,50,100,200,500 (mV/s) within a voltage range of 1V-3V. The data was used to extract the apparent lithium diffusion constant by plotting the peak current vs the square roots of scan rates at different CV cycles. A galvanostatic charge and discharge (GCD) was carried out graph using current density 2/4/10/20 (A/g) to measure the 2capacity density of the electrode. For a rate performance test a series of five GCD cycles are performed sequentially at 1, 2, 4, 10, 20, 1, A/g. Then plot capacity at different current densities against current density was made. Also measure the specific volumetric capacitance *F/cm3* vs the cycle number and plot a cycle life curve of the pseudocapacitor.

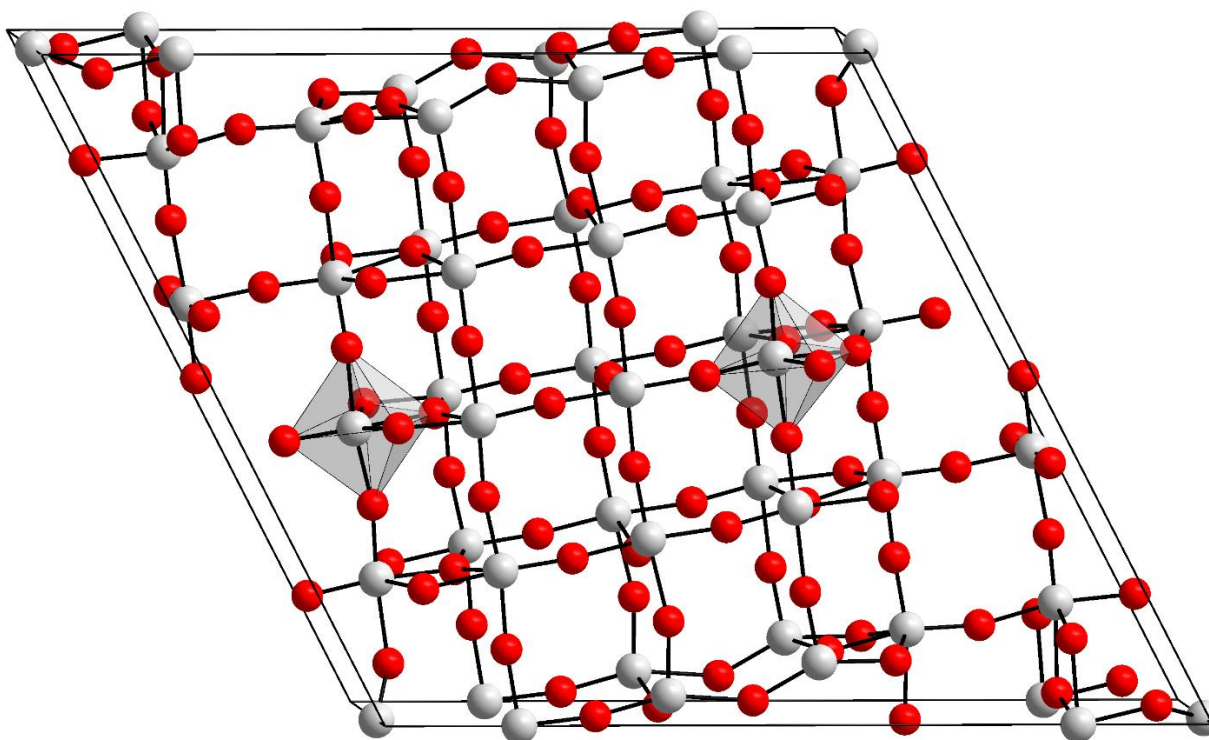


Figure 1. orthorhombic structure of T-Nb₂O₅, lithium ions can travel through the space between atoms above.

Another method is EIS mapping, which is very useful for determining impedance contributions from EDLC and pseudocapacitance. The test was carried out by applying an AC current of 10mV on the T-Nb₂O₅-NiO electrode in the chamber and vary the frequency of the AC current from 1kHz to 1MHz. The resulting current density at some point is composed of migration, diffusion, and convection term at different voltage steps. A Nyquist plot can be mapped by simply dividing the potential $V(\omega)$ by the instantaneous current $i(\omega)$, get the impedance Z . The magnitude of the impedance Z_0 equals to the potential amplitude E_0 divided by the current amplitude i_0 . Plot the vector Z with magnitude Z_0 on a 2-D plot while its real part (x component on a 2-D coordinate) is the impedance get from measured V/i at a certain time, which symbols the resistance simply forms $R=V/i$; its imaginary part (y component) is the active part that comes from the capacitors or limits of ion/electron diffusion. A fast ion diffusion and smaller resistance reflect in the imaginary region at the first half circle but not the real region in a pseudocapacitor half-cell. After the first cycles a fastened ion diffusion will shows up with a smaller impedance.

To test how the pseudocapacitive part and the EDLC part contribution to the whole battery, two variant controlled experiments are performed: capacitive charge storage process which focuses on the surface capacitance; and ion diffusion-controlled process which targets at the diffusion of the ions in the electrodes. The instantaneous current at different scan rate is measured and is compared to Cottrell's equation of battery like behaviors and capacitor like behaviors. [5] After linearization, the equation for capacitive materials is:

$$i(v) = k_1 v + k_2 \sqrt{v}$$

While in a pseudocapacitor, the instantaneous current versus instantaneous voltage becomes:

$$\frac{i(v)}{\sqrt{v}} = k_1 \sqrt{v} + k_2$$

A simpler way to identify is take logarithm of both i and v , make a plot of $\ln(i)$ versus $\ln(v)$, if the slope is near 0.5, it is pseudocapacitive; if the slope nears 1, it is more EDLC mechanism.

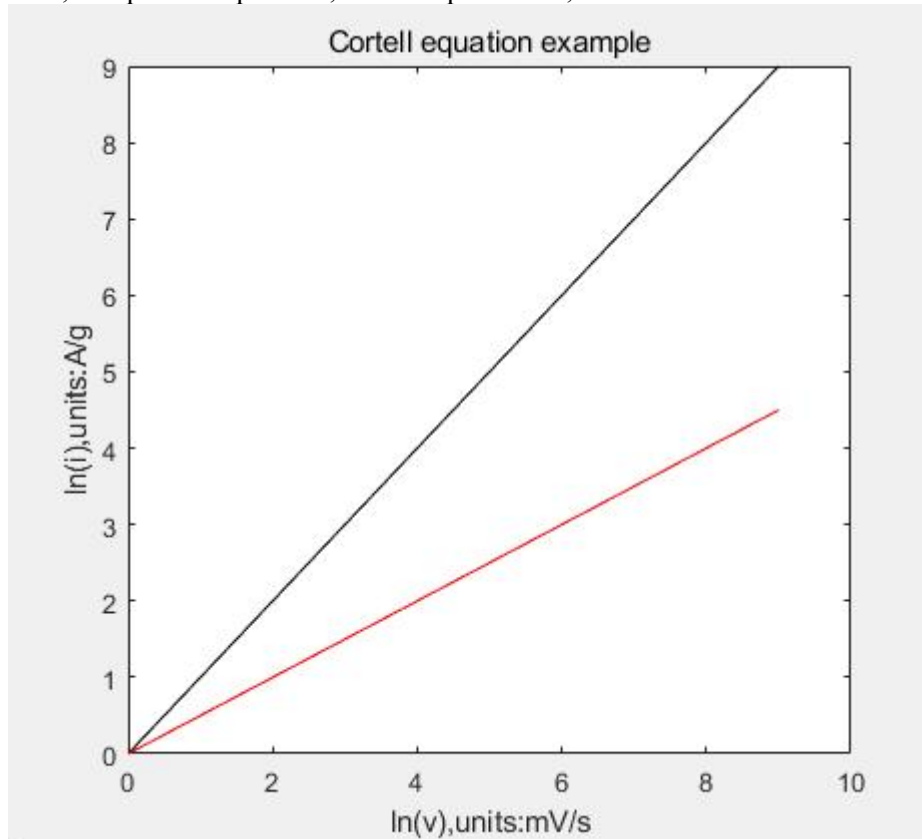


Figure2. the Cortell equation $\ln(i)$ versus $\ln(v)$ of EDLC (black, slope=1) and pseudocapacitive (red, slope=0.5) mechanisms.

To test how the doping level of the cathode material affect the performance of the pseudocapacitor, dope the cathode with same synthesis procedure I mentioned before with different ratios of NiO :(3,6,10,20,30 percents). Use same tests (CV and GCD) to conclude its capacity, energy density and power density.

As the temperature changes, the doped structure of T-Nb₂O₅-NiO electrode may not be orthorhombic anymore, may even collapse at higher temperature and cannot be conductive. As a result, changing the reaction condition is an important method to test the actual functionality of the T-Nb₂O₅-NiO pseudocapacitor. For instance, changing the environmental temperature and test the performance of the cell. Set the environmental temperature to 0°C, 10°C, 20°C, and 50°C, and use CV and GCD cycles to experiment the capacity, energy density and power density at each temperature. There will be one or more temperature to optimize the Coulombic efficiency because the holes of the cathode porous structure may be optimized to fit in lithium ions or at this temperature the conductivity is optimized.

3. Conclusion and discussion

In this research I have dived into the doping method of NiO to T-Nb₂O₅ as a pseudocapacitor's cathode and tested how the different doping levels affect the Coulombic efficiency as well as the impedance. Also I tested the full cell's performance in its capacitance, impedance and power / energy density. As a conclusion, popular cathode materials have many possibilities to improve in many aspects, and targeting problems like a smaller energy density than lithium-ion batteries are direct and clear. With the target and problem may meet, researchers can use methods like doping or using new adhering methods to make more porous structure and generate a bigger surface area can improve the

performance. Lithium-ion batteries, in contrast have smaller areas to improve because it is already a mature technology. By studying the natures of pseudocapacitors and Lithium-ion batteries, I inspected that some areas like car batteries or laptop batteries will remain lithium ion while they need to perform a longer operation time, while some accessories and phones can use pseudocapacitors as their energy support which is more time-saving when charging. Pseudocapacitors' energy density cannot exceed Lithium-ion batteries not because lacking in technology or researches, just because Lithium is the least heavy metal and performs best energy density theoretically by simple calculations, which no metal can exceed it. However, a pseudocapacitor has its own advantage which remains high power density just like a EDLC and exceeds EDLC as its energy density is comparable with lithium-ion batteries.

References

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