Using Vanadium Oxide Electrodes in Pseudo-Capacitors

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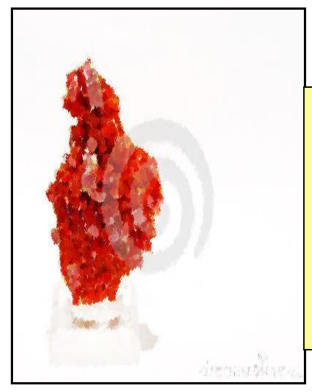


Abstract:

One of the most significant areas of research today is the study of energy. Economic growth in third world countries means a rise in fossil fuel usage, while availability decreases. This creates an increased need for new energy resources. Scientists are looking into electrochemical energy production as a viable option if it is sustainable and more environmentally friendly. Batteries, fuel cells and electrochemical capacitors are the systems currently being studied. The common feature of these three systems is that the energy providing process takes place at the phase boundary of the electrode/electrolyte interface and that electron and ion transport are separated. The differences in these systems are; fuel cells are high energy systems, super-capacitors are high power systems and batteries are considered intermediate energy and power systems. In the future, scientists would like to replace the battery, which is our most widely used energy source, with fuel cells and super-capacitors. Studies are being conducted to research using lower cost electrodes which are carbon- or metal-based (manganese, vanadium) as well as stable, water soluble electrolytes at room temperature.

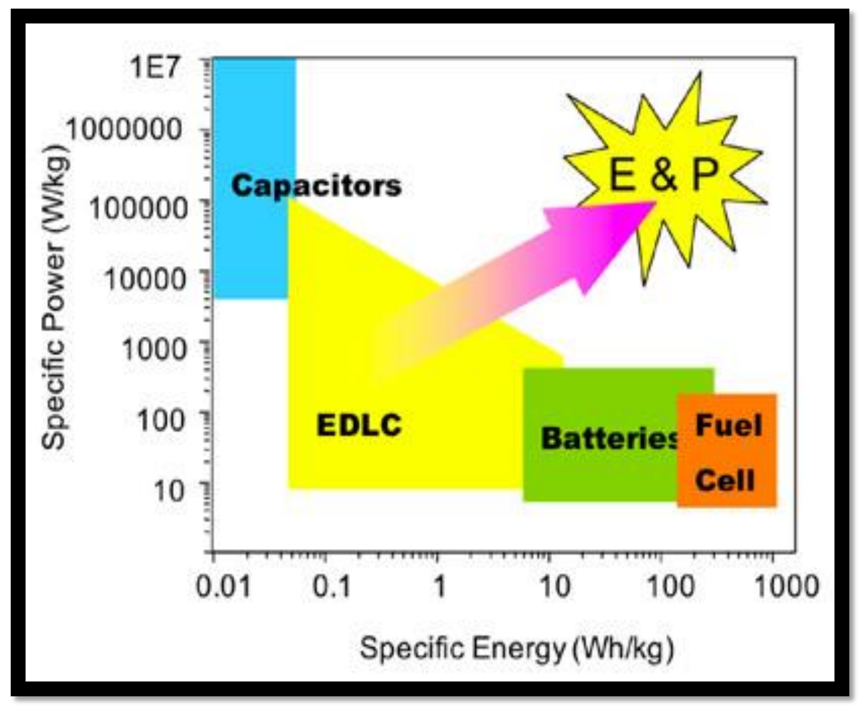
Introduction/Background:

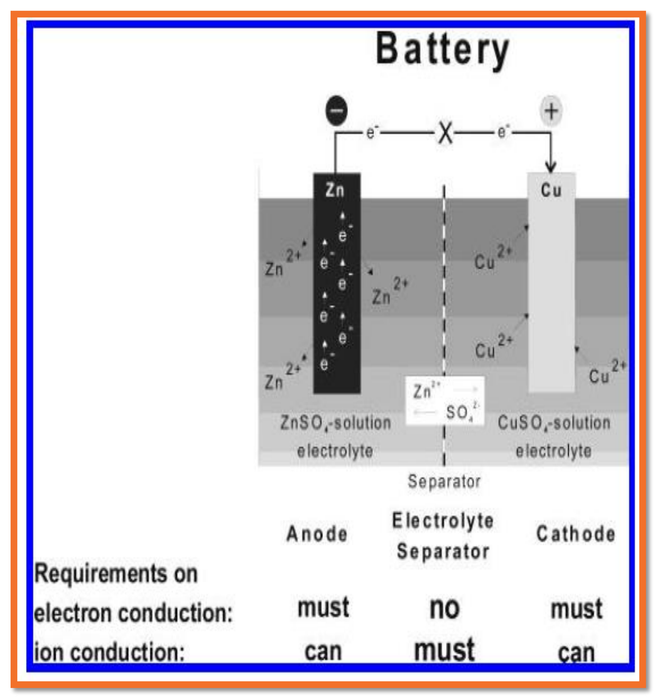
Vanadium is the 23rd element on the periodic table, the 22nd most abundant element in the Earth's crust and is found in 65 minerals and in fossil fuel deposits. It is a hard, silver-gray, ductile and malleable transition metal. It is also the lightest d-transition metal, with a low density and high melting point.

It can be isolated easily in the laboratory to form an oxide layer which stabilizes the free metal somewhat from further oxidation. Vanadium can be produced as a by-product from steel smelter slag, or from the dust of heavy oil or as the by-product of uranium mining, making it relatively cheap as compared to other transition metals like Titanium, Manganese, Ruthenium or Platinum. It is currently used primarily to produce ferrovanadium, which is a steel alloy, which is found in high speed tools. If added to aluminum in titanium alloys, vanadium increases its strength making it suitable to be used in Jet engines. The other major use of vanadium is as a catalyst in the production of sulfuric acid.

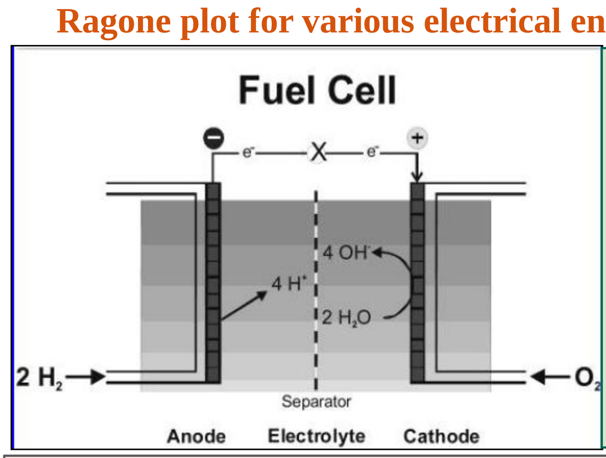
Vanadium has one naturally occurring isotope; Vanadium-51 @ 99.75% and one radioactive isotope Vanadium-50 @ 0.25% with a half-life of $1.5X10^{17}$ years. Vanadium has 4 stable oxidation states; +2 to +5, but the most commercially important one is the Vanadium (V) oxide. Therefore, the Vanadium (V) oxide compound is being used as an electrode in pseudo-capacitors and batteries.

Differences Between A Battery, Fuel Cell & Capacitor:





Ragone plot for various electrical energy storage devices:



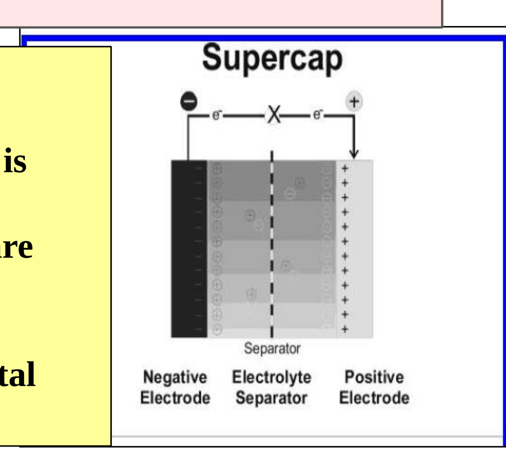
Battery: Closed system . Energy and storage conversions occur in the same compartment
High energy, intermediate power

Fuel cells: Open system
Energy storage is in the tank and energy conversion in the fuel cell is separated.
Space applications.

TYPES OF SUPERCAPACITORS:

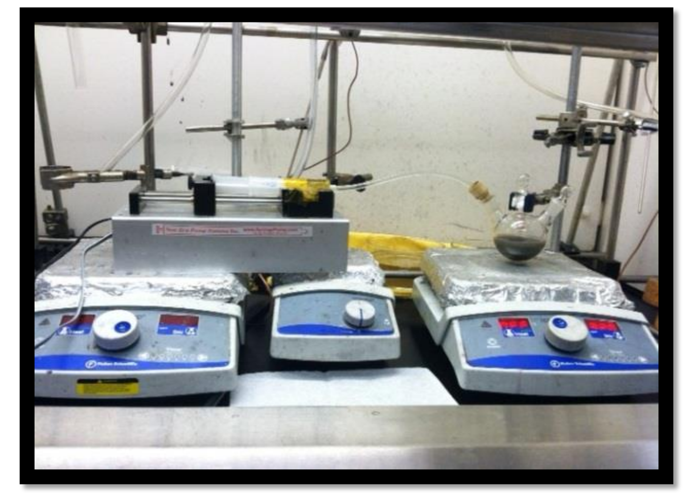
Electric Double Layer Capacitors (EDLCs):
Charge storage occurs by charge separation across the electrical double layer. This is dependent on the electrolyte used and the material on the surface of the electrode. These electrodes have high surface area and are usually made up of activated carbon. This is a non-faradaic and the double layer at the electrode surface forms and relaxes almost instantaneously; responds more rapidly to potential changes than a battery or fuel cell and has a longer life cycle and is more stable.

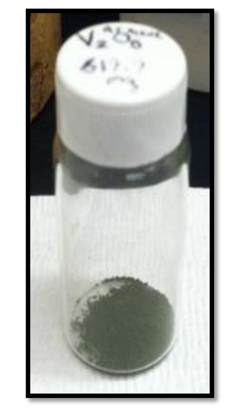
Pseudo-capacitors:
These capacitors undergo a Faradaic reaction (redox reaction) at the electrochemical interface, using an electrolyte, causing storage of charge. It is near-surface
- Symmetric capacitors (also known as ultra-capacitors) - both electrodes are made up of the same material, usually carbon polymers
- Asymmetrical capacitors (also known as pseudo-capacitors) - one of the electrodes is made up of carbon (anode) and the other is made up of a metal oxide.



Methods & Materials:

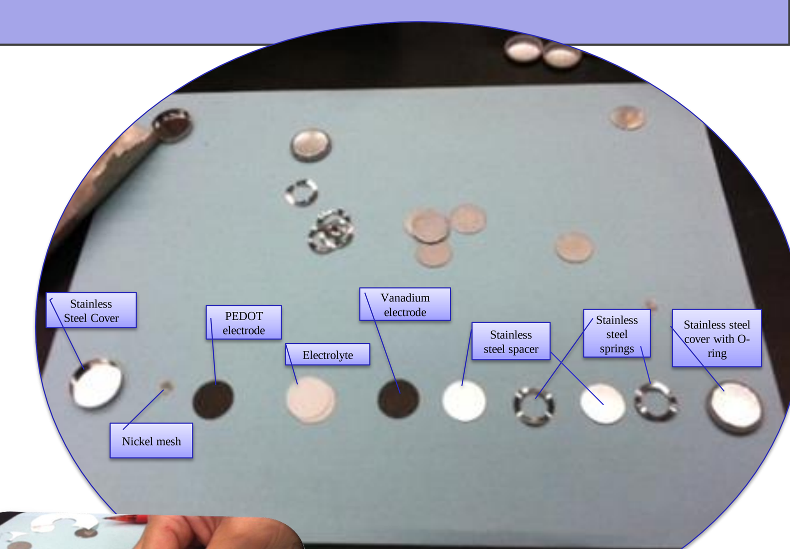
Synthesis of V_2O_5 or some derivative:
Using 280 mg of $VOSO_4$ X $H_2O_{(s)}$ is dissolved in 28mg of de-ionized (DI) water. This is placed in a round bottom flask over a stir plate and a stirring bar is placed into the solution. Stir at an intermediate speed to avoid splattering. 242.2 mg of KOH (roughly 2 pellets) is dissolved in 14 mL of DI water and is placed into a syringe. This will be added to the Vanadium solution via an injector and syringe. When 10 mLs of KOH is added, the injector will stop and the material will then be mixed for an additional ½ an hour. It will then be collected into centrifuge vials and 3 separations will be done. The first two with DI water and the last with ethanol. The remaining solid will then be put into the oven/vacuum for approximately 2-3 days to dry. The V_2O_5 solid was massed at 59.5 mg.
This material will be crushed and placed into a ceramic dish to be cooked at 450°C for two hours and then cooled to room temperature. This material can then be weighed out and used to make the electrodes for the capacitor.

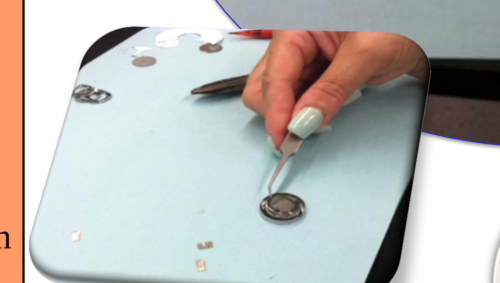


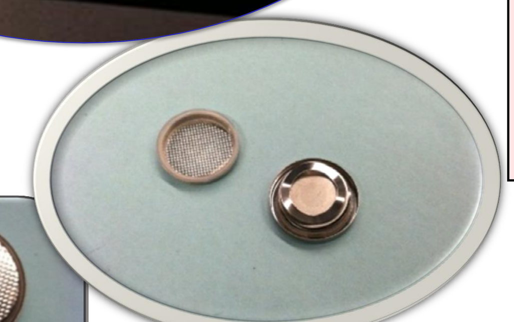


Electrode Production Process:
The empty pre-cut carbon paper electrodes are massed before the layering of the vanadium mixture and PEDOT occurs. The V_2O_5 is placed into a jar and some 3.5% PEDOT (conductive polymer), is added in a 3:1 ratio, a little ethanol (about 1 mL) is added to the jar and it is stirred in the sonicator. The mixture is layered at 50 µL onto each electrode and allowed to dry in the oven under low temperature and vacuum. Upon drying another layer is applied until the mass of the electrode increases by approximately 8 mg. The other electrode is layered only with 3.5% PEDOT and is dried in the oven at low temperature and vacuum. Upon drying another layer is applied until the mass of the electrode has increased by 15 mgs.

Assembly of capacitors:
Once the electrodes were massed and had a mass of approximately 8 mgs of the vanadium and approximately 15 mg of PEDOT (**conductive polymer**), the capacitor could be assembled. A bottom container was placed on a dry flat working area and a small piece of nickel mesh was placed on the bottom, next the PEDOT electrode is placed facing up. 2 pieces of filter paper cut into a circle, which is slightly larger than the electrode is placed on top. 2 drops of the electrolyte is added to the filter paper (we used KCL on our first set, LiOH on the second set). The vanadium electrode is placed on top of the filter paper with electrolyte face down. A stainless steel disc separator is placed on top then a stainless steel spring and another separator and spring is added. A stainless steel top cover with O-ring is placed on top and carefully moved to a press, where it is all forced together to make up a cylinder super-capacitor. Once inspected it is placed on the battery analyzer to check for capacitance (can it be charged and recharged). It cycle for 5-10,000 times.



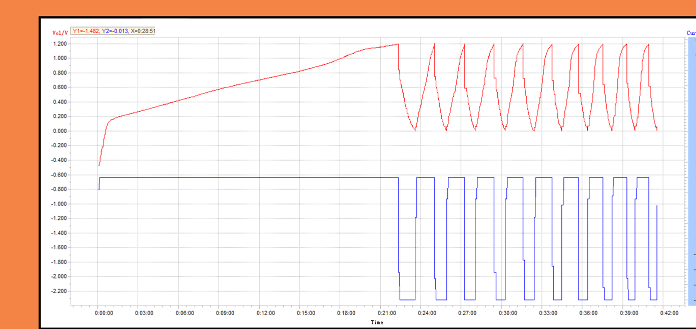




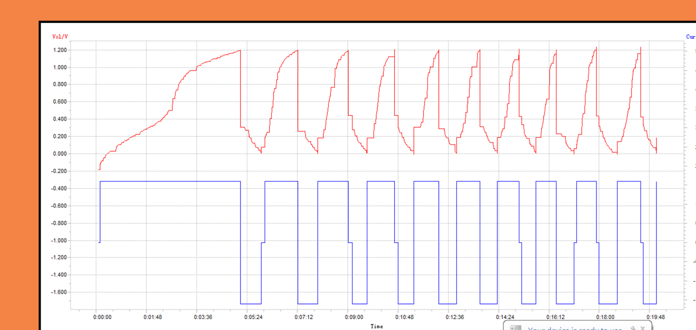
Results & Discussion:

To calculate the capacitance we use the following formula:
C = charge ÷ voltage or Q ÷ V , where Q = current X time or I X t, where i(t)
Note: current is constant over the cycle. We ran these capacitors on the anode side.
So : C = ((I X t) ÷ V) X 2

KCl



LiOH



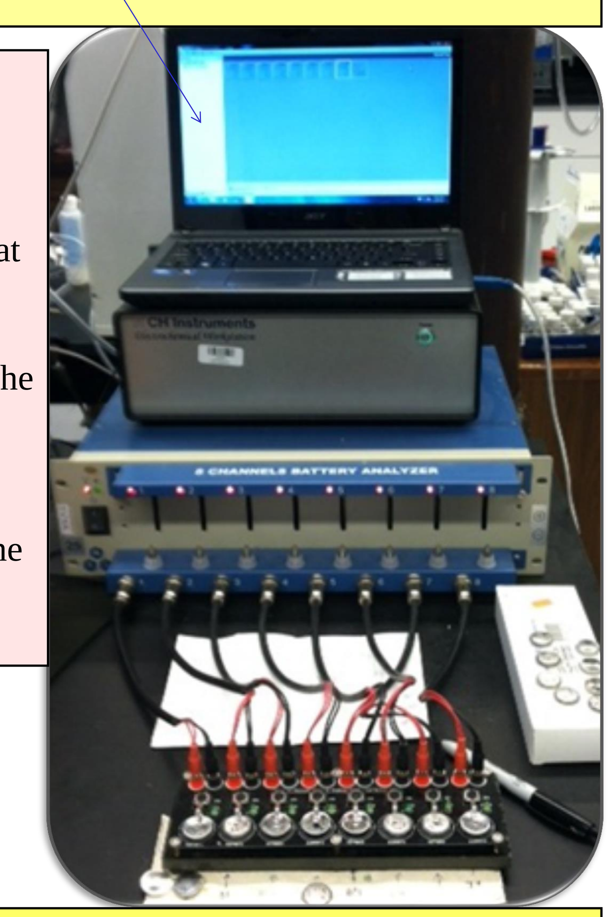
For the KCl electrolyte the capacitance at the 10th discharge cycle is:
C = ((2.0 X 10^{-3} A X 36 s) ÷ 1.2 V) X 2 = 0.12
We need to take into account the amount of Vanadium (V) oxide used on the electrode to produce this capacitance so we use the mass of vanadium on the electrode and divide it by the capacitance to get the capacitance per gram of the capacitor.
C/g = 0.12 ÷ 6.6 mg = 0.12 ÷ 6.6 X 10^{-3}g = 18.2 F/g

For the LiOH electrolyte the capacitance at the 10th discharge cycle is:
C = ((1.6 X 10^{-3} A X 34 s) ÷ 1.2 V) X 2 = 0.09066
C/g = 0.09066 ÷ 6.0 mg = 0.09066 ÷ 6.0 x 10^{-3}g = 15.1 F/g

REDOX REACTION THAT ARE OCCURRING:

$V_2O_5 + xK^+ + xe^- \rightarrow K_xV_2O_5$ using $KCl_{(aq)}$ electrolyte
Vanadium is at a +5 oxidation state and will be reduced to a different oxidation number (+4, +3)
More tests, runs need to be done to fully understand the complex mechanism that is going on here, as it is not a simple redox reaction, the electrolytes complicate things.
$V_2O_5 + xLi^+ + xe^- \rightarrow Li_xV_2O_5$ using $LiOH_{(aq)}$ electrolyte
The LiOH as an electrolyte seem to make the redox reaction even more complex than KCl and therefore it does not seem to be as good of an electrolyte as the KCL.

Based on this data, we can say that KCl is a better aqueous electrolyte than LiOH in these capacitors. Many more capacitors will need to be tested at different voltages and currents. The two graphs above show only the first 10 cycles of the 10,000 cycles that were run. The two capacitors were run as anodes and many more capacitors will be tested as cathodes. Further research will be needed in order to understand the redox reactions that occur with the different electrolytes. The vanadium used will also be analyzed to make sure the same vanadium structure is used so data can be compared.
Other stable aqueous electrolytes will be studied and tested with the vanadium oxide electrodes in the future.



Literature Cited:

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Winter, M., & Brodd, R. J. (2004). What Are Batteries, Fuel Cells, and Supercapacitors? *Chemical Reviews*, 4245-4269.

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