

Testing the Limits of Urban's Method for Voltage Calculation

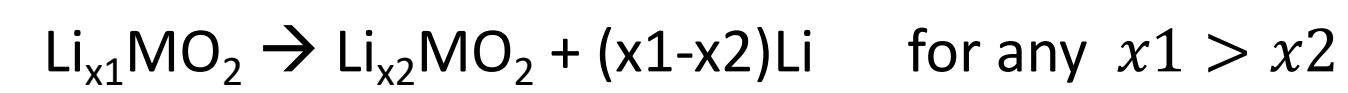
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Motivation

Lithium-ion batteries (LIB) show much promise for energy storage mechanisms but are far from being perfected. Sensitivity to ambient oxygen and moisture, low energy density, dendrite growths, and short battery life are all problems that plague LIB on the market today. To solve these issues, the Mo group uses atomic-scale modeling of LIB materials to gain insight on reaction pathways of both existing and theoretical materials. One aspect of this research is on the voltage of cathode materials, which is the subject of this project. In 2016, Urban et al published a paper studying the voltages for lithium metal oxides of the form $LiMO_2$, and their thermodynamic stabilities against various electrolytes was further studied by Nolan et al (2019). This project examined whether this formula could be extended to polyatomic oxyanions and found that formula-calculated results were highly precise but reliably 1.0V below the theoretical value for that average. On its own Urban's method was not accurate, but a slightly modified version of it would work phenomenally. Usage of this much simpler formula will allow future researchers to gain a reasonably accurate estimate of voltage of a theoretical material without needing to do a full Molecular Dynamics Simulation (MDS), which saves time, power, computer memory, and other relevant resources.

Abstract

Urban's method to calculate voltage applies to the following chemical reaction with the equation written below:



$$V = -\frac{E(Li_{x_1}MO_2) - E(Li_{x_2}MO_2) - (x_1-x_2)E(Li)}{(x_1-x_2)}$$

Literature voltage values were provided by the Materials Project, which has already done full MDS with the Vienna Ab-initio Simulation Package (VASP) to produce highly accurate results. Total energy values were also given by the Project, and these were the values put into Urban's formula. Percent error was then evaluated to judge the accuracy of the simple calculation method. Four different types of polyatomic oxides were examined: phosphates, sulfates, silicates, and carbonates. Many transition metals were involved, the most abundant sample sizes being Fe, Mn, Co, and Cr.

Transition Metals

The data on transition metals was much less clear-cut than that of the oxide categories. Much of this was because there were many more metals involved in the overall data pool than there were oxide types, meaning that the sample size for each metal was much smaller. The metals with the greatest sample sizes were Fe, Co, and Mn, closely followed by Cr. Other metals included in this project were V, Ti, Ni, and Cu; the latter two are popular for use in Li batteries. More work will be needed to study these categories in depth because I did not have enough time to do this myself.

Metal	Average	Median	Standard Deviation	Sample Size
Co	25.72	7.061	44.74	22
Cr	21.52	12.58	25.41	14
Cu	11.21	0.7798	25.60	7
Fe	19.80	5.948	29.56	15
Mn	25.95	15.77	29.51	17
Ni	2.494	0.3715	4.248	7
Si	0.2761	0.2761	0.000	1
Ti	4.655	3.166	4.607	4
V	9.048	5.705	10.09	6
Zn	21.12	21.12	20.37	2

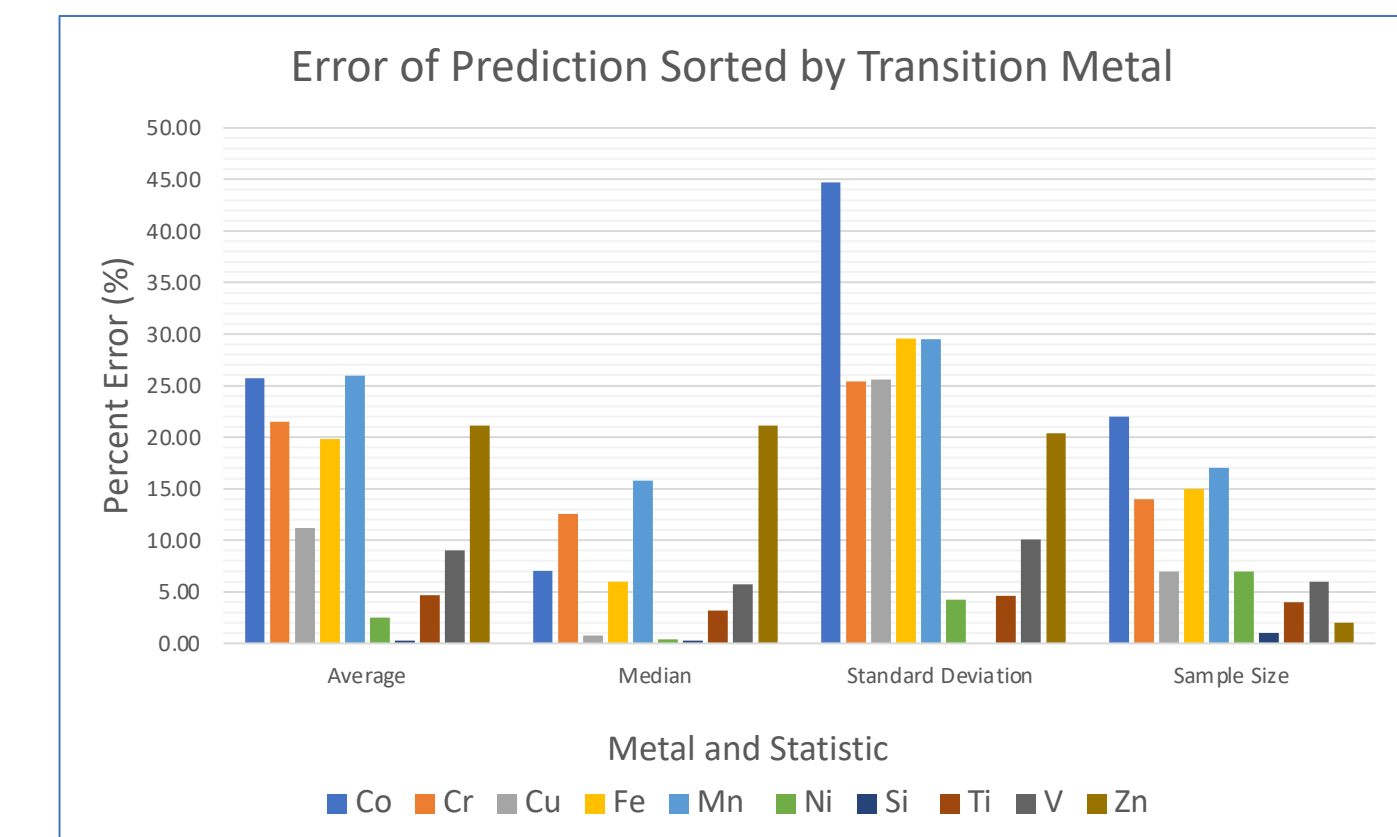


Table 1. Statistics for each transition metal.

Figure 3. Table 1 shown in a bar graph. Medians consistently lower than the average show that all sets of data have a positive skew of error, and that most metals except Mn and Cr can be trusted. Judgement should be withheld for Zn and Si because their sample sizes are too small to establish a pattern.

Many Outliers in Overall Data Set

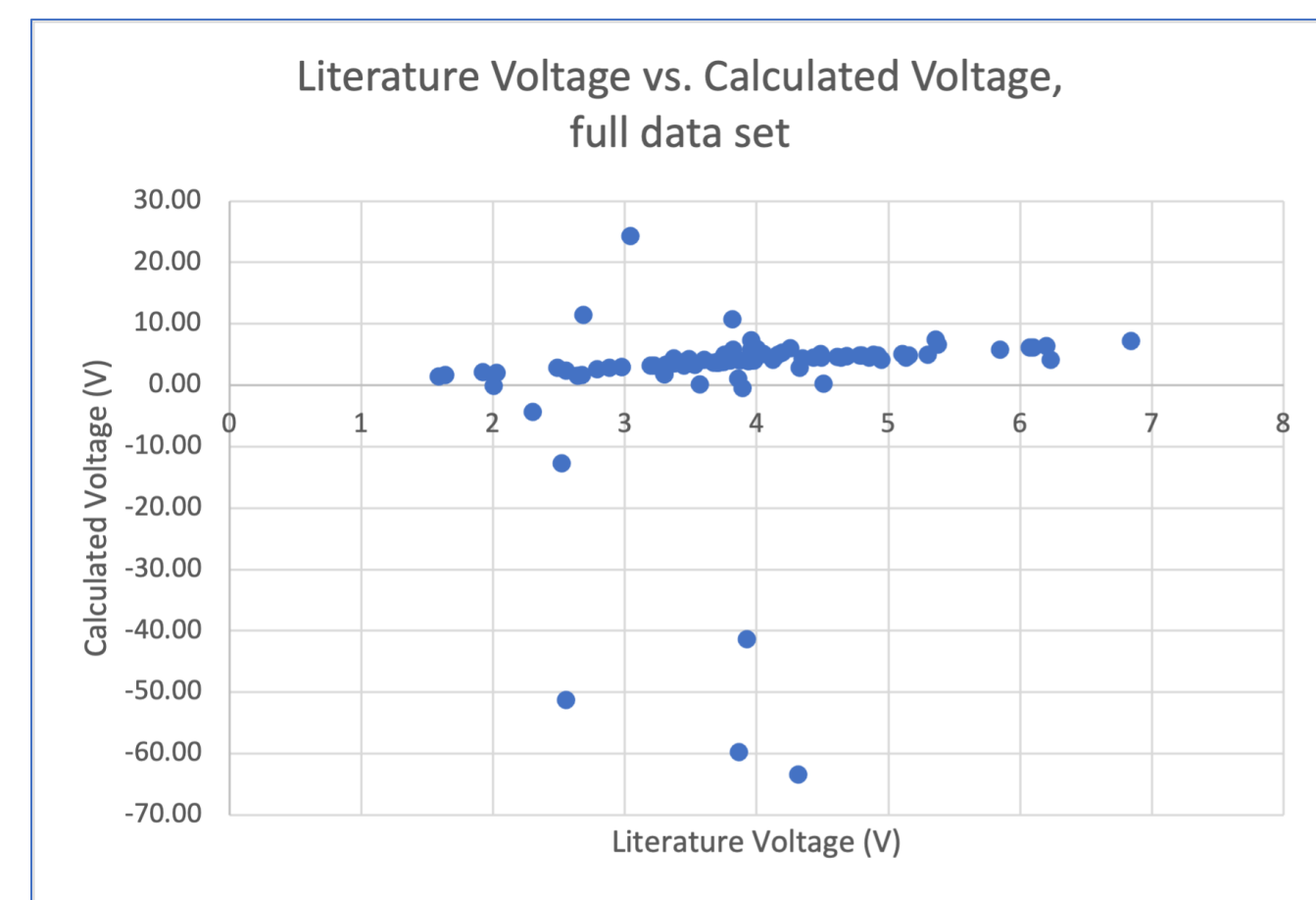


Figure 1a. In the full data set, most of the calculated values produce somewhat reasonable estimates of voltage, being below 10V. However, there were many extreme outliers that produced values that were either negative in value, close to zero, or some enormous magnitude that could not possibly be produced by these sorts of LIB.

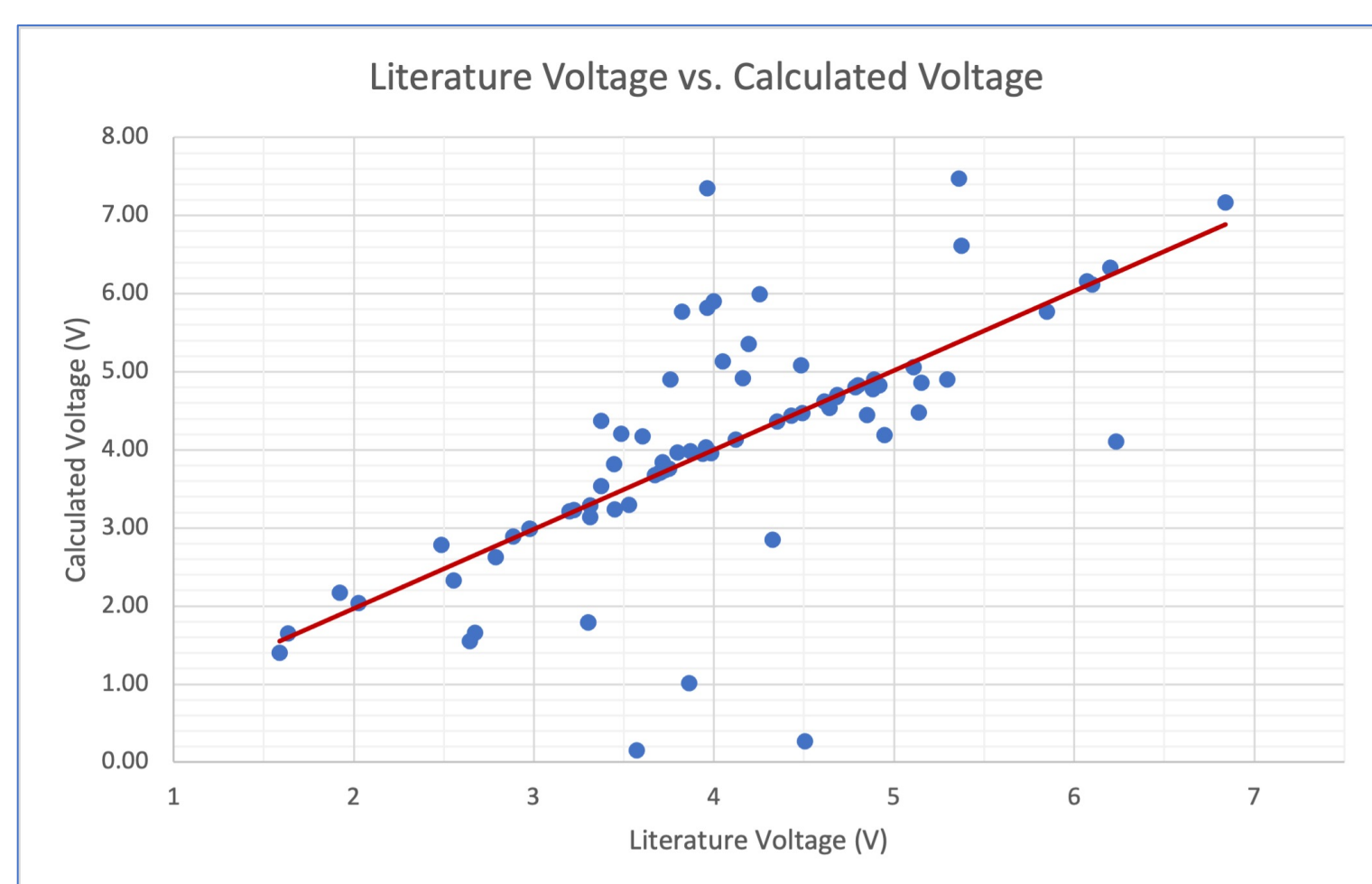


Figure 1b. Removing the extreme outliers mentioned above shows a clear relationship between the predicted voltage and the literature voltage, following the relationship $L = 1.058 * C - 0.0611$, where L represents the literature and C represents the calculations. There are still many exceptions to this trend.

Oxide Classification Contributes to Percent Error

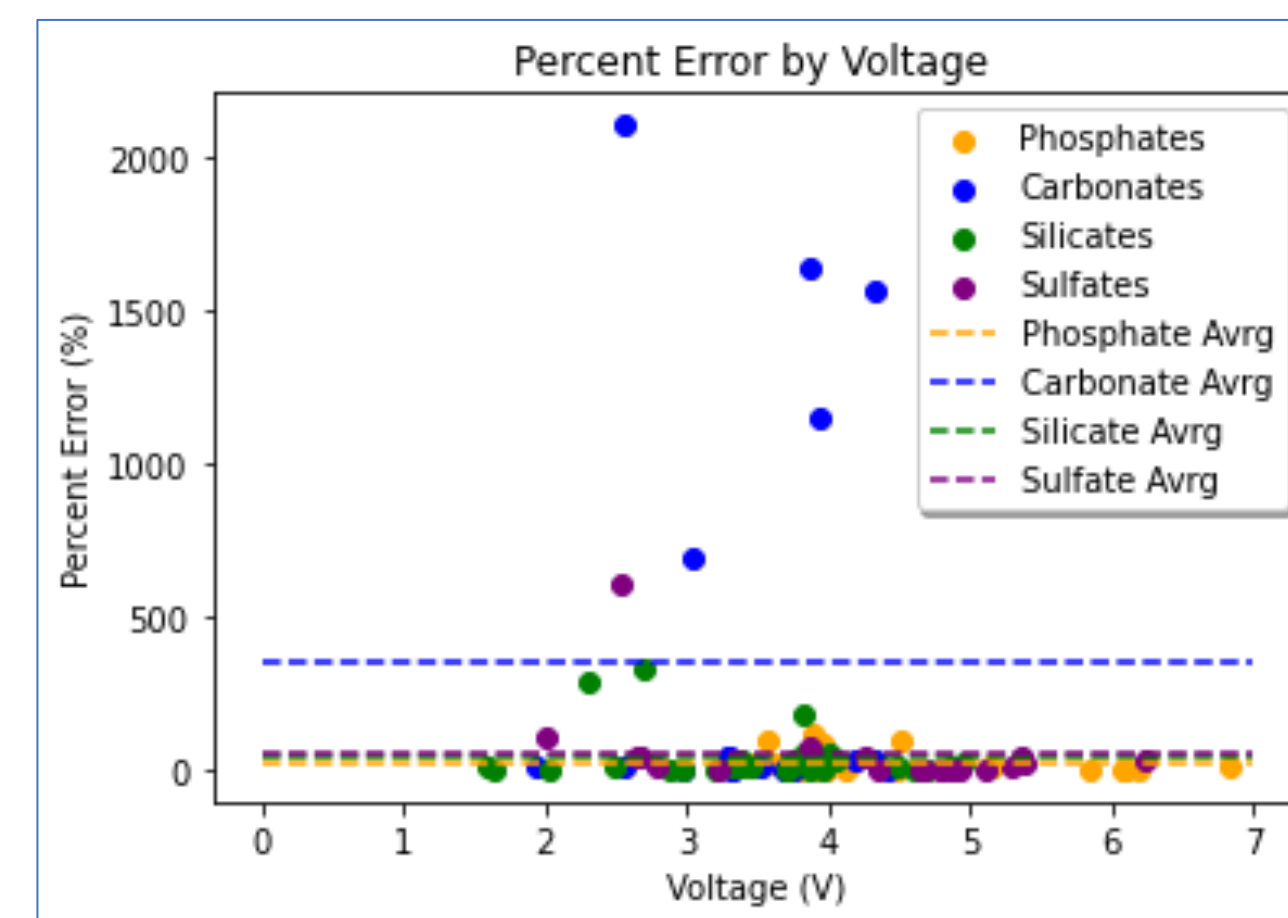


Figure 2a. Out of all the oxide classifications, carbonates are the highest contributor to the outlandish outliers. This could potentially be due to the different oxidation state of carbonates, as the ion has a trigonal-planar structure while phosphates, silicates, and sulfates all have tetrahedral structures.

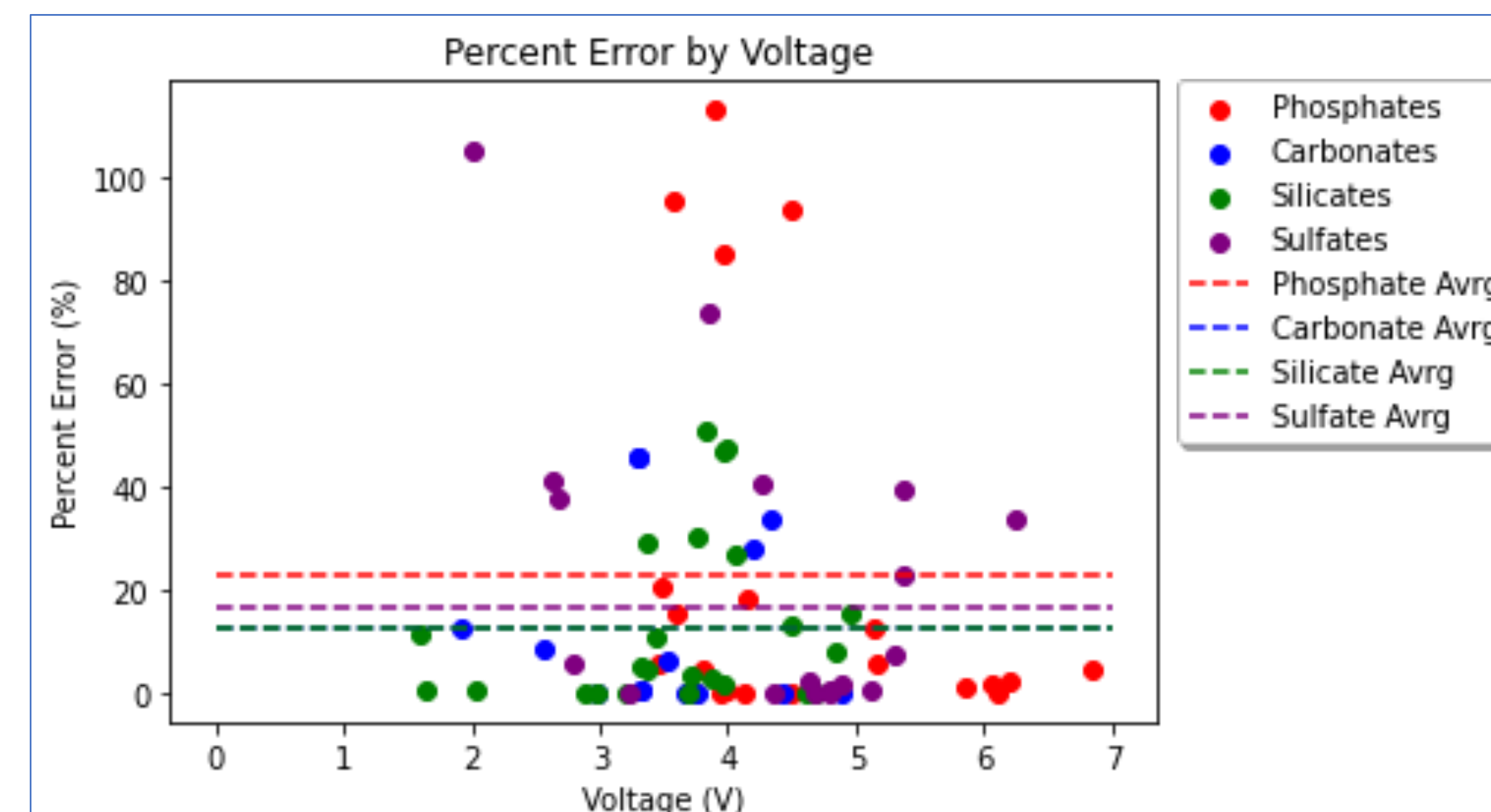


Figure 2b. When the extreme carbonate voltages are removed, phosphates become the least well-behaved group. Silicates and carbonates become tied for the lowest average percent error. However, the extremely low median value for phosphates (not pictured) indicates that this group is either accurate or wildly off.

Conclusions:

This study showed that Urban's method was generally accurate but not enough to be completely relied on. If one is evaluating the voltage for a material not within the Materials Project database, they would be better off not using Urban's method at all and doing the full MDS, even though such a computation is much more resource-intensive. It could still be useful to relax the crystals and use Urban's method to gain a general ballpark, but the outcome of the equation should by no means be prioritized over the VASP-computed values. Sources of systematic error included carbonates, which contained the highest amount of egregiously incorrect values, but beyond that there are no clear-cut sources of either systematic nor random error. The median percent error for all tested groups was much lower than the averages, indicating that the calculated values were generally close to the theoretical voltage. The average error was not a good metric because one or two outliers could position the average at double the median and would therefore make it not representative of the data set it belonged to. More research could certainly be done to expand the data, especially to include more robust counts of the transition metals discussed above.

Lessons Learned

There are several lessons I will take away from this REU. The first is that materials research is a prime example of the idiom 'easier said than done.' With a system as delicate as a LIB, there are many checkboxes a material (or combination of materials) must meet to be considered a viable candidate for testing in a physical laboratory environment. Finding a new material to fit the job is like playing whack-a-mole. For example, LGPS has high efficiency and energy density but is highly reactive to ambient moisture; $LiFePO_4$ (LFP) is stable and lightweight but has a lower energy density; and so on. This has been very eye-opening in terms of the open-ended problem-solving process of research, and that there isn't necessarily a 'right answer' like there might be to the worksheets and homework one will see in classroom settings. Additionally, I have gained experience in tools that are popular in chemical and material research. Pymatgen and VASP are key tools for computational modelling of all sorts of substances and not just LIB, which makes them transferrable to other research positions that I might hold in the future.

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Citations

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