**Title:**

I'm today’s speaker, YMW. And, I would like to share with you some of my research progress, and the topic is Alkyl chain effect of quaternary ammonium ionic liquids on capacitance of graphene electrode.

**Factors of Changing Interfacial Structure to Enhance Energy Storage:**

First of all, the main focus of my research project is the electrical double layer formed between electrode and electrolyte. Before I move on to my research result, I will first motivate the reason why we are particularly interested structures and properties of these electrical double layers and electrochemical interfaces. Here, what I'm showing to you is a supercapacitor device and a picture of interfaces between electrode and electrolyte by simulation. These electrochemical interfaces in SC devices play a fundamental role because energy storage is done by the formation of the electrical double layer.

**Factors of enhancing the energy storage of SC:**

In general, the formation of EDL characterizes the performance of energy storage in SC. So, having a good understanding of these EDL structures is important to enhance energy storage performance. Here are some factors to modulate different types of EDL, such as using different nano-structured carbon electrodes and different types of electrolytes. In my project, I will particularly focus on different types of long alkyl chains quaternary ammonium ionic liquids and graphene electrode and study their interfacial structures.

**Importance of Nonpolar Functional Groups for Like-charge Ions Clustering on Electrochemical Interface:**

Before moving on to my research result, I would like to motivate why we want to use ionic liquids with different long alkyl chains quaternary ammonium. Here is a previous research of computational works in our group. This paper shows that anions with nonpolar functional groups like trifluoromethane can show nonpolar packing and push all these anions clusters together during the formation of EDL. This anion-anion clustering can facilitate the separation of cations and anions at the positive polarized electrode. As you can see, the capacitance of TFSI ionic liquids system shows a significant increase at positive polarized electrode. So this nonpolar interaction between functional groups motivates us to study the long alkyl chains, which can facilitate the accumulation of like charge ions at interface, which plays an important role in energy storage performance.

**Cation effects on EDL capacitance:**

Previous work has demonstrated (found) the effect of nonpolar functional groups on double layers capacitance. Here we want to compare the effect of different types of cations on the double layer capacitance. As you can see, this capacitance profiles from impedance spectroscopy experiments show different cations capacitance at different voltages. In particular, the butyltrimethylammonium ionic liquids shows a significant increase of capacitance at negative polarized electrode. So this kind of tetra alkyls cation may increase the capacitance at negative polarized electrode.

**Long Alkyl Substituents of Quaternary Ammonium can increase Capacitance on Positive Electrode Significantly:**

For the same group, they studied the double layer capacitance of quaternary ammonium and it also conducted by impedance spectroscopy. They used different types of quaternary ammoniums with different long alkyl chains and they displayed different differential capacitance behavior. Here is a result when they used methyltrioctylammonium, they found out better enhancement of capacitance at positive electrode than other tetra alkyls ammonium. This probably caused by long alkyl chains that can soften the repulsion between anions based on the conclusion of the article.

**Motivation:**

We are also curious about the interaction between these long alkyl groups and how they affect structures and capacitances of electrical double layers.

**Supercapacitor systems of interest:**

Here are some supercapacitor system I will investigate in this project. I will use graphene electrodes to be my electrode material and different tetra alkyls ammonium with different anions to study their interfacial structures and capacitances at different applied voltages.

**Computer Simulation Method:**

Here we study electrical double layer in this voltage response using the computer simulation method called Fixed-Voltage MD simulation. So basically, we set the voltage drop across two electrodes at different applied voltages and solve the electrostatic boundary condition for each atom from electrode surface. Here is one of a Fixed-Voltage MD simulation snapshot of SC systems of interest. The right hand side of this picture is our electrochemical cell and on the other hand, the vacuum gap separate the cathode from the periodic image to offset electrostatic potential from it so the full simulation cell has zero voltage drop between periodic boundary.

(Here are snapshots of cell setup and this setup is for 3D PME to speed up the simulation and before running the fixed-voltage MD simulation I will use the Hybrid Monte-Carlo MD to equilibrate the electrolyte density.)

**Trajectory Analysis:**

In order to understand the interfacial structures, properties and even capacitance, they can be done by following trajectory analysis. First of all, 1D density distribution profiles of functional groups, they can characterize the spatial orientation of functional groups related to electrodes and use RDFs to show the interaction between ions at interface. We can also integrate the 1D Charge density distribution of ionic liquids and use electrostatic boundary conditions solved from Fixed-Voltage MD simulation to calculate the Poisson’s profiles and its voltage drops. Finally, we can calculate differential capacitance by dividing by the difference of electrode surface charge by difference of voltage drops at different applied voltages to plot the differential capacitance profiles.