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# Designing Graphene-Based Electrodes that Show Selective Adsorption of Metal Cations Aiming at Metal Resource Recovery from Industrial Effluents

Graphene is expected to be a key material of new functional devices because of its high electro-conductivity and two-dimensional structure. We seek for application of graphene-based porous materials as the electrode for selective adsorption of ions aiming at metal resource recovery from industrial effluents. Recently, capacitive de-ionization (CDI) is drawing attention as a water purification technology that employs electrochemical adsorption of ions on the electrode. In CDI, ions in aqueous electrolytes are adsorbed on the electrode by way of formation of electric double layers to obtain deionized water. Activated carbons are often used as the electrode material of CDI because of their large specific surface. On the other hand, it has been shown that, when the pore size of the electrode is comparable to the ion size, the electrode can show selective adsorption of ion species. Selective adsorption of ions could be used for metal resource recovery from industrial effluents. Currently, industrial effluents is often simply disposed, although it contains a lot of metal cations and it could cause environmental problems. Graphene-based porous electrode materials have great potential for the use of the selective adsorption because the pore size could be finely tuned. In this study, we investigated the dependency of adsorption performance of the electrode material on the ion species and the pore diameter of the electrode material by using molecular dynamics (MD) simulation [1]. Our simulation system (Fig. 1) consists of a unit of metal salt $MCl_X$ (where "M" is Al, Cr(III), Fe(II), Fe(III), Ni, Cu(II), Zn, Sn or Ba and "X" is 2 or 3, depending on the valence of the metal)[2-5] , 1440 water molecules[6] and the graphene electrodes[7] that have slit pores periodic that the diameters, $d$, are 8, 9, 10 and 11 Å. We calculated the potential of mean force (PMF) of the cations as a function of the distance from the entrance of the pore, the radial distribution function (RDF) with respect to the cation and oxygen of water molecules and the density distribution of water. We performed these calculations for two cases; with and without applying the voltage of 1 V between the anode and the cathode. We also estimated the potential barrier that the cations need to overcome in order to be adsorbed in the slit pore from the obtained PMFs. The PMF for each cation species without applying voltage is shown in Fig. 2. In the case where $d$ is 8 Å, we observed clear difference in the PMFs between divalent and trivalent cations. We also observed another clear difference between divalent cations, Sn and Ba, and the other divalent cations studied here. As a result, we the PMFs were categorized into three groups. The differences between the groups are caused by the difference in the valence and the size of the cation. Furthermore, in these groups, it was found that the height of the potential barrier of each group is correlated with the tendency of the cation to attract water molecules. In other words, the weaker the attractive force is, the lower the potential barrier is: each cation must be partially dehydrated when it enters the slit pore. Therefore, we found that the accessibility of cations to the slit pore depends on the valence, the size and the magnitude of the attractive force of each cation. In the case where $d$ is 9, 10 and 11 Å, the order of the height of the potential barrier for those cations changed because the effect of the factors that associate with the accessibility of cations to slit pore becomes complex. It was found that Sn is overall the most easily absorbed to electrodes in the cations studied here. In this study, we found that we can isolate a cation species from an aqueous solution that contains multiple cation species by CDI with the electrodes of controlled pore sizes, utilizing the difference in the valence and the size of the cation species. In the presentation, we will also discuss the case where voltage of 1 V is applied in detail.

# References

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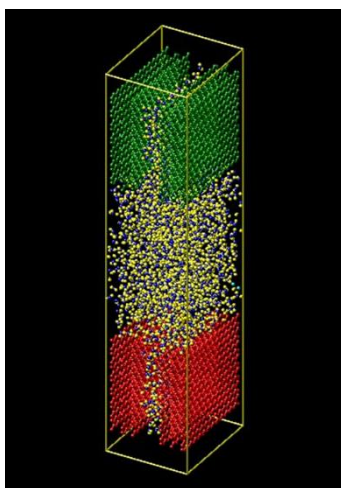
# Figures



**Figure 1:** Snapshot of the simulation box. Water molecules are shown in blue (oxygen) and yellow (hydrogen). The cation and the anion are shown in purple and blue, respectively. The anode and the cathode are shown in red and green, respectively.
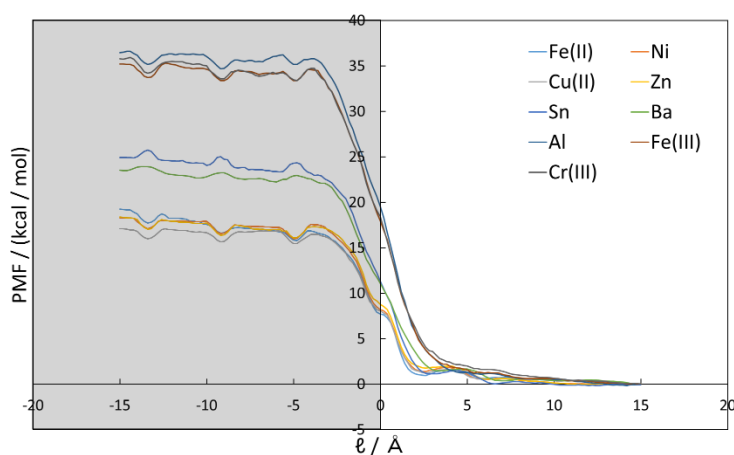


**Figure 2:** Potential of mean force (PMF) in case of the pore diameter is 8 Å. The shaded area shows positions of the inside of the pore of the carbon electrode.