
Yuji Yamamoto¹

Kenji Kiyohara^{1,2}

¹Kwansei Gakuin University, 669-1337, Sanda, Japan

²National Institute of Advanced Industrial Science and Technology (AIST), 563-8577, Ikeda, Japan

k.kiyohara@aist.go.jp

Selective Adsorption of Monovalent Cation in Aqueous Solution with Slit-Porous Carbon Electrode

Use of graphene-based materials as slit-porous electrodes has great potential because of its tunability of the pore size. Here we propose the use of graphene-based electrodes for selective adsorption of ions from an aqueous solution of multiple ion species. Slit-porous electrodes such as activated carbon have been used as electrodes for electric double layer capacitors (EDLC) and capacitive de-ionization (CDI), because of their large specific surface area^[1,2]. Recently, it has been shown that, when the pore size of the electrode is comparable to the size of the electrolyte ions, the capacitance per surface area significantly depends on the change of the pore size of the electrode at the scale of angstrom. This effect implies that such electrodes would show selectivity of ion species. In order to use the selectivity for practical applications, we need precise knowledge of the free energy profile of the ions near the electrode surface that incorporates hydration and dehydration. We conducted molecular dynamics simulations (MD) and electrochemical experiments to acquire the conditions that enable selective adsorption of monovalent cations from an aqueous solution of multiple ion species. In MD, we used a model composed of slit-porous electrodes made from several graphene sheets, water molecules and 1 pair of electrolyte ions, which is Li^+ , Na^+ , K^+ or Cs^+ and Cl^- . The model is shown in Figure 1. We computed the average force acting on the cation over 2 ns at different positions including the inside and the outside of the pore. We then computed Potential of Mean Force (PMF) for each cation as a function of distance from the electrode surface by integrating the average force. Those were computed for different pore sizes; 6 Å, 7 Å, 8 Å, 9 Å and 10 Å of the slit-porous electrode with and without applying 1V between the positive and negative electrodes. All the simulations were conducted at the condition of 300 K and 1 atm. In electrochemical experiments, we fabricated an electrochemical cell to adsorb ions and aqueous solution of monovalent cations were circulated inside the cell. The voltage of 1 V was applied between the electrodes. This experimental setup showed in Figure 2. The cell contains activated carbon fiber with controlled pore-size as the electrode. Figure 3 shows the graph of PMFs as a function of the position of Li^+ and Cs^+ for porous electrodes with pore size 8 Å or 9 Å with applying the voltage of 1 V. When the pore size is 8 Å, there are two free energy barriers when Li^+ gets close to and inside the pore of the electrode. The magnitude of barriers of the first and the second barriers shown in Figure 3 are $0.46 \text{ kcal}\cdot\text{mol}^{-1}$ and $0.84 \text{ kcal}\cdot\text{mol}^{-1}$, respectively. Comparing those barriers with the thermal energy of $0.6 \text{ kcal}\cdot\text{mol}^{-1}$ in 300 K, Li^+ surpasses the first barrier easily but the second barrier with difficulty. On the other hand, Cs^+ surpasses the barrier easily and gets inside of the pore because the largest barrier is $0.38 \text{ kcal}\cdot\text{mol}^{-1}$. To summarize, Cs^+ gets the inside of the pore of 8 Å more easily than Li^+ in aqueous solution of Li^+ and Cs^+ and we could see selectivity of adsorbed ions. We also computed hydrated radii of those cations to find out the reason why those behaviors of the barriers were observed. Positions of the first and the second barrier in Figure 2 correspond to the positions where hydrating water molecules are removed from the cation. In other words, the free energy barriers as above correspond to the work needed to remove the hydration shell. The magnitude of the barriers change if the pore size and voltage change. So, by adjusting the voltage and the pore size, we could see selective adsorption of ion species in the porous carbon electrode. In the result of the experiment which use the aqueous solution dissolved Li^+ and Cs^+ with electrodes of about 8 Å pore, Cs^+ is adsorbed more easily than Li^+ . So, this result coincides the result of simulations.

References

- [1] M. A. Anderson et al, *Electrochim, Acta* **55** (2010) 3845-3856
- [2] S. Porada et al., *Prog Mater. Sci.*, **58**, (2013) 1388-1442.

Figures

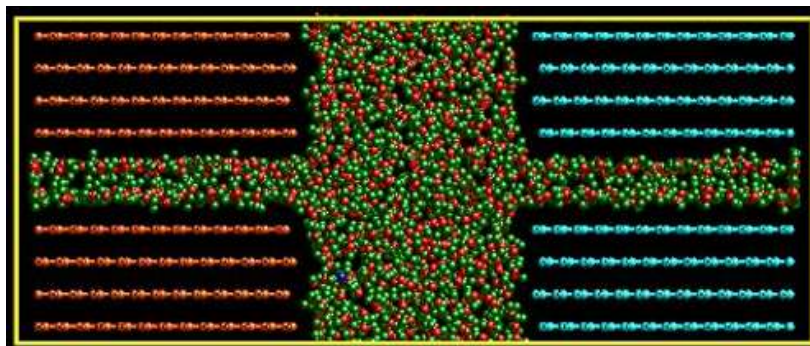


Figure 1: Schematic picture of the simulation model. Orange and light blue molecules are the positive and negative electrodes, respectively. Red and green molecules are oxygen and hydrogen, respectively. Yellow and blue molecules are the cation and the chloride ion, respectively.

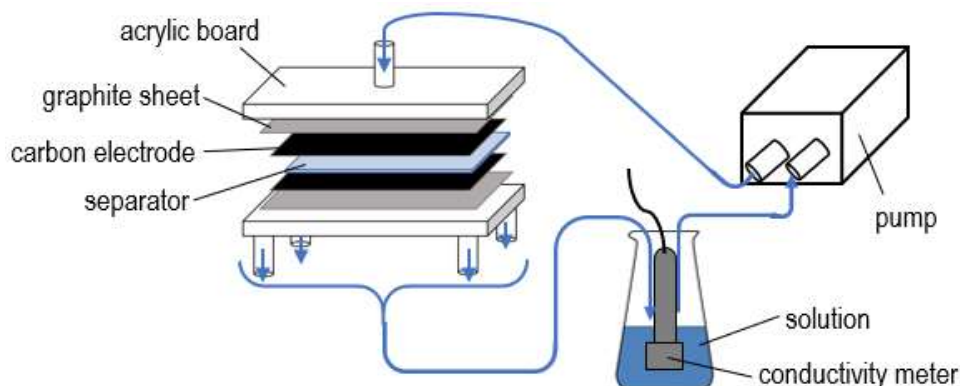


Figure 2: Schematic picture of the experimental setup. Graphite sheets are used as current collectors. Blue lines show the flow of the solution.

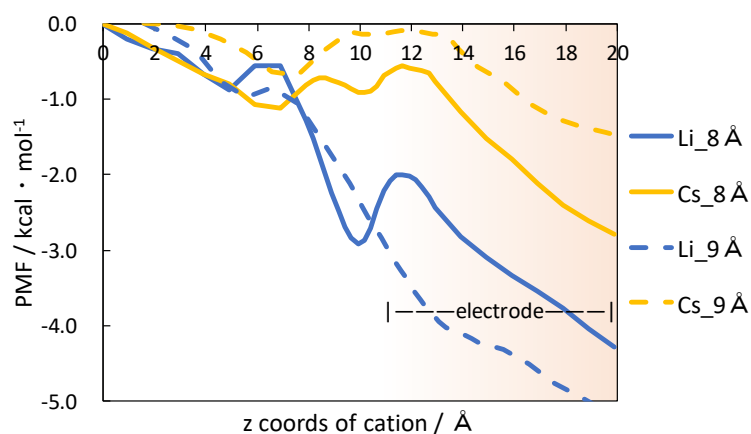


Figure 3: PMFs as a function of the position of Li^+ and Cs^+ for slit-porous electrodes with pore size 8 Å and 9 Å. Shaded area indicates the inside of the electrode.