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Table of contents

1	Introduction.....	3
2	Methodology.....	4
2.1	Mean square displacement and the extraction of the diffusion coefficient.....	4
2.2	Kinetic Monte Carlo model adaptation for mean square displacement.....	4
2.2.1	Translation event and translation rate.....	5
2.2.2	Rotation event and rotation rate.....	5
2.2.3	Multimerization event and multimerization rate.....	6
2.2.4	Disproportionation event and disproportionation rate.....	6
2.3	Extraction of viscosity from MSD algorithm.....	7
3	Results and discussions of the MSD model.....	7
4	Conclusions and perspectives.....	11
5	References.....	11



1 Introduction

In this deliverable report, we present our advancement of Task 3.5, the upscaling strategy of the kinetic Monte Carlo (kMC) model. In the previous kMC model, we have applied a 3-dimensional grid configuration to explicitly illustrate each ion of all the active material species, including the methyl viologen (MV) and the chloride ion. The developed kMC model simulates the discharging process of the MV anolyte by stochastically selecting the possible event and advancing the simulation clock by random step sizes. The considered event type in the kMC model includes ion displacement, electrochemical reaction, and the degradation of MV molecules [1]. Each event is assigned an event rate based on the process mechanisms. Meanwhile, a double layer model is coupled with the kMC model to complete the simulation and consider the electrostatic field distribution. For a more detailed modelling methodology, please refer to Deliverable 3.1.

In our previous analysis of the kMC model, the ion displacement event takes much computational power due to its significant amount in both the event list and the rate list. Meanwhile, from the experiment side, we have noticed the nonignorable impact of electrolyte concentration on the diffusion coefficient of the organic compounds. We have reported the measurement of the diffusion coefficient of MV in different concentrations in Deliverable D3.2. By calculating from the Randels Sevcik equation, the diffusion coefficient of MV increases from $3.51 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ to $5.39 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ while the electrolyte concentration drops from 0.1 M to 1 mM . Furthermore, due to the dimerization of MV^+ , the anolyte viscosity changes a lot during the discharging process, which can be linked to the decrease of the diffusion coefficient of active species.

Therefore, we developed our MSD algorithm based on the previous kMC model to extract the diffusion coefficient in anolyte solutions with different concentrations. Unlike the typical molecular dynamic model, which simulates single-molecule trajectory in a relatively diluted solution, we applied the MSD algorithm in the kMC model to take the concentration effect into account. As a result, the electrochemistry process is no longer considered with the MSD approach to stabilize the ensemble.

This report first presents our methodology of the MSD algorithm and our approach to estimating the viscosity of solution from the diffusion coefficient extracted from the MSD algorithm. Then, anolyte with three different concentrations were tested, and the results obtained from the MSD approach are reported later in Section 3.



2 Methodology

2.1 Mean square displacement and the extraction of the diffusion coefficient

The MSD, derived from statistical mechanics, is a measure of the deviation of the position of a particle concerning a reference position over time, which is well applied in the estimation of the diffusion coefficient of Brownian Motions [2]. The MSD function is defined by the molecule position at time t , $x(t)$, and its initial position, $x(0)$,

$$MSD = |x(t) - x(0)|^2 . \quad (1)$$

From MSD, we can also extract the diffusion coefficient after a long enough simulation time t with:

$$D_{MSD} = \frac{1}{2N} \frac{dMSD}{dt} . \quad (2)$$

N is the dimension of the system. In this study, $N = 3$. Under ideal conditions, the MSD simulation field is without limit, which leads to an almost linear MSD curve, as the translation distance of the simulation target molecule is unlimited. Therefore, the diffusion coefficient can be extracted by fitting the slope of the MSD curve. However, an extensive simulation box is not available to limit the concentration conditions, and requires a significant amount of computational power. Thus, in this study, all the diffusion process is tested in a simulation box with a constraint of 500 ns. The diffusion coefficient is then extracted from the beginning of the MSD curve, as discussed later in the results section.

In this study, the kMC model simulated the trajectory of target ions, and the MSD algorithm analyzed each ion's trajectory and extracted desired information.

2.2 Kinetic Monte Carlo model adaptation for mean square displacement

The simulated species in this study includes MV^+ , MV^{2+} , Cl^- , and $(MV_n)^{n+}$, where the latter is the formed MV multimer. In order to calculate the MSD of the desired system, the previous kMC model needs to be adapted accordingly. Since the previous kMC model focused on the electrochemistry process of the MV anolyte solution, the electron transfer event was the target process. However, we target the impact of concentration on the diffusion coefficient of MV and the viscosity of the anolyte in this study. Thus, the discharging/charging event is removed from the event list. In the meantime, the dimerization event of MV species is reformed into a multimerization event, which



contains the formation of not only dimers but also multimers. Accordingly, the rotation of the formed dimers and multimers can no longer be ignored in the kMC model.

2.2.1 Translation event and translation rate

The translation event considered in the study is the hopping of ion with a step size equating the mesh size in six different directions perpendicular to the surface of the cubic mesh. Since we do not include the electron transfer process in this study, the migration driven by electrical field distribution is no longer included in the translation event. Thus, the only driving force for the translation is diffusion. We implement the diffusion coefficient of MV measured from electrolyte of 1 mM concentration solutions as the initial diffusion coefficient, $D_0 = 5.86 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ (Levich equation).

It is important to clarify here that the initial diffusion coefficient injected in the model does not represent the final diffusion coefficient, D_{MSD} , extracted from the MSD algorithm. We took D_0 from the most diluted solution as the intrinsic value, which is later impacted by the increase of concentration and the multimerization process.

The translation rate is then calculated through,

$$K_{diff} = \frac{D_{diff}}{A}, \quad (3)$$

where A is the cross-sectional surface area of the considered species.

2.2.2 Rotation event and rotation rate

In the previous kMC model, all the active species only occupied one cubic mesh. Thus, the rotational Brownian motion event can be ignored. However, in this study, we include the multimerization of MV^+ ions, which produce dimers and multimers occupying more than one cubic mesh. Therefore, the rotation of multimers needs to be taken into account.

The rotation event is considered the reform of the multimer chain. For each multimer occupying more than one cubic mesh, a specific cube is set to be the base point of the rotation. When a rotation event is chosen, the rest of the cube mesh occupied by the multimer will be relocated randomly around the base point, as shown in Figure 1. For each multimer, we labelled its sub-molecules by numbers, and the sub-molecule with the number 0 is the base point.

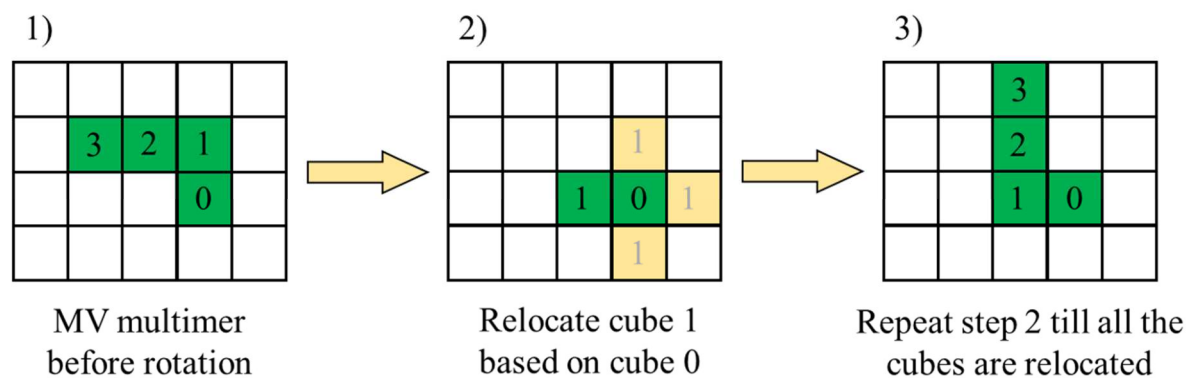


Figure 1. Illustration of the rotation event in the kMC model

Both rotation and translation are driven by diffusion. The rotation rate is then calculated the same way as the translation event, while the cross-sectional surface area is related to the entire surface of the considered multimer.

2.2.3 Multimerization event and multimerization rate

From our practical knowledge, multimerization is quite common in MV^+ solutions due to the fast kinetics. Dimerization was firstly reported as a side reaction of methyl viologen, and then the concept emerged of multimerization event, which is frequently observed.

The multimerization event is considered in the kMC model when two MV^+ are neighbors or a multimer $(MV_n)^{n+}$ is next to an MV^+ . Then, the product from the multimerization is one multimer occupying all the cubic mesh of both reactants.

The multimerization event is assigned a fast kinetic rate of $K_{mm} = 1 \times 10^{14} \text{ s}^{-1}$, which is much faster than the translation event rate.

2.2.4 Disproportionation event and disproportionation rate

From our experience with the previous kMC model, the kinetics for a disproportionation event is relatively slow, leading to a rare observation of such an event during the simulation. Thus, the disproportionation event is excluded from this study for the moment. We intend to include this event for future development.



2.3 Extraction of viscosity from MSD algorithm

From the Stokes-Einstein equation, the relation between the diffusion coefficient, D_0 , of certain species, and the viscosity of the fluid media, η , is described as follows:

$$D_0 = \frac{k_B T}{6\pi\eta r}. \quad (4)$$

r is the radius of the solvation shell. k_B and T are the Boltzmann constant and the temperature, respectively. From this equation, Einstein linked the diffusion coefficient of a 'Stokes' particle undergoing Brownian motion to the dynamic viscosity of a quiescent liquid.

Therefore, by substituting the diffusion coefficient obtained from the MSD algorithm, D_{MSD} , the viscosity of the electrolyte is estimated. Furthermore, considering the multimerization event leading to the change of component in the solution, we only track the trajectory of ions without reactions to estimate the viscosity of the electrolyte (Cl^- and MV^{2+}).

3 Results and discussions of the MSD model

We first tested the MSD model with a diluted anolyte solution of 1 mM and two different states of charge. For this case, the simulation box size is set at 50 x 50 x 50 cubic meshes with a unit cube length of 0.3 nm. Figure 2 a) and c) present the simulation box and the MSD results for SoC = 100, where only one MV^+ and one Cl^- ion are randomly diffusing inside the box. Figure 2 b) and d) present the simulation box and the MSD results obtained for SoC = 0. Since our simulation is carried out in a limited volume, the MSD curves reach a steady plateau after a specific time (around 50 ns in this case), which is due to the diffusion limit. We then fit the first five nanoseconds of the MSD curve with a linear tendency line. The values of slopes are also presented in Figure 2 a) and b). Finally, the MSD diffusion coefficient is obtained from Equation 2 and shown in Figure 5.

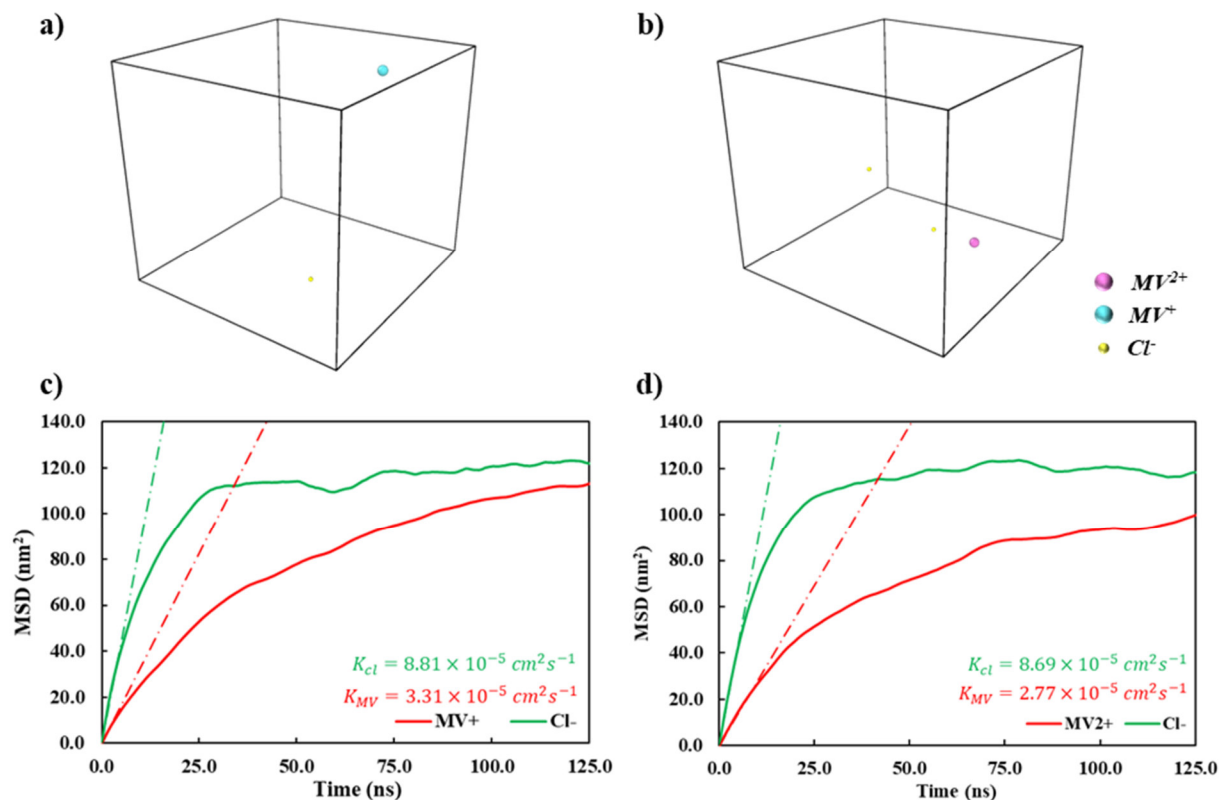


Figure 2. MSD obtained from 1 mM case study. a) simulation grid of SoC 100; b) simulation grid SoC 0; c) MSD results extracted from SoC 100; d) MSD results extracted from SoC 0.

Figure 3 and Figure 4 present the results obtained from anolyte with 10 mM and 100 mM, respectively. The simulation of 100 mM pres was carried out in a 25 x 25 x 25 cubic mesh grid simulation box to save computational power. In the kMC grid, the difference in concentration leads to an exponential increase in computational power demand. Figure 3 a) and Figure 4 a) show that the MV dimers and monomers dominate the system after a long enough simulation time, especially for high concentration cases. As seen from the simulation of 100 mM simulation (Figure 4 a), no MV monomers are left after 500 ns. Therefore, the trajectories of the MV⁺ ions are not obtained for this case. However, considering the lack of the disproportionation event and the constant event rate assigned to the multimerization event, the multimerization could be overestimated in the kMC model. Hence, we believe that future parameterization and the refinement of the model are required.

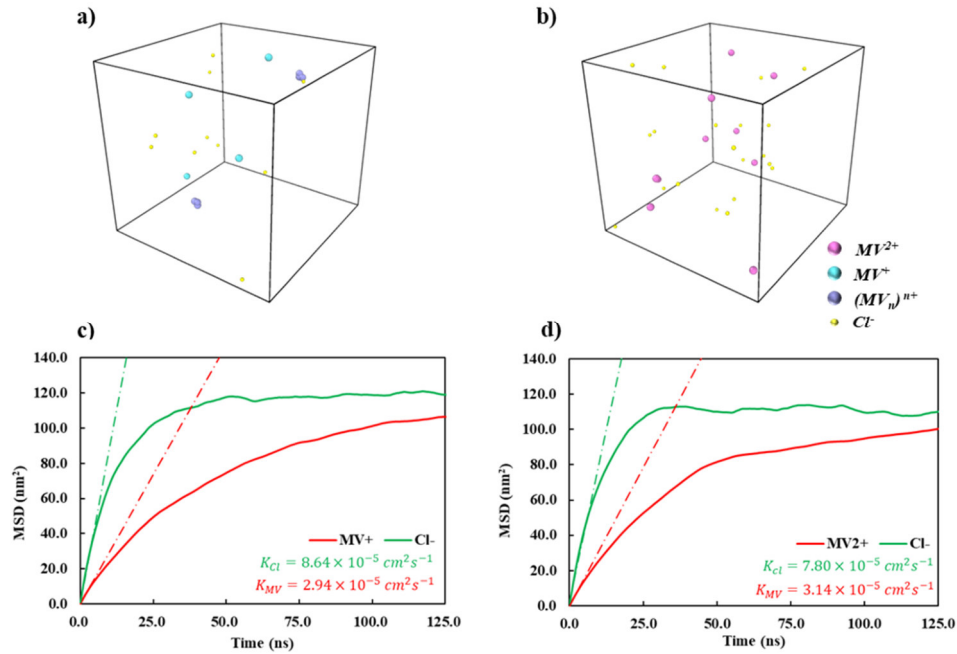


Figure 3. MSD obtained from 10 mM case study. a) simulation grid of SoC 100; b) simulation grid SoC 0; c) MSD results extracted from SoC 100; d) MSD results extracted from SoC 0.

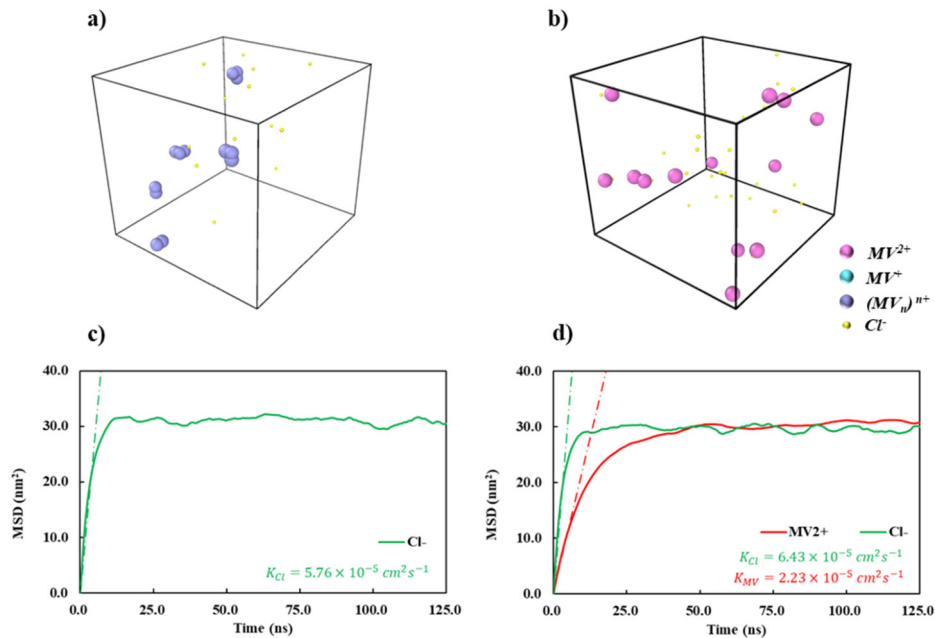


Figure 4. MSD obtained from 100 mM case study. a) simulation grid of SoC 100; b) simulation grid SoC 0; c) MSD results extracted from SoC 100; d) MSD results extracted from SoC 0.

Figure 5 presents the extracted diffusion coefficient from the MSD algorithm and the experimentally measured values. For the SoC 100 cases, the diffusion coefficient calculated by the MSD approach fall in the range of experimental measurement, which could firstly validate our modeling approach. Due to the missing points for the SoC0 at 100 mM concentration, we couldn't expand our observation into a general conclusion.

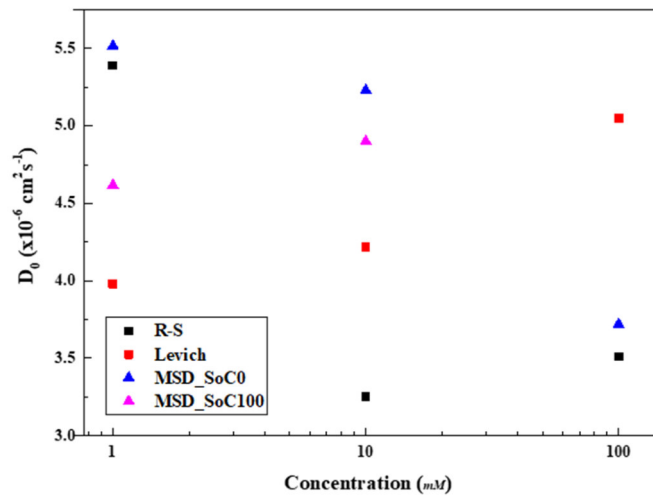


Figure 5. Comparison of diffusion coefficient obtained from MSD and experiments.

From Equation 4, we calculated the viscosity for each species based on their MSD diffusion coefficient. Then we estimate the electrolyte viscosity through the component number.

Table 1. electrolyte viscosity calculated based on D_{MSD}

CONCENTRATION (MM)	SOC	η_{MV} mPa's	η_{Cl} mPa's	η_{ele} mPa's
1	0	1.57	0.95	1.15
1	100	1.31	0.89	1.1
10	0	1.39	1.01	1.13
10	100	1.48	0.91	1.20
100	0	1.96	1.21	1.45
100	100	/	1.38	/



4 Conclusions and perspectives

A MSD approach to extracting the diffusion coefficient from our kMC model and estimating the viscosity of MV analyte with different concentrations is presented in this report. Furthermore, to adapt the kMC model to the implementation of MSD, a series of changes regarding the event list and the event rate calculations are added.

Analytes with three different concentrations were tested with the new kMC model coupled with the MSD algorithm. The simulated MSD diffusion coefficient corresponds to the experiment values and demonstrates the decreasing trend while the concentration increases. Moreover, the results demonstrate a strong tendency of multimerization in high concentration solution, which increases the dynamic viscosity.

We will calibrate the model with more experimental data for future aspect, and expand the simulation range in order to get more stable MSD results.

5 References

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