Supporting Information

Electrochemical Characterisation and Comparison of Transport in Nafion Films and Particles

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I Determination of the MV-Nafion thin film dry thickness on GC

0.1 μL of MV-Nafion stock mixture was drop-cast on the GC electrode and the film dry thickness can be determined as followed:

Mass of 0.1 μL Nafion is

$$m = V \cdot \rho \cdot wt\% = 0.1\mu L \times 0.921 g / cm^3 \times 5\% = 4.61 \times 10^{-6} g$$

where ρ is the density of Nafion perfluorinated resin solution, whose value obtained from the supplier Sigma-Aldrich.

The density of dry Nafion is relevant to its storage and drying conditions and in this case the dry density of Nafion, $\rho_{DryNafion}$, is 1.965 g cm^{-3}.[1]

Therefore the dry volume of Nafion is

$$V = \frac{m}{\rho_{DryNafion}} = 2.48 \times 10^{-12} m^3$$

The diameter of GC electrode is 3 mm, hence the area is $A = D^2 / 4 = 7.07 \times 10^{-6} m^2$

The dry thickness for 0.1 μL of MV-Nafion thin film on the GC electrode is

$$h = \frac{V}{A} = \frac{2.48 \times 10^{-12} m^3}{7.07 \times 10^{-6} m^2} = 0.35 \mu m$$

Similarly, the dry thickness for 0.5 μL and 1.5 μL of MV-Nafion thin film on the GC can be determined as 1.75 μm and 5.26 μm respectively.

II Determination of the number of MV-Nafion particle layers drop-cast on glassy carbon electrodes

For single MV-Nafion particle, the average radius is 0.43 ± 0.26 μm and the density of Nafion in water, $\rho_{DryNafion}$, is 1.858 g cm^{-3}.[1]

Hence the mass for single particles is

$$m_{Nafion} = \frac{4}{3}\pi r^3 \rho_{Nafion} = 6.36\times10^{-13} g$$

Total mass of Nafion used to synthesize Nafion particles is

$$m_{total} = V \cdot \rho \cdot wt\% = 50\mu L \times 0.921 g / cm^3 \times 12.5\% = 5.76\times10^{-3} g$$

The number of Nafion particle synthesized is

$$N = \frac{m_{total}}{m_{Nafion}} = \frac{5.76\times10^{-3} g}{6.36\times10^{-13} g} = 9.05\times10^{9}$$

Final Nafion particle suspension volume is 0.5 mL.

Then the concentration of Nafion particle suspension is

$$C = \frac{N}{V} = \frac{9.05\times10^{9}}{0.5mL} = 1.81\times10^{10}\ particles / mL$$

Hence the number of Nafion particle drop-casted on the GC electrode is

$$N_{GC} = C \cdot V_{GC} = 1.81\times10^{10}\ particles / mL \times 10\mu L = 1.81\times10^{8}\ particles$$

Number of layers Nafion particles is

$$N_{layers} = \frac{A_{particles}}{A_{GC}} = \frac{\pi\times(0.43\mu m)^2 \times 1.81\times10^{8}}{7.07\times10^{-6} m^2} = 15 layers$$

III Simulation of the cyclic voltammetry of MV^{2+}/MV^{+} via the single Nafion particle model

To explore the ion transport property of MV^{2+}/MV^{+} in Nafion particles, we measured the cyclic voltammetry of immobilized Nafion particles with different drop-casting amounts under variable scan rates. As the redox species are confined in Nafion particles, the single particle model is applied when simulating multiple layers of immobilized Nafion particles. The experiment data is analysed via the single Nafion particle model, by which the approximate ion transport time τ_{it}, the diffusion difference between the reactant and the product D_{MV+}/D_{MV2+} , and the contacting area where the immobilized particle attached on the electrode are determined.

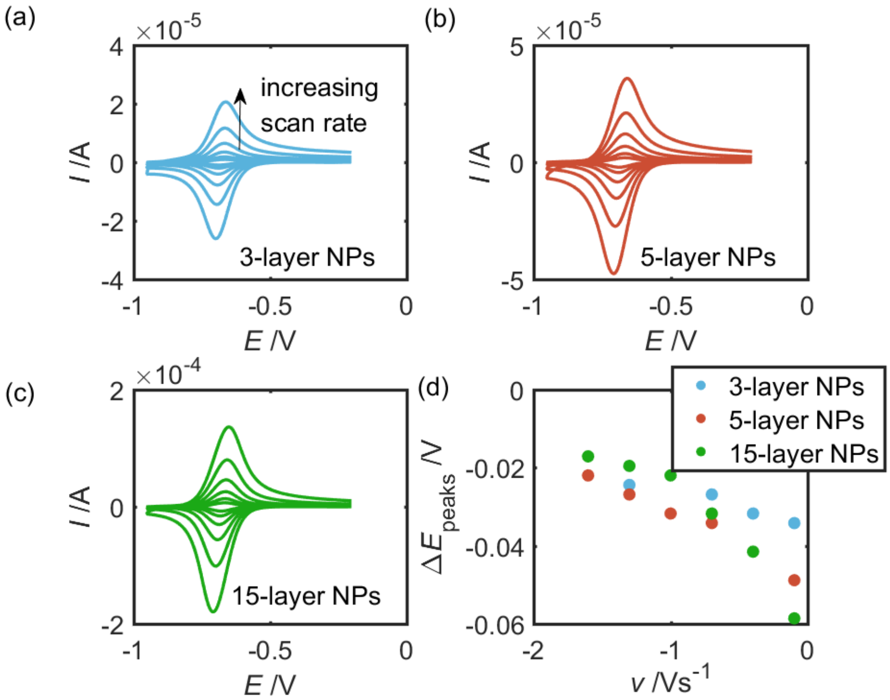

Figure S1 *(a) Cyclic voltammograms of 3-layer Nafion particles modified electrode under various scan rates of 0.025, 0.05, 0.1, 0.2, 0.4, 0.8 V* s^{-1}*; (b) Cyclic voltammograms of 5-layer Nafion particles; (c) Cyclic voltammograms of 15-layer Nafion particles; (d) Scan rate dependence of the peak-to-peak separation of the 3-layer, 5-layer and 15-layer Nafion particles. Experiment conditions are mentioned in the main text.*

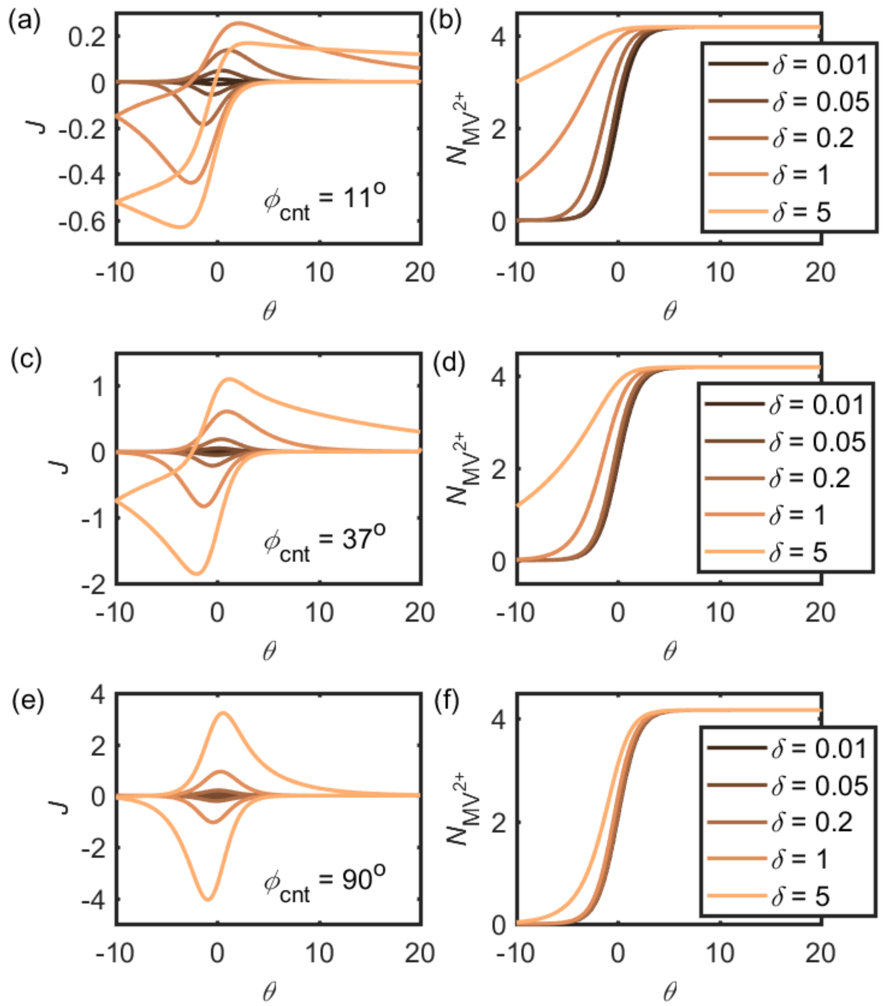

Figure S2 *(a) Dimensionless cyclic voltammogram simulated for one particle of 11° contacting angle under a series of scan rates. (b) Dimensionless mass variation of the reactant during the reaction. (c) and (d) are the cyclic voltammogram and the mass variation for one particle of 37° contacting angle; (e) and (f) are the cyclic voltammogram and the mass variation for one particle of 90° contacting angle. In the simulation* D_{MV+}/D_{MV2+} *is set to be 0.5 and other simulation conditions are the same as in the main text.*

The cyclic voltammetry of 3, 5 and 15 layers of MV^{2+} doped Nafion particles under variable scan rates is presented in Figure S1 a, b and c. The scan rate implemented in the experiment for each electrode is 0.025, 0.05, 0.1, 0.2, 0.4, 0.8 V s^{-1}. The scan rate dependence of the forward and backward peak currents has been shown in Figure 7 in the main text and the peak-to-peak separation ΔE_{peaks}, the difference between the forward and backward peak potentials, is shown in Figure S1 d. Comparing to the current-time response measured from the single particle experiment, the immobilized particles provide three fitting features, the forward peak current, the backward peak current and the peak-to-peak separation, which can be used as the fitting objectives.

In the single particle simulation model, as explained in the main text, not only the ion transport time τ_{it} and the diffusion coefficient difference between MV^{+} and MV^{2+} D_{MV+}/D_{MV2+} but also the contacting angle of the particle ϕ_{cnt} are unknown. To explore the scan rate dependence of the cyclic voltammogram in the Nafion particles, Figure S2 shows the simulation results of various scan rates and three different contacting angles. The simulation results are presented in the dimensionless format, where J is the flux, θ is the overpotential, δ is the scan rate and N_{MV2+} is the mass of MV^{2+} in one Nafion particle. The dimensionless MV^{2+} mass in one particle is 4/3π before the electrochemical reaction. Figure S2 a and b are the simulation results in which the contacting area between the particle and the electrode is relatively small. In Figure S2a, the waveshape of the cyclic voltammogram with a small contacting area varies when the scan rate increases and only at low scan rate, the simulated waveshape is similar to that observed in the experiment. Figure S2b explains the waveshape variation as a function of the scan rate. It is found that only when the reactant can be fully assumed, for instance the case of δ = 0.01, the experiment-like waveshape can be observed in the simulation. Similar phenomena can be found in simulations with larger contacting areas as shown in Figure S2 c-f.

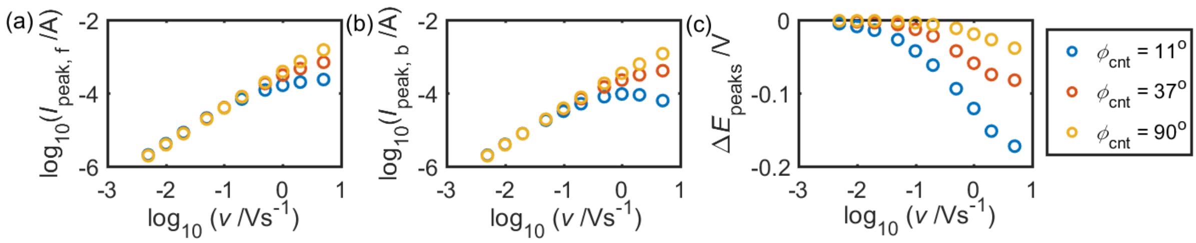

Figure S3 *Scan rate dependence of (a) simulated forward peak currents, (b) simulated backward peak currents, (c) simulated peak-to-peak separations. Three different contacting angles are presented, 11°, 37° and 90°. In the simulation,* τ_{it} *is set as 0.025 s and* D_{MV+}/D_{MV2+} *= 0.5. The reaction charge Q applied is measured from the 15-layer Nafion particle experiment and Q = 4.0x10*$^{-5}$ *C.*

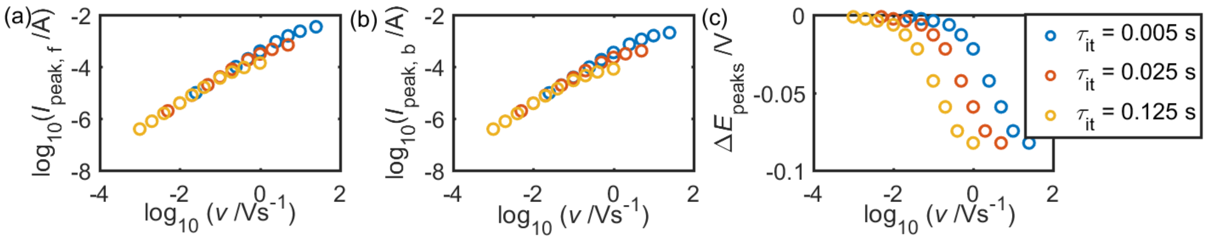

Figure S4 *Scan rate dependence of (a) simulated forward peak currents, (b) simulated backward peak currents, (c) simulated peak-to-peak separations. Three different ion transport time are presented, 0.005, 0.025 and 0.125 s. In the simulation,* ϕ_{cnt} *is set as* 37^o *and* $D_{MV+}/D_{MV2+} = 0.5$*. The reaction charge Q applied is measured from the 15-layer Nafion particle experiment and* $Q = 4.0x10^{-5}$ *C.*

To determine the unknown parameters τ_{it}, D_{MV+}/D_{MV2+} and ϕ_{cnt}, we need to compare the forward peak current, the backward peak current and the peak-to-peak separation. The transformation between the dimensionless and dimensional variables has been explained in the main text. Figure S3 illustrates the scan rate dependence of the simulated peak currents and peak-to-peak separation in the dimensional format. Three contacting areas with the same τ_{it} (0.025 s) and D_{MV+}/D_{MV2+} (0.5) are compared. It is found that only at low scan rate the peak current increases linearly as a function of the scan rate; and the scan rate dependence of the peak-to-peak separation varies with the contacting area. Figure S4 illustrates the scan rate dependence with constant contacting angle ϕ_{cnt} (37^o) and D_{MV+}/D_{MV2+} (0.5). Three ion transport times are applied in Figure S4. Varying τ_{it} alters the peak current increasing region while the scan rate dependence of the peak-to-peak separation is irrelevant to the value of τ_{it}. In the data fitting procedure, not only the scale of the fitting objectives but also the dependence on certain variables needs to be taken into consideration. As shown in Figure S1 and Figure 7 in the main text, the experimental peak currents increases with the scan rate and the peak-to-peak separation varies among the three Nafion particle modified electrodes. Therefore, combining the simulation result with the experiment data, it can be determined that τ_{it} is approximately 0.025 s for MV^{2+} in Nafion particles, D_{MV+}/D_{MV2+} is ca. 0.5 and the contacting angles for the 3-layer, 5-layer and 15-layer Nafion particles to be ca. 45^o, 30^o and 18^o.

IV Supplementary Experimental Data

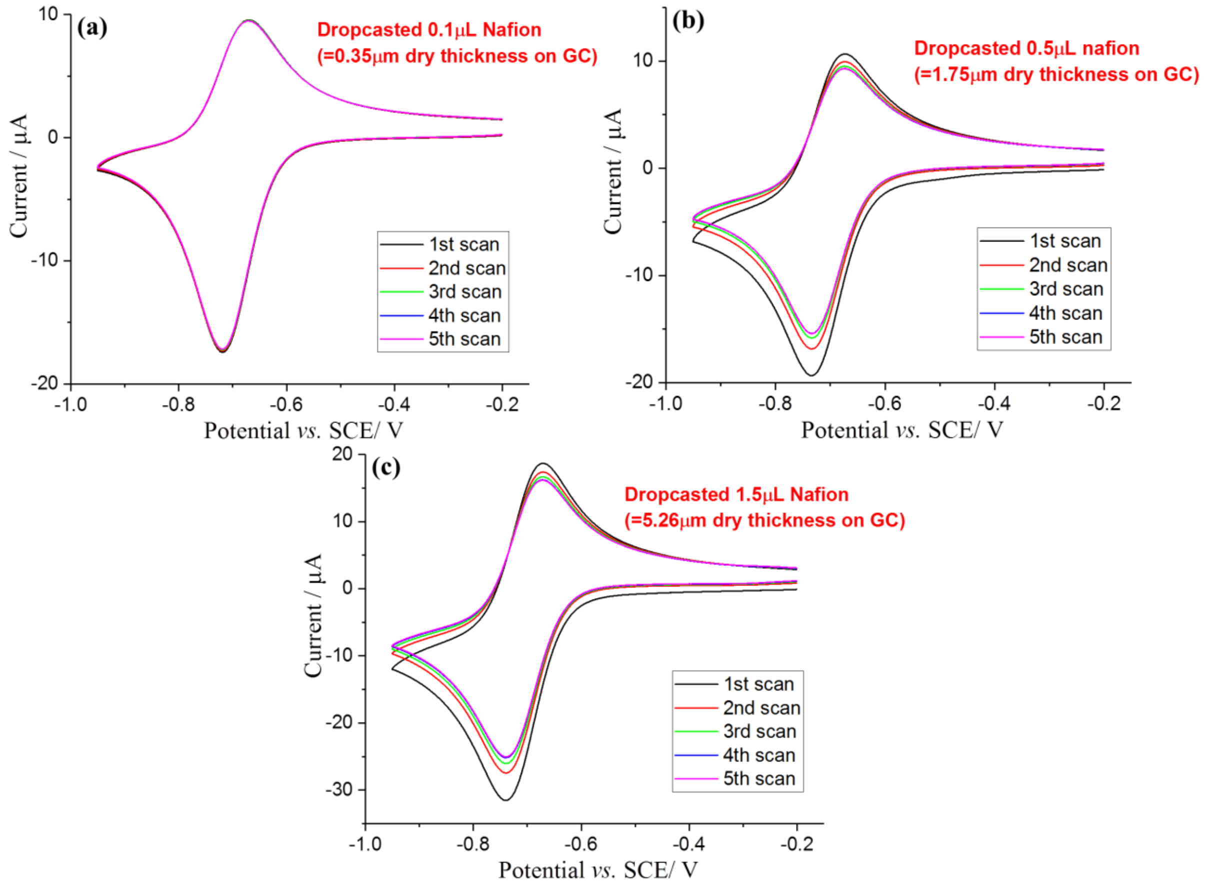

Figure S5 *Multiple-scan experimental CVs for (a) film 1, of which the dry thickness is 0.35 μm (b) film 2, of which the dry thickness is 1.75 um (c) film 3, of which the dry thickness is 5.26 μm; scan rate = 0.1 V/s*

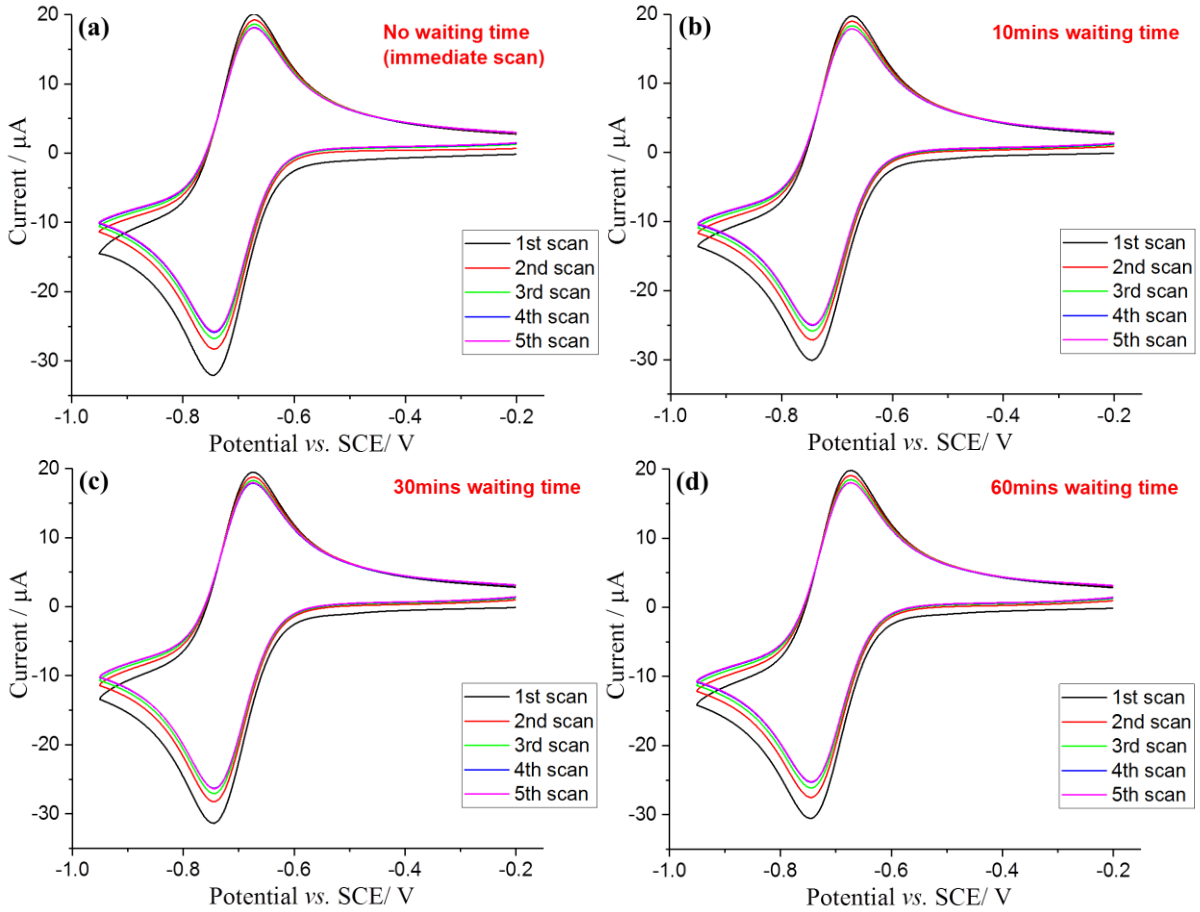

Figure S6 *Multiple-scan experimental CVs of film 3(with dry thickness 5.26 μm) for different waiting time after immersing the films into the buffer solution (a) no waiting time (b) 10mins waiting time (c) 30mins waiting time (d) 60mins waiting time; scan rate = 0.1 V/s*

References

1. T. Takamatsu and A. Eisenberg, *Journal of Applied Polymer Science*, 1979, 24, 2221-2235.