Electrochemical Characterisation and Comparison of Transport in Nafion Films and Particles

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Abstract

The diffusional transport of the dication and monocation of methyl viologen, MV^{2+} and MV^+ , in hydrated Nafion films and particles is studied electrochemically. Methodology is established for characterising the relative rates of transport and for evaluating the diffusion coefficient of the two ions. The transport in the particles – is shown to be significantly faster than in films of similar thickness whilst the diffusion of MV^{2+} is confirmed to be faster than that of MV^+ .

1 Introduction

As a well-known perfluorosulfonated, cation exchange polymer, Nafion has been widely applied in the field of energy and catalysis, including fuel cells, solar cells, electrocatalysts and electrochemical sensors.¹⁻⁵ In previous papers, we synthesised, characterised and studied the electrochemical responses of Nafion particles doped with different redox active species with an aim of developing new electrocatalysts.^{6, 7} The focus of these previous studies was on the reaction kinetics of the electrochemically activated doped Nafion particles with reactants present in solution such as oxygen. In this paper we address the dynamics of the charge transfer processes *within* the particles. The behaviour of Nafion materials is known to strongly depend on the preparation procedures. As reported in the literature, the morphology and properties of bulk Nafion materials are quite different from thin films even when similarly prepared.^{8, 9} It is inferred that when Nafion films are immersed into water, phase separation takes place with each phase domain of the size of a few nanometres, depending on the hydration degree.¹⁰ In comparison to Nafion particles, Nafion films are more commonly investigated and used in practical applications.^{11, 12} Comparative studies of the electrochemical behaviour of Nafion films and the ion transport property of Nafion materials in general including Nafion particles are of potential value.⁸ This interest is driven by both practical and fundamental needs: one is to understand the ion transport behaviour of Nafion in the electrode system and to explore the origin of any differences related to the structure of the material; the other is to develop an electrochemical characterisation approach which helps to understand the structure-functionality of Nafion (or related ionomers).

In this work, we measure and analyse the electrochemical signals of the one-electron-transfer reaction of methyl viologen (MV) ions $MV^{2+} + e^- = MV^+$ in both Nafion thin films and sub-micron sized particles. Two simulation models are built up for two geometries; first of the film and second for a single particle to allow investigation of the ion transport properties of the Nafion materials in the two different forms. Combining experiment with simulation, it is found that the ion transport of MV^{2+} and MV^+ is much faster in Nafion particles than in Nafion films, showing that the preparation of the material has a non-negligible influence on transport and by implication the material structure.

2 Experimental

2.1 Chemical reagents and instrumentation

Scheme 1 Structure of MV^{2+} .

Methyl viologen dichloride ($MVCl_2$, $\geq 98\%$) was purchased from Aldrich and used as received. The structure of the methyl viologen ion MV^{2+} is shown in Scheme 1. All other chemicals were obtained from Sigma-Aldrich at the highest purity available. Nafion perfluorinated resin solution (5 wt% in lower aliphatic alcohol and water, with a water content of 45%) was heated in a water bath at $52 \pm 0.5^\circ\text{C}$ to obtain a concentrated 12.5 wt% Nafion solution. Phosphate buffered saline buffer solution (PBS, pH = 7.4) was

composed of 137 mM sodium chloride, 2.7 mM potassium chloride, 10 mM sodium phosphate dibasic and 1.8 mM potassium phosphate monobasic. All solutions were made up using ultrapure water (Millipore) with a resistivity of 18.2 M Ω cm at 25°C and degassed thoroughly with argon (99.998%, BOC Gases plc) before use.

Electrochemical experiments were performed with a μ Autolab Type II potentiostat (Utrecht, Netherlands) using a standard three-electrode system in a thermostatted (25.0 $\pm$ 0.2 °C) Faraday cage. A glassy carbon (GC) macroelectrode (diameter 3.0 mm, CH Instrument), a saturated calomel electrode (SCE; by BASi, Japan) and a graphite rod were used as working, reference electrode and counter electrodes respectively. Prior to voltammetric experiments, the working electrode was polished using three grades of alumina (1.0, 0.3 and 0.05 μ m, Buehler, UK) in a decreasing particle size order followed by sonication in water and drying with nitrogen.

2.2 Preparation and Electrochemical Characterisation of MV-Nafion films on electrodes

A MV-Nafion stock solution containing MV²⁺ with a MV²⁺:SO₃⁻ ratio of 1:20 were prepared by directly dissolving 0.7 mg of MVCl₂ into 1.30 mL of 5 wt% Nafion perfluorinated resin solution. The mixture was shaken on a vortex (Whirlmixer, Loughborough, UK) for 3 min.

MV-Nafion thin films were obtained by evenly drop-casting 0.1 μ L of MV-Nafion stock solution on a GC electrode and left to dry under an N₂ atmosphere. The dry thickness of the thin films was determined to be 0.35 μ m (see Supporting Information). Note that the Nafion film prepared is uniform and its estimated thickness is accurate, as verified by

AFM imaging.¹³ Before measurements in PBS buffer, the latter was vigorously bubbled with argon to remove dissolved O₂ and an atmosphere of argon was maintained during the experiment. Cyclic voltammetry was then conducted at selected scan rates of between 25 mVs⁻¹ to 800 mVs⁻¹. Similar experiments were conducted with 0.5 μ L and 1.5 μ L MV-Nafion film, corresponding to 1.75 μ m and 5.26 μ m dry thicknesses.

2.3 Preparation and Electrochemical Characterisation of single MV-Nafion particles

Nafion particles doped with MV²⁺ were synthesized by the re-precipitation method.¹⁴ Specifically, 5 μ L of 300 mM MV²⁺ aqueous solution was added into 50 μ L concentrated 12.5 wt% Nafion, followed by stirring with the pipette tip for 200 circles. The mixture was injected into 1 mL ultrapure water dropwise under stirring by magnetic vortexing at 600 rpm for 5 minutes. The resulting mixture was subjected to sonication (FB15050, Fisher Scientific, 50/60 Hz, Germany) for 30 min at room temperature. The suspension was then centrifuged (Eppendorf Centrifuge 5430 R) at 14000 rpm for 10 min and the precipitate was washed with water thoroughly to remove excess MV²⁺. This washing-step was repeated three times. The obtained MV-Nafion particles were characterised as previously described giving an average radius of 0.43 ± 0.26 μ m with a doping amount (ratio of MV²⁺:SO₃⁻) of 1:20.^{7, 15} The doping ratio of 1:20 is called “fully-doped” and the doping ratio of 1:40 is called “half-doped” when discussing the doping concentration variation in the following text. The MV-Nafion particles were dispersed evenly in 0.5 mL water by sonication for 5 min.

For the single MV-Nafion particles study, chronoamperometry was performed with a home-fabricated carbon microcylinder electrode¹⁶ (diameter 7.0 μm , Goodfellow, Cambridge, UK) as the working electrode. Note that the potentiostat used in this work accurately conserves the charge transferred arising from a particle-impact process.¹⁷ 500 μL of MV-Nafion stock suspension was added into 4.5 mL of degassed PBS buffer. The cell was sealed and sonicated for 1 min to obtain a well dispersed suspension, followed by immediate chronoamperometric scans under an atmosphere of argon during the measurements.

2.4 Preparation and Electrochemical Characterisation of dropcast layers of MV-Nafion particles on electrodes

For the drop-cast experiments of MV-Nafion particles, the same MV-Nafion stock suspension containing MV^{2+} of a $\text{MV}^{2+}:\text{SO}_3^-$ ratio = 1:20 was applied (see above). 10 μL of stock suspension was drop-cast on the GC electrode left to dry. 15 layers of Nafion particles were determined on the surface of GC electrode (see Supporting Information). Cyclic voltammetry was recorded at selected scan rates of between 25 mVs^{-1} to 800 mVs^{-1} at degassed PBS buffer. Similar experiments were also performed for 3 layers and 5 layers of MV-Nafion particles by drop-casting diluted stock suspension.

3 Theory and Simulation

To study the electrochemical behaviour of the redox species doped in the Nafion thin-films and the Nafion particles, two simulation models are developed: one is a one-dimensional thin-film model for simulating cyclic voltammetry on a Nafion film coated

electrode; the other is a two-dimensional particle model for simulating the current-time and cyclic voltammetric response corresponding to one Nafion particle when instantaneously subjected to a reducing potential sufficient to reduce the MV^{2+} under the potential. The simulation procedure is introduced and key parameters in understanding the ion transport in Nafion materials are derived.

3.1 Nafion thin-film simulation

Figure 1 Illustration of the Nafion thin-film simulation in a single dimension x . Simulation equations and boundary conditions are listed. x_{film} is the thickness of the Nafion film. f_{BV} refers to the Butler-Volmer equation. c is concentration, D is the diffusion coefficient, x is the dimension perpendicular to the electrode surface, t is the reaction time, x_{film} is the film thickness.

Figure 1 illustrates the simulation model of the Nafion thin-film coated electrode. The thin-film model is well established in the study of mass transport inside a coating layer,¹⁸ in which the electroactive species are confined in the film. We assume that the reactant diffuses in Nafion and the electron transfer only takes place at the electrode surface which is $x = 0$ in Figure 1. The mass transport of the reactant MV^{2+} and the product MV^+ in the Nafion thin-film is described by the diffusion equation:

$$\frac{\partial c}{\partial t} = D \nabla^2 c = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where c is the concentration, t is the reaction time, D is the diffusion coefficient and x is the distance from the electrode surface. For the reactant and the product, the diffusion coefficients are typically not the same in Nafion.¹ The redox reaction studied in this work is a one-electron-transfer reaction $MV^{2+} + e^- = MV^+$ and MV^{2+} is the species initially doped in Nafion. On the electrode surface, the electron-transfer kinetics is described by the Butler-Volmer equation and the surface concentrations of the redox species follows:^{19, 20}

$$-D_{MV^{2+}} \frac{\partial c_{MV^{2+}}}{\partial x} \Big|_{x=0} = -k_0 \exp\left(-\frac{\alpha F (E - E_f)}{R_{\text{gas}} T_r}\right) c_{MV^{2+}} \Big|_{x=0} + k_0 \exp\left(\frac{\beta F (E - E_f)}{R_{\text{gas}} T_r}\right) c_{MV^+} \Big|_{x=0} \quad (2)$$

$$-D_{MV^+} \frac{\partial c_{MV^+}}{\partial x} \Big|_{x=0} = k_0 \exp\left(-\frac{\alpha F (E - E_f)}{R_{\text{gas}} T_r}\right) c_{MV^{2+}} \Big|_{x=0} - k_0 \exp\left(\frac{\beta F (E - E_f)}{R_{\text{gas}} T_r}\right) c_{MV^+} \Big|_{x=0} \quad (3)$$

where F is the Faraday constant, R_{gas} is the gas constant, T_r is the room temperature, E is the applied electrode potential and E_f is the formal potential of the MV^{2+}/MV^+ redox reaction within the film, k_0 is the standard electron-transfer rate constant. As the electron transfer is fast in this redox reaction, k_0 is assigned a large value and both the cathodic and anodic transfer coefficients, α and β , are treated as 0.5. The initial concentration of the reactant MV^{2+} is c^* and there is no product MV^+ in the Nafion film before the redox reaction. By solving the diffusion equation with given boundary conditions, the current can be calculated by:

$$I = F \pi r_{\text{el}}^2 \left(D_{MV^{2+}} \frac{\partial c_{MV^{2+}}}{\partial x} \Big|_{x=0} \right) \quad (4)$$

r_{el} is the radius of the substrate electrode on which the Nafion film is coated. The electrode potential used in the cyclic voltammetry is a function of the reaction time and the scan rate v , described as:

$$E = \begin{cases} E_{\text{ini}} - vt, & t < \frac{|E_{\text{ini}} - E_{\text{rev}}|}{v} \\ E_{\text{rev}} + v \left(t - \frac{|E_{\text{ini}} - E_{\text{rev}}|}{v} \right), & t > \frac{|E_{\text{ini}} - E_{\text{rev}}|}{v} \end{cases} \quad (5)$$

where $[E_{\text{ini}}, E_{\text{rev}}]$ is the potential window.

3.2 Single Nafion particle simulation

Figure 2 (a) Illustration of the single Nafion particle model in the two-dimension (r, ϕ) coordinates. The contacting area where electron transfer is assumed to take place is marked by red. (b) Simulation model, where ϕ_{cnt} is the angle corresponding to the edge of the contacting area.

Next we simulate the current signal after a Nafion particle is suddenly subjected to a potential for example by hitting an electrode after diffusion to it within a solution. The model is illustrated in Figure 2a, where the Nafion particle is treated as a sphere. In the experiments reported below, the dry radius of the particles was characterised via transmission electron microscopy (TEM) as $0.46 \pm 0.40 \mu\text{m}$.⁶ Upon the impact the soft particles are presumed to partially distort and we assume that there is certain well-defined contacting area between the electrode and the Nafion particle where the redox reaction of the MV^{2+} takes place, shown by the red area marked in Figure 2a. The diffusion of MV^{2+} inside the Nafion particle is modelled in spherical coordinates (r, ϕ, φ) , where r is the radial distance, ϕ is the polar angle and φ is the zenith angle, as shown in Figure 2b. Due to the symmetry, the diffusion equation inside a spherical particle is written as:

$$\frac{\partial c}{\partial t} = D \nabla^2 c = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} + \frac{1}{r^2} \frac{\partial^2 c}{\partial \phi^2} + \frac{1}{r^2 \tan \phi} \frac{\partial c}{\partial \phi} \right) \quad (6)$$

The equation is solved in the range of $r \in [0, r_{\text{NP}}]$ and $\phi \in [0, \pi]$. At the contacting area, under the high overpotentials assumed applied, the reactant is fully consumed $c_{\text{MV}^{2+}}(r_{\text{NP}}, 0 < \phi < \phi_{\text{cnt}}) = 0$ and $c_{\text{MV}^{2+}}(r_{\text{NP}}, \phi_{\text{cnt}}) = c^*$ (c^* : bulk concentration), where ϕ_{cnt} is the polar angle corresponding to the end of the contacting area. The current measured from the electrode via the electron transfer at the contacting area can be calculated by the time derivative of the amount of reactant:

$$I = F \frac{\partial}{\partial t} \left(2\pi \int_0^{\phi_{\text{cnt}}} c \cdot r \sin \phi \, d\phi \right) \quad (7)$$

The single-particle model in Figure 3 can be used to simulate both the current-time response of single particles (chronoamperometry) and the current-potential response

of layers of particles (cyclic voltammetry, see below). The boundary condition at the contacting area also follows the Butler-Volmer equation as in Eqn.(2) and Eqn.(3). For comparison with the experiments reported below, the simulated current-time response is further filtered by a simple first-order low pass filter with a cutoff frequency f_{cutoff} of 50 Hz and resampled according to the sampling frequency f_{sampling} applied in the experiment (2 kHz). Note for practical applications the filtering of the signal in the potentiostat needs to be characterised via fitting the current pulse signal output by the potentiostat. By fitting to a simple first-order low-pass filter, $f_{\text{cutoff}} = 50$ Hz is measured for the experimental potentiostat. The details of the filter characterisation have been reported in the literature.^{17, 21}

In the simulation, the diffusion equation Eqn.(6) was solved by the finite difference method in Matlab 2018a. The alternating direction implicit method was applied to solve the two-dimensional problem, of which the details can be found in the textbook.²² The validation and the convergence of the simulation conditions were tested before fitting to the experimental data.

3.3 Dimensional and dimensionless simulation

By solving the diffusion equation with the boundary conditions shown in Figure 1 and Figure 2, the current response can be calculated. To avoid selecting the exact experimental conditions for the simulation, dimensionless parameters are first applied when building up the two models. The transformation between the dimensional and dimensionless parameters used in both the thin-layer and the single particle models are shown in Table 1. In the thin-layer model, the dimensionless current flux J is calculated

from solving the equations listed in Table 2. J is a function of the dimensionless scan rate δ , overpotential θ and the diffusion coefficient d_{MV^+} :

$$J = f(\delta, \theta, d_{MV^+}) \quad (8)$$

Similarly, the current-potential response of a single particle can be written as:

$$J = f(\delta, \theta, d_{MV^+}, \phi_{\text{cnt}}) \quad (9)$$

where one more parameter, the contacting angle ϕ_{cnt} , needs to be considered. The current-time response of a single particle is a function of the dimensionless T and the contacting angle ϕ_{cnt} :

$$J = f(T, \phi_{\text{cnt}}) \quad (10)$$

Note that the current-time response of particle impacts cannot reflect the changed diffusion coefficients between the reactant and the product. Thus d_{MV^+} is not involved in Eqn.(10).

When fitting to the real experimental data, the current expressions can be written as:

$$I = M \cdot \frac{D_{MV^{2+}}}{x_{\text{film}}^2} \cdot f\left(\frac{Fv}{R_{\text{gas}} T_r} \cdot \frac{x_{\text{film}}^2}{D_{MV^{2+}}}, \frac{F\eta}{R_{\text{gas}} T_r}, \frac{D_{MV^+}}{D_{MV^{2+}}}\right) \quad (11)$$

$$I = \frac{3Q}{4\pi} \cdot \frac{D_{MV^{2+}}}{r_{\text{NP}}^2} \cdot f\left(\frac{Fv}{R_{\text{gas}} T_r} \cdot \frac{r_{\text{NP}}^2}{D_{MV^{2+}}}, \frac{F\eta}{R_{\text{gas}} T_r}, \frac{D_{MV^+}}{D_{MV^{2+}}}, \phi_{\text{cnt}}\right) \quad (12)$$

$$I = \frac{3Q}{4\pi} \cdot \frac{D_{MV^{2+}}}{r_{\text{NP}}^2} \cdot f\left(\frac{Ft}{R_{\text{gas}} T_r} \cdot \frac{r_{\text{NP}}^2}{D_{MV^{2+}}}, \phi_{\text{cnt}}\right) \quad (13)$$

$M = F\pi r_{el}^2 x_{film} c^*$ is the charge associated with the full one-electron-transfer reaction of all the MV^{2+} in the Nafion film and the value of M can be measured from the current response at a low scan rate. $Q = 4/3\pi F r_{NP}^3 c^*$ is the charge associated with the full one-electron-transfer of all the MV^{2+} doped in one Nafion particle and Q can be measured from the current response in single Nafion particle experiment. From Eqn.(11), Eqn. (12) and Eqn.(13), it can be found that the combined parameter $x_{film}^2/D_{MV^{2+}}$ ($r_{NP}^2/D_{MV^{2+}}$ for the Nafion particle) is the key parameter with unit of time (s) to understand ion transport in Nafion materials. Physically it gives the order of magnitude of the time response of the film or the particle to potential induced concentration perturbations.

It is possible to calculate a diffusion coefficient according to the dry thickness or the average particle radius measured from TEM images. However, as the Nafion material uptakes water the real volume will vary after immersing into water.^{23,24} Accordingly the combined parameter $x_{film}^2/D_{MV^{2+}}$ can better describe the ion transport. The ion transport time (unit: s) is defined as $\tau_{it} = x_{film}^2/D_{MV^{2+}}$ ($r_{NP}^2/D_{MV^{2+}}$ for the Nafion particle) in this work. In the following text, the value of τ_{it} will be measured via fitting the experiment data by simulation, where the electrochemical response from a series of electrodes modified by Nafion films or particles; and the physical insights revealed by the combined parameter will be discussed.

Table 1 Dimensionless transformation.

Variable	Dimensionless Variable	Variable	Dimensionless Variable
x (film)	$X = x/x_{\text{film}}$ (film)	t	$T = tD_{\text{MV}^{2+}}/x_{\text{film}}^2$ (film) $T = tD_{\text{MV}^{2+}}/r_{\text{NP}}^2$ (SNP)
r (SNP)	$R = r/r_{\text{NP}}$ (SNP)		
c	$C = c/c^*$	I	$J = Ix_{\text{film}}/(F\pi r_{\text{el}}^2 D_{\text{MV}^{2+}} c^*)$ (film) $J = I/(Fr_{\text{NP}} D_{\text{MV}^{2+}} c^*)$ (SNP)
D	$d = D/D_{\text{MV}^{2+}}$	E	$\theta = F(E-E_f)/(R_{\text{gas}} T_r)$
v	$\delta = Fv x_{\text{film}}^2/(R_{\text{gas}} T_r D_{\text{MV}^{2+}})$	k_0	$K_0 = k_0 x_{\text{film}}/D_{\text{MV}^{2+}}$ (film) $K_0 = k_0 r_{\text{NP}}/D_{\text{MV}^{2+}}$ (SNP)

SNP= Single Nafion Particle

Table 2 Equations and boundary conditions in dimensionless form for the Nafion film modelling.

Conditions	Equations
$X > 0$	$\frac{\partial C_{\text{MV}^{2+}}}{\partial T} = \nabla^2 C_{\text{MV}^{2+}}; \frac{\partial C_{\text{MV}^+}}{\partial T} = d_{\text{MV}^+} \nabla^2 C_{\text{MV}^+}$
$X = 0$	$\frac{\partial C_{\text{MV}^{2+}}}{\partial X} = -d_{\text{MV}^+} \frac{\partial C_{\text{MV}^+}}{\partial X} = K_0 \exp(-0.5\theta) C_{\text{MV}^{2+}} - K_0 \exp(0.5\theta) C_{\text{MV}^+}$
$X \rightarrow \infty$	$C_{\text{MV}^{2+}} = 1; C_{\text{MV}^+} = 0$

Table 3 Equations and boundary conditions in dimensionless format for the single Nafion particle modelling.

Conditions	Equations
$0 < R < 1$ and $0 < \phi_{\text{cnt}} < \pi$	$\frac{\partial C_{\text{MV}^{2+}}}{\partial T} = \nabla^2 C_{\text{MV}^{2+}}; \frac{\partial C_{\text{MV}^+}}{\partial T} = d_{\text{MV}^+} \nabla^2 C_{\text{MV}^+}$
$R = 1$ and $\phi \leq \phi_{\text{cnt}}$	$\frac{\partial C_{\text{MV}^{2+}}}{\partial R} = -d_{\text{MV}^+} \frac{\partial C_{\text{MV}^+}}{\partial R} = K_0 \exp(-0.5\theta) C_{\text{MV}^{2+}} - K_0 \exp(0.5\theta) C_{\text{MV}^+}$
$R = 1$ and $\phi_{\text{cnt}} < \phi < \pi$	$\partial C / \partial R = 0$
$0 < R < 1$ and $\phi = 0$	$\partial C / \partial \phi = 0$
$0 < R < 1$ and $\phi = \pi$	$\partial C / \partial \phi = 0$

4 Results

The electrochemical responses of doped Nafion thin-film and Nafion particles are reported in this section. Cyclic voltammetry on Nafion thin-film coated electrodes is measured for Nafion films of 0.35 μm , 1.75 μm and 5.26 μm dry thicknesses. The electroactive species MV^{2+} is confined in the Nafion film and the one electron transfer reaction $\text{MV}^{2+} + e^- = \text{MV}^+$ takes place at the electrode surface. To explore the contrasting electrochemical behaviour of the MV^{2+} doped Nafion particles, the current responses of individual Nafion particles of average 0.46 μm TEM radius are recorded; then the cyclic voltammetry of multi-layer Nafion particle modified electrodes is measured and analysed.

4.1 Ion transport in Nafion thin-film coated electrodes

In previous studies, the cyclic voltammetry (CV) of $MV^{2+} + e^- = MV^+$ was reported for the free MV^{2+} in aqueous solution and for the MV^{2+} doped Nafion particles.^{7, 15} The formal potential of $MV^{2+}/^+$ in both cases was found to be -0.69 V vs SCE. For comparison with the simulation models introduced above, the overpotential $E-E_f$ is reported where the formal potential $E_f = -0.690$ V. Note that MV^+ can be further reduced to MV^0 at more negative potentials, but in this work only the redox reaction between MV^{2+} and MV^+ is considered since initial experiments showed that neutral MV^0 is rapidly lost from the Nafion to the solution phase, consistent with the electrostatic binding of MV^+ and MV^{2+} .

Figure 3 shows the cyclic voltammogram of the MV^{2+} -doped Nafion film coated on a glassy carbon substrate electrode of radius 1.5 mm. The film is made from 0.1 μ L Nafion suspension drop-casted on the substrate electrode. Both experiment (shown by solid lines in Figure 3) and simulation (dashed lines) are combined to analyse the ion transport conditions in the Nafion film and the value of the ion transport time τ_{it} is measured by fitting to voltammograms measured at different scan rates. The influence of the doping concentration of the electroactive species is also explored. Two different MV^{2+} doping concentrations are considered, one is the “fully-doped” case ($MV^{2+}:SO_3^{2-} = 1:20$) shown in Figure 3 a-c and the other is “half-doped” ($MV^{2+}:SO_3^{2-} = 1:40$) as shown in Figure 3d.

Figure 3 (a) Experimental CV (black line) of a fully-doped Nafion thin-film coated electrode at 0.1 V s^{-1} scan rate with simulated voltammograms (dashed lines) of various $x_{\text{film}}^2/D_{\text{MV}2+}$ (0.125, 0.25, 0.50, 1.0, 1.50 s) and a fixed $D_{\text{MV}+}/D_{\text{MV}2+} = 0.1$. (b) 0.1 V s^{-1} experiment CV with simulation voltammograms of various $D_{\text{MV}+}/D_{\text{MV}2+}$ (0.05, 0.1, 0.2, 0.4) and a fixed $x_{\text{film}}^2/D_{\text{MV}2+} = 0.50 \text{ s}$. (c) Experiment CVs (solid lines) of the fully-doped Nafion film various scan rates ($v = 0.05, 0.10, 0.20, 0.40, 0.80$), simulated by $x_{\text{film}}^2/D_{\text{MV}2+} = 0.50 \text{ s}$ and $D_{\text{MV}+}/D_{\text{MV}2+} = 0.1$ (dashed lines); (d) Experiment (solid lines) and simulation (dashed lines) CVs of for the half-doped Nafion film. For the fully-doped film used in (a), (b) and (c), $M = 2.0 \times 10^{-5} \text{ C}$; for the half-doped film used in (d), $M = 1.0 \times 10^{-5} \text{ C}$.

The experimental CV was simulated by the 1D thin-layer model as introduced in Section 3.1. To infer suitable values for the key fitting parameters $\tau_{\text{it}}(x_{\text{film}}^2/D_{\text{MV}2+})$ and $D_{\text{MV}+}/D_{\text{MV}2+}$, Figure 3a compares the experimental CV of the fully-doped Nafion film at

0.1 V/s scan rate with several simulation results of different τ_{it} ; Figure 3b compares the same experiment CV with simulated results of different D_{MV+}/D_{MV2+} . In Figure 3a and 3b, the parameters used in the thin-film CV are determined as $\tau_{it} = 0.5 \pm 0.05$ s and $D_{MV+}/D_{MV2+} = 0.1 \pm 0.05$. To obtain the values of M (M , the total amount of chemicals doped in the thin film) for the Nafion films used in Figure 3, the forward peak of the fully-doped CV at the slowest scan rate 0.025 V/s is integrated and the charge is approximately 2.0×10^{-5} C. Similarly, for the half-doped CV, $M = 1.0 \times 10^{-5}$ C is measured. Figure 3c shows the experiment (solid line) and simulation (dashed line) CVs of the fully-doped film under different scan rates, where the simulation is implemented with the fitting parameters mentioned above. Figure 3d shows the CVs of the half-doped film. The key modelling parameter τ_{it} used in the simulation for the fully-doped Nafion film and the half-doped film has the same value of 0.5 ± 0.05 s, indicating that the ion transport is independent of the doping concentration in the cases studied.

Figure 4 Multiple-scan CVs for (a) film 1, of which the dry thickness is $0.35 \mu\text{m}$, $\tau_{it} = 0.5$ s, $D_{MV+}/D_{MV2+} = 0.1$; (b) film 2, of which the dry thickness is $1.75 \mu\text{m}$, $\tau_{it} = 12.5$ s, $D_{MV+}/D_{MV2+} = 0.1$; (c) film 3, of which the dry thickness is $5.26 \mu\text{m}$, $\tau_{it} = 60.0$ s, $D_{MV+}/D_{MV2+} = 0.1$. The 1st scan and the 5th scan are presented in the figure and the CVs of the two scans overlap in Figure 4a. Black solid lines are the experiment results and blue dashed lines are from the simulation fitting. τ_{it} and $D_{MV+}/D_{MV2+} = 0.1$ are determined by fitting the experimental data.

Figure 4 shows the multi-scan cyclic voltammograms of three Nafion films with different thicknesses. The dry thickness of the three films can be calculated from the Nafion density and was approximately $0.35\ \mu\text{m}$ for film 1, $1.75\ \mu\text{m}$ for film 2, $5.26\ \mu\text{m}$ for film 3. Film 1 is the “fully-doped” film shown in Figure 3 while film 2 and film 3 are thicker films with the same MV^{2+} doping ratio. It is noted that the dry thickness reflects the amount of Nafion doped on the electrode surface but not the “true” thickness of the coating film, as the Nafion is known to swell after immersion into aqueous solution.^{25, 26}

Applying multiple scans in the voltammetry allows us to examine if the redox species, both the reactant and the product, are fully confined inside the Nafion film during the experiment and that no leaching of either takes place. Figure 4a shows the multiple-scan CV of the film 1, where the experiment is shown by the black line and the simulation is the blue dashed line. For both the experiment and the simulation, the voltammogram does not change after multiple scans, showing that the redox species $\text{MV}^{2+}/\text{MV}^+$ can be fully cycled in the thin film 1. Integrating the forward and backward peak leads to the same charge for the reductive and the oxidative processes, confirming that there is no depletion of the redox species in film 1 during the reaction. However, Figure 4b and 4c are the multi-scan CVs of film 2 and film 3, where the current decreases after the 1st scan. It is also observed that after a few cycles, the current stops decreasing (See Figure S5), showing that the current decrease is not caused by the redox ions depletion during the reaction. As revealed by the simulation, the current decrease is attributed to the slow mass transport speed of the product MV^+ , which however can be easily misunderstood as the chemical depleting from the thin-film. Comparing the τ_{it} values obtained from the three Nafion films with different thickness, it is found that:

$$\frac{\tau_{it, \text{film 1}}}{0.35^2} = \frac{\tau_{it, \text{film 2}}}{1.75^2} > \frac{\tau_{it, \text{film 3}}}{5.26^2} \quad (14)$$

As τ_{it} is proportional to the true film thickness in the reaction, Eqn (14) indicates that the variation of the film thickness and the reactant diffusion speed is identical for the thinner films 1 and 2 but different from the thickest film 3. Taking the water-sorption of the Nafion films into consideration, it is possible that the two thinner films (1 and 2) can quickly adsorb solvent and the film reaches a stable state or a quasi-steady state scan after immersing into water solution; in contrast the thickest film (film 3) may not fully equilibrate in the same solution. Note that film 3 gives essentially unchanged electrochemical responses even after immersion into the buffer solution for up to 60 minutes (Figure S6).

The similar ion transport properties measured in film 1 and film 2 shows that in these cases the diffusion of the reactant is independent of the film thickness. The ion transport time τ_{it} is also proved to be independent of the doping concentration in Figure 3, indicating that the charge transport mechanism in these Nafion films is likely to be ion self-diffusion rather than electron hopping.²⁷ Figure 3 and Figure 4 both show that the diffusion of the product MV^+ is much slower than the reactant MV^{2+} ($D_{MV^+}/D_{MV^{2+}} = 0.1$), despite the lower ion charge. The interaction between the redox species and Nafion is both ionic and hydrophobic for methyl viologens.²⁸ In comparison to MV^{2+} , MV^+ is more hydrophobic and this is a possible reason explaining why MV^+ moves slower in the water-saturated Nafion film.²⁹

4.2 Ion transport in single Nafion particles

The one-electron-transfer reaction $MV^{2+} + e^- = MV^+$ in a single MV^{2+} -doped Nafion particle was next investigated via the nano-impact technique. The dry radius of the Nafion particles used was on average of $0.46\ \mu\text{m}$. The chronoamperometry measured at the substrate electrode immersed in the Nafion particle suspension is recorded under high overpotential where $E = -1.0\ \text{V}$ vs SCE and the overpotential $E - E_f$ is $-0.3\ \text{V}$. Note that MV^{2+} can be only reduced to MV^+ at this overpotential.⁷ The current responses (“spikes”) of single particles observed in experiment is analysed by the single particle simulation model to infer the ion transport condition in sub-micron Nafion particles.

Figure 5a shows some examples of the single particle signals measured. Figure 5b shows four individual spikes each of which corresponds to reduction of an individual Nafion particle, where the black line refers to the experimental data and the dashed lines are from simulations. In the single-particle simulation model as introduced in section 3.2, it is assumed that there is a “contacting” area between the particle and the electrode, where the electron transfer occurs on the surface of the contacting area. In contrast to the thin-film model, the two unknown parameters in the single-particle model are τ_{it} and the contacting area which is characterised by the contacting angle ϕ_{cnt} , which both contribute to the signal current. Therefore, any one spike signal can be simulated by either a short τ_{it} (faster ion transport) combined with a small ϕ_{cnt} (smaller electron-transfer area) or a long τ_{it} (slower ion transport) with a large ϕ_{cnt} (larger electron-transfer area). However, whilst the exact value of τ_{it} cannot be unambiguously measured, the ion transport speed can be still estimated relative to that in the film.

To explore the possible ion transport speed in single particles, τ_{it} is calculated with different ϕ_{cnt} . Figure 5b shows two simulation conditions which are both able to fit the experimental spikes well. The red line is the simulation result of $\phi_{cnt} = 30^\circ$ where the particle relatively minimally distorted on impact and the blue one is the extreme one of $\phi_{cnt} = 90^\circ$ corresponding to the particle flattening to a hemisphere on impact with the electrode. When the contacting area is fixed, the value of τ_{it} can be calculated via fitting the spike, as explained in Eqn.(13). Figure 5c shows the distribution of τ_{it} measured for 70 independent, individual Nafion particles under the assumptions of $\phi_{cnt} = 30^\circ$ (red) and $\phi_{cnt} = 90^\circ$ (blue). As each individual particle is not identical, a distribution of τ_{it} can be recorded under a fixed ϕ_{cnt} . For $\phi_{cnt} = 30^\circ$, τ_{it} is from 10^{-5} s to 10^{-2} s; for $\phi_{cnt} = 90^\circ$, τ_{it} is from 10^{-4} s to 10^{-1} s. Although the contacting area is not clear, it is apparent that the ion transport time τ_{it} (most of which are much smaller than 0.1 s) in Nafion particles is much faster than measured from Nafion thin layers (0.5 s).

Figure 5 (a) Chronoamperometry measured in Nafion particle suspension; (b) Four individual Nafion particle experiment signals (black) with simulations of 30° (red) and 90° (blue) contacting angles; (c) Distribution of the measured τ_{it} in the simulations of 30° (red) and 90° (blue) contacting angles. In the simulation, the charge Q of each particle is calculated from their experimental current spikes.

4.3 Ion transport in Nafion particle modified electrodes

To further appreciate the difference observed between the Nafion thin film and the Nafion particles, the cyclic voltammetry of the Nafion particles modified electrode was recorded experimentally and analysed with the aid of simulation. Three Nafion particle modified electrodes were made by drop-casting different amounts of Nafion particles, which correspond to approximately 3, 5 and 15 layers of particles on the glassy carbon substrate electrode of 1.5 mm radius. The estimation of the number of layers of particles loaded on the electrode is approximated from the dry radius of the Nafion particle hence may not fully reflect the number of particles contributing to the electron transfer on the electrode. The reactant MV^{2+} is doped in the particles and the doping concentration is $MV^{2+}:SO_3^{2-} = 1:20$ ("fully-doped"). The one-electron-transfer reaction $MV^{2+} + e^- = MV^+$ was studied on these Nafion particle modified electrodes and the single Nafion particle model was applied to the analysis of the experimental cyclic voltammetry on these particles. We develop the analysis by first assuming that the electrochemical response of each particle is independent and the redox species are all confined in the particles during the reaction so as to get an initial point of comparison with experiment. To understand the ion transport property in Nafion particles, we measure the cyclic voltammetry of immobilized particles with different drop-casting amounts and the current-potential response of the immobilized Nafion particles is compared with a Nafion film, in which the ion transport speed has been determined.

Figure 6a shows the cyclic voltammetry of MV^{2+} -doped Nafion particle modified electrodes with 3, 5 and 15 layers respectively at scan rate of 0.1 V/s, where the method of estimating the layer thickness is given in the supporting information. Figure 6b compares the voltammetric waveshape between a Nafion thin film (film 1) and a

particle-modified electrode (15 layers). Figure 6c is the normalized current response of Figure 6b. If the ion transport speed in the two materials were similar, the same diffusion-controlled feature would be observed on the particles modified electrode, which is contradictory to experiment.

Figure 6 (a) Cyclic voltammetry recorded on three Nafion particles modified electrodes at 0.1 V/s scan rate. Blue line: 3 layers of Nafion particles are drop-casted on the glassy carbon macroelectrode; Red line: 5 layers; Green line: 15 layers. (b) Cyclic voltammetry of MV^+/MV^{2+} redox reaction in MV^{2+} doped Nafion film and Nafion particles (15 layers) modified electrode at 0.1 V/s scan rate. (c) Normalized current-potential responses in Nafion film and particles. For comparison, the current I in (c) is normalized by the forward peak current I_{peak} .

The single particle model is applied to simulate the data from the three electrodes on which *ca.* 3, 5 and 15 layers of Nafion particles are modified. Figure 7 shows the experiment and simulation peak currents for the three electrodes. The fitting of the simulation model to the experiment data can be found in the Supporting Information. The simulations of the 3, 5 and 15 layers of modifying particles employ the same τ_{it}

(0.025 s) and $D_{MV^+}/D_{MV^{2+}}$ (0.5) but different contacting area ϕ_{cnt} . The identical τ_{it} found for the three electrodes suggests that there is probably only one layer of Nafion particles contributing to the electron transfer on the electrode as the particle-particle contact seemingly play little role in districting the response. The fitting parameter of the contacting angle ϕ_{cnt} decreases when fewer amounts of particles are drop-casted on the electrode, hinting that the more particles are stacked on the electrode, the less area of the particles can contact with the electrode. The similarity of τ_{it} among the three electrodes confirms that there is only the first layer of particles triggering the redox reaction while the difference in ϕ_{cnt} may explain why the number of the particles involved in the reaction is different for the three electrodes.

Figure 7 Experimental (solid circles) and simulated (open circles) peak currents under various scan rates. (a) Forward peak current, $I_{\text{peak, f}}$; (b) backward peak current, $I_{\text{peak, b}}$. Blue: 3 layers of Nafion particles modified electrode under the simulation of $\tau_{\text{it}} = 0.025$, $\phi_{\text{cnt}} = 45^\circ$ and $D_{MV^+}/D_{MV^{2+}} = 0.5$; Red: 5 layers modification under $\tau_{\text{it}} = 0.025$, $\phi_{\text{cnt}} = 30^\circ$ and $D_{MV^+}/D_{MV^{2+}} = 0.5$; Green: 15 layers modification under $\tau_{\text{it}} = 0.025$, $\phi_{\text{cnt}} = 18^\circ$ and $D_{MV^+}/D_{MV^{2+}} = 0.5$.

Figure 6 highlights the difference in the ion transport speed between the Nafion thin layer and the Nafion particles, where diffusion-controlled features are found in the thin-film voltammetry (from intra-film diffusion) but thin-layer features are found in the particle voltammetry. Via simulation, the parameters τ_{it} are also found to be different for the two Nafion materials, $\tau_{it} = 0.5$ s for the film with dry thickness of $0.35\ \mu\text{m}$ and $\tau_{it} = 0.025$ s for the particles with dry radius of $0.46\ \mu\text{m}$, reflecting different hydration of particles and of films. Another interesting change is the difference of $D_{MV^+}/D_{MV^{2+}}$ between Nafion films and particles. In Nafion particles, the ion transport speed of MV^+ is still slower than MV^{2+} ($D_{MV^+}/D_{MV^{2+}} = 0.5$) but not as much as in the film ($D_{MV^+}/D_{MV^{2+}} = 0.1$). Combining with single Nafion particle signals shown in Figure 6, it can be concluded that the ion transport of MV^{2+} and MV^+ is faster in Nafion particles than in Nafion thin films.

5 Discussion and Perspectives

The ion transport speed in two types of Nafion materials is measured and used to characterise the structure-functionality of Nafion materials. The ion transport speed, marked by τ_{it} , and the relative speed of MV^+ and MV^{2+} , marked by $D_{\text{product}}/D_{\text{reactant}}$, was derived via fitting the experiment data with the theoretical models of Eqn(11), (12) and (13). It was seen that the ion transport speed for the redox species MV^{2+} in Nafion particles is much faster than in the thin film of similar sizes. As mentioned in Section 4.1, a possible explanation for this is the water-sorption influence on the ion transport property in Nafion materials. For the hydrophilic ions such as Na^+ and Cl^- , higher water contains lead to faster ion diffusion speeds;³⁰ while for hydrophobic ions such as MV^{2+}

and MV^+ , higher water content is suggested to lead to slower ion diffusion speeds.²⁹ The faster ion transport speed in Nafion particles may indicate that the water-sorption in the particles is much less than that in the films, showing that material preparation and processing has significant influence in the material structure and properties. A larger $D_{MV^+}/D_{MV^{2+}}$ ratio measured in Nafion particles also suggests a structure difference between the particles and the films.

The combined voltammetry/impact approach offers applications beyond the present work. On the one hand, the ion transport properties of Nafion or other ionomer materials can be quantified and investigated directly in electrode systems. These can be influenced by many factors, such as the charges of the redox ions, the sizes of the redox ions, the doping concentration, the film thickness, the structure and component of the ionomer, the supporting substrate et al.^{1,8} In real applications, varying redox species or materials may lead to other charge transport mechanisms, such as electronic hopping, of which differ from the ion transport of MV^{2+}/MV^+ . However, only little modification to the current simulation model is needed to include more complex situations, such as the permeability of the ions or the conductivity of the materials. Moreover the key modelling parameter τ_{it} generally describes other type of charge transport speed in ionomer materials.

6 Conclusions

Contrasting transport in Nafion films and particles has been demonstrated and quantified. The observation of faster diffusion of MV^{2+} as compared to MV^+ has been confirmed with the relative rates again sensitive to the physical form of Nafion. The work highlights the existence of diverse transport behaviour from Nafion processed in different ways.

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