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## Methods—Meso-Scale Electrodes for Characterizing Diffusion-Reaction Properties of Redox-Active Organics in Viscous Electrolytes

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Deep Eutectic Solvents (DESs) have recently gained interest as flow battery electrolytes. Their advantages include a wider electrochemical stability window compared to aqueous electrolytes, higher solubility for redox-active species, and negligible volatility. However, DESs are often highly viscous, and suffer from low ionic conductivities. This can make assessing redox kinetics difficult when attempting to determine their viability for energy storage. In classical voltammetric measurements, low ionic conductivity manifests as high solution resistance, thereby requiring "live" compensation of the electrolyte ohmic drop when performing fast-scan voltammetry. An uncompensated or inadequately-compensated ohmic drop leads to misinterpretation of the voltammetric behavior, e.g., assessing reversibility vs. irreversibility of a redox reaction. Here, we present micro-fabricated electrodes as facile "meso-scale" electrodes, which overcome these issues by nearly eliminating the ohmic drop while retaining uniformity of the current distribution over the electrode surface. Their use in precise transport-kinetics measurements is demonstrated using a redox-active organic, i.e., 4-Hydroxy-TEMPO in an aqueous medium and in ethaline, which is a viscous DES. This study provides a methodical approach to design and to implement voltammetry experiments using meso-scale electrodes leading to reliable measurements of diffusion-reaction properties of 4-Hydroxy-TEMPO.

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Redox Flow Batteries (RFBs) are promising stationary grid-scale energy storage devices, particularly due to their ability to decouple energy and power. Recently, a class of non-aqueous electrolytes called "Deep Eutectic Solvents" (DESs) have emerged as promising candidates for RFB applications due to their low cost, high thermal stability, low volatility, and wider electrochemical stability window when compared to aqueous electrolytes.<sup>1,2</sup> To determine the suitability of DESs as electrolytes for RFBs, it is crucial to examine both the charge transfer kinetics and the transport properties<sup>3,4</sup> of redox-active molecules added to the DES electrolyte. A common technique used to assess these properties is cyclic voltammetry (CV); however, the high viscosity and low conductivity of DES electrolytes poses significant challenges in extracting reliable transport-kinetics parameters via CV.<sup>5</sup> As shown by Shen and coworkers, implementing CVs in resistive DES media requires "live" compensation of the ohmic drop  $(IR_{\Omega})$ , which develops between the working and reference electrodes, and which evolves non-linearly with time as the potential is scanned. Correcting for this non-linear ohmic drop during the potential scan is essential to satisfy the condition of a "linear" change of the surface potential  $E = V - IR_{0}$ , where V is the applied potential) with time assumed in theoretical treatments of  $CVs.^6$  Live  $IR_{\Omega}$  compensation is performed using potentiostats equipped with positive feedback where the varying current is continuously monitored and is utilized to adjust the applied potential V such that the post-compensated surface potential E varies linearly with time.<sup>7-10</sup> This requires a priori knowledge of the solution resistance  $R_{\Omega}$ , which may be obtained from independent measurements such as electrochemical impedance spectroscopy (EIS).

On macro-scale electrodes, it is well known that inadequate  $IR_{\Omega}$  compensation can lead to the misinterpretation of CV data. For example, shifts in the peak potential due to uncompensated ohmic resistance during fast scan voltammetry<sup>11,12</sup> may lead to incorrect conclusions regarding the extent of reversibility of a redox reaction.<sup>10,13</sup> While convolutive or semi-integrative methods can

help extract kinetic parameters without suffering from the effects of uncompensated  $IR_{\Omega}$ ,<sup>9</sup> these techniques are uncommon in practice. An alternative method is to employ ultra-micro-electrodes (UMEs), which eliminate  $IR_{\Omega}$  because of their small size. This allows for small currents and thus negligible  $IR_{\Omega}$  to be realized.<sup>8,10,14</sup> UMEs come with their own complexities, e.g., the nano-ampere currents at UMEs are prone to noise interference, and UMEs deviate from linear one-dimensional diffusional transport assumed in classical models of cyclic voltammetry at macro-electrodes.<sup>15</sup>

Electrode geometries obtained via micro-fabrication or thin-film printing methods, where the electrode dimensions are in the "mesoscale" range ( $\sim 0.1$  cm) present an intriguing compromise between conventional macro-scale ( $\sim$ 1 cm) electrodes and aforementioned UMEs ( $\sim 10^{-3}$  cm) for electrochemistry in viscous electrolytes. Such commercially available electrodes (Fig. 1) present several advantages: (i) They offer more uniform current distribution on account of their small size compared to macro-scale electrodes such as macro-disk electrodes; and (ii) They have optimally-placed reference probes, which as shown below nearly eliminate the ohmic drop between the working electrode and the reference probe, negating completely the need for live  $IR_{\Omega}$  compensation. Additionally, such electrodes are compatible with small-volume electrolytes, which is advantageous in high-throughput screening of designer redox compounds that are synthesized only in small proportions. In this contribution, guidelines are developed to employ such meso-scale electrodes for quantitative studies of the diffusionreaction properties of redox active species in viscous electrolytes. Specifically, using a redox-active organic, i.e., 4-Hydroxy-TEMPO, we demonstrate how meso-scale electrodes enable precise and reliable measurement of the diffusion coefficient and the chargetransfer kinetics of 4-Hydroxy-TEMPO. The approaches developed herein are generic, and the best practices recommended can be applied to electrochemical studies of DESs and other viscous ionic liquids.

#### **Experimental Methods**



Figure 1. Top-down optical microscopy image of the micro-fabricated chip. WE = Pt, CE = Pt, and RE = Ag/AgCl.

(ChCl, 99% purity, Acros Organics), sodium chloride (NaCl, >99% purity, Sigma Aldrich), 4-Hydroxy-TEMPO (HT,  $C_9H_{18}NO_2$ , >98% purity, Alfa Aesar). The viscous DES "ethaline" was prepared by mixing ChCl and EG in a 1:2 molar ratio at 80 °C on a hot plate while being stirred for 8 h.<sup>16</sup> Solutions of 10 mM HT in ethaline were prepared by adding appropriate amounts of HT to the premixed ethaline. Aqueous solution of 10 mM HT in 0.5 M NaCl were prepared using Millipore ultrapure (18.2 MΩ·cm) deionized water.

Electrochemical measurements.—Pre-fabricated chips (Fig. 1) were procured from Conductive Technologies Inc.<sup>17</sup> Each chip consisted of a 0.254 mm thick PET substrate with a thin film (~50 nm) of sputter-coated polycrystalline platinum that was patterned via laser ablation technique (WE and CE). The reference electrode (RE) was a thick film printed Ag/AgCl fabricated using DuPont 5870 (BQ162) Ag/AgCl ink. Experiments were performed by immersing the chip in a vial containing 2-5 milliliters of the prepared electrolyte solution. The aqueous solutions were de-aerated by purging Ar and then tightly sealing them for storage before starting experiments. Ethaline-based electrolytes were not de-aerated, since de-aeration does not alter the experimental results as reported in literature.<sup>18</sup> A Princeton Applied Research PARSTAT-4000 potentiostat was used for all experiments. Connections were made from the chip's contacting leads to the potentiostat using an edge connector. Linear scan voltammograms for oxidation of HT were collected with and without live  $IR_{\Omega}$  compensation at various scan rates as indicated below.

#### **Results and Discussion**

**Benefits of using "Meso-scale" electrodes.**—We first performed numerical simulations to determine the secondary current distribution uniformity at the surface of the meso-scale working electrode. Simplifying the actual 3D geometry to 2D (Figs. 2a and 2b), we solved the Laplace's equation governing the potential ( $\varphi$ ) distribution in the electrolyte phase:

$$\nabla^2 \varphi = 0 \tag{1}$$

At the working electrode, we use the Tafel approximation to describe the electrode kinetics:

$$-\kappa \nabla \varphi = i_0 \exp[\alpha_a f (V - \varphi)]$$
<sup>[2]</sup>

where f = F/RT (F = Faraday's constant, R = ideal gas constant, and T = temperature). At the counter electrode, the potential was

fixed at 0.3 V. The insulating walls represented a no flux boundary condition:  $\nabla \varphi = 0$ . Simulations were performed at various values of the working electrode applied potential V, corresponding to various applied current densities  $i_{avg}$  at the working electrode. Equation 1 was numerically solved using the coefficient form PDE module in COMSOL<sup>\*</sup> version 6.1. An extremely fine ( $\sim$ 50  $\mu$ m sized) physicscontrolled mesh was selected, and a "stationary" study with a tolerance of  $10^{-3}$  was performed. The values of the exchange current density  $i_0 = 0.8 \ \mu\text{A cm}^{-2}$  and  $\alpha_a = 0.9$  were taken from literature for 4-Hydroxy-TEMPO.<sup>18,19</sup> Electrolyte conductivity was set at 8 mS cm<sup>-1</sup> representative of resistive DES electrolytes such as ethaline.<sup>20</sup> Figure 2c shows the current distribution over the WE, which becomes increasingly non-uniform as the value of  $i_{avg}$ increases as expected for secondary current distribution. Figure 2d shows the simulated equipotential lines for  $i_{avg} = 0.6 \text{ mA cm}^{-2}$ . Figure 2d highlights that the placement of the RE within 1 mm of the WE, but on the opposite side of the WE as compared to the CE, enables a negligibly small ohmic drop between the WE and RE of around 3 mV. This suggests that the RE truly senses the potential very close to the WE surface and that  $IR_{\Omega}$  compensation as needed in classical macro-electrode measurements is not required.

In addition to negligibly small ohmic drop, a second advantage of the meso-scale electrodes is that they provide fairly uniform current distribution at relevant operating conditions even in viscous electrolytes. The secondary current distribution uniformity can be assessed using the Wagner number, which for a disk of radius a embedded in an infinite insulating place (Fig. 2b), takes the form:

$$Wa = \frac{4RT\kappa}{\pi\alpha_a Fi_{avo} a}$$
[3]

For  $a = x_0/2 = 0.7$  mm, Wa = 6.9 for  $i_{avg} = 0.6$  mA cm<sup>-2</sup>, which provides a uniform current distribution as seen in Fig. 2c. This is a significant advantage over conventional macro-disk electrodes because, under similar conditions of electrolyte conductivity and  $i_{avg}$ , a 0.25 cm macro-disk electrode experiences non-uniform current distribution because the Wagner number is low (Wa = 1.94). In conclusion, uniform current distribution and small  $IR_{\Omega}$  both can be obtained on a meso-scale electrode at applied current densities ( $i_{avg}$ ) of practical interest for studying redox reactions in DESs.

**Voltammetry on "meso-scale" electrodes.**—To demonstrate that  $IR_{\Omega}$  compensation is small and thus not required on a meso-scale



**Figure 2.** (a) Schematic of the top-view of the pre-fabricated chip with meso-scale electrode dimensions. (b) Cross-section of the chip that runs through the diameter of the WE. (c) Current density distribution over the WE simulated for various values of  $i_{avg}$  (X-axis is position on the electrode normalized to the electrode diameter  $x_0$ ). The deviation of the maximum current density from the corresponding  $i_{avg}$  is small for  $i_{avg} = 0.6$  mA cm<sup>-2</sup> indicating relatively uniform current distribution. (d) Equipotential lines for the case of  $i_{avg} = 0.6$  mA cm<sup>-2</sup>, showing that the potential drop between the WE and the RE (placed adjacent to the WE, but on the opposite side of the CE) is negligible (~3 mV).

electrode, linear scan voltammetry was performed with and without live  $IR_{\Omega}$  compensation. Figure 3 shows voltammetric curves for HT oxidation in DES and in aqueous NaCl media. As expected, the voltammetry is unaffected by  $IR_{\Omega}$  compensation in both media, i.e., the peak currents and the behavior of the peak potentials with scan rate is independent of whether  $IR_{\Omega}$  compensation is applied or not. This is not surprising given that  $IR_{\Omega}$  is negligibly small at a mesoscale electrode. For example, in ethaline, for current density of 0.6 mA cm<sup>-2</sup> (I = 0.012 mA), and for  $R_{\Omega} = 260 \Omega$  (measured using EIS, see Fig. S1 in supplementary information), the ohmic overpotential correction is merely 3.12 mV and thus  $IR_{\Omega}$  compensation can be ignored in acquiring voltammetric scans. To demonstrate the versatility of the proposed electrode arrangement, a similar study on HT oxidation was performed in a more viscous "reline" DES (a 1:2 molar ratio mixture of choline chloride and urea). Similar to the ethaline system, no difference in voltammetric behavior was observed with our without  $IR_{\Omega}$  compensation (Fig. S2, supplementary information). For ethaline, note that the value of  $R_{\Omega}$  is consistent with that estimated from numerical simulations (Fig. 2d), where  $R_{\Omega}$ is  $\Delta V/I = (3 \text{ mV})/(0.012 \text{ mA}) = 250 \Omega$ . In ethaline, the peak potentials for HT oxidation are relatively independent of the scan rate, but they depend on the scan rate in the aqueous medium. This is due to the fact that higher current densities are reached in the aqueous medium on account of the higher diffusivity (lower viscosity) of HT in this medium. The higher current densities induce irreversibility that manifests in a shift in the peak potential with higher scan rates. This is discussed further in the subsequent section.

In LSV, note that the voltammetric current response represents an average current over the entire electrode surface. Thus, it is important to choose conditions, i.e., the redox species concentration and the potential scan rate, that provide a uniform current density distribution particularly when the measured current is at its maximal (peak) value. Figure 4. shows how the redox species concentration and the potential scan rate modulate the peak current and thus the Wagner number (Eq. 3). For example, for solutions of 10 mM HT in ethaline, scan rates below 0.4 V/s generate peak current densities of 0.83 mA cm<sup>-2</sup> or lower, representing uniform current distribution (Wa > 5, typical criterion for uniformity of the secondary current distribution<sup>21</sup>). Conditions were chosen in Figs. 3a and 3b to be consistent with this criterion to ensure that uniform current distribution during voltammetry was always preserved. A similar analysis was performed for the aqueous medium so that voltammetric



**Figure 3.** (a) & (b) Linear Scan Voltammetry (LSV) of the oxidation of HT at different scan rates, with and without live  $IR_{\Omega}$  compensation, performed using the meso-scale electrode in viscous ethaline medium consisting of 10 mM HT. (c) & (d) LSV of HT oxidation, also at different scan rates with and without live  $IR_{\Omega}$  compensation performed in an aqueous (0.5 M NaCl) medium consisting of 10 mM HT. Results show that application of live  $IR_{\Omega}$  compensation does not appreciably alter the voltammetric response compared to that without live  $IR_{\Omega}$  compensation. This is due to the fact that meso-scale electrodes of the type depicted in Fig. 1 facilitate negligible ohmic overpotentials under conditions employed in this study. This fact is unique to meso-scale electrodes and does not apply to macro-electrodes.

analysis in Figs. 3c and 3d conforms to the criterion of uniformity in the secondary current distribution.

Applying micro-fabricated electrodes for diffusion-reaction studies.—The meso-scale electrodes can be assumed to exhibit linear 1D diffusion analogous to macro-electrodes even at low sweep rates. As discussed in Fig. S3 in supplementary information, voltammetric response at a meso-scale electrode is very similar to that at a macro-scale electrode confirming linear diffusion. Thus, the peak current densities  $(i_p)$  at these electrodes obey the Randles-Sevcik equation (for reversible redox reaction), or the Nicholson-Shain equation (for irreversible redox reaction):<sup>15,22</sup>

$$i_{\rm p,irreversible} = 0.4958 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} \alpha_{\rm a}^{\frac{1}{2}} D_{\rm HT}^{\frac{1}{2}} C_{\rm b} \nu^{\frac{1}{2}}$$
 [4]

$$i_{\rm p,reversible} = 0.4463 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D_{\rm HT}^{\frac{1}{2}} C_{\rm b} \nu^{\frac{1}{2}}$$
[5]

where  $\alpha_a$  is the anodic charge transfer coefficient,  $D_{\rm HT}$  is the diffusion coefficient of HT,  $C_{\rm b}$  is the bulk concentration, and  $\nu$  is the scan rate. Additionally, irreversibility manifests as a dependence of the peak potential on the potential sweep rate whereas reversible system do not exhibit such dependence. Previous studies have shown that oxidation of HT in ethaline leads to reversible behavior at low scan rates or low current densities; however, irreversibility sets in on account of surface adsorption phenomena at higher scan rates or currents.<sup>23</sup> We chose to assess these effects using the meso-scale electrodes proposed herein. First, we assessed HT oxidation in ethaline (Fig. 5) and found that its voltammetry response closely agrees with the Randles-Sevcik equation if the diffusion coefficient is selected to be  $2.4 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>. This observation in Fig. 5, together with the observed weak dependence of the peak potential on the scan rate (Figs. 3a and 3b) suggests that HT oxidation in ethaline, under the conditions employed in this study, is reversible. Also, the best fit value of  $D_{\rm HT}$  agrees with the known diffusion coefficient of HT in ethaline obtained in previous studies.<sup>18</sup> In addition to transport property characterization, the meso-scale electrodes can also enable measurement of the kinetics properties, i.e., the charge transfer



**Figure 4.** Peak current densities calculated using the Randles-Sevcik equation for various HT concentrations (assuming  $D_{\rm HT} = 2.4 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>), and then correlated to the Wagner number using Eq. 3. The scan rate and the species concentration are the two parameters that establish an upper bound on the current density that can be reached during LSV while preserving relatively uniform current distribution (Wa > 5).

coefficient. Figure 6a depicts a linear dependence of the peak current  $i_p$  on the square-root of  $\nu$  for HT oxidation in an aqueous medium. The linear dependence agrees well with the Nicholson-Shain equation Eq. 4 for  $\alpha_a = 0.89$  and  $D_{\rm HT} = 6 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>. This suggests that HT oxidation at higher currents encountered in less-viscous aqueous medium exhibits kinetic irreversibility. Nicholson and Shain provide the following dependence of the peak potential  $E_p$  on scan rate for an irreversible system:<sup>15,22</sup>

$$E_{\rm p} \propto \frac{RT}{\alpha_{\rm a} F} \left[ \ln \left( \frac{\alpha_{\rm a} F \nu}{RT} \right)^{\frac{1}{2}} \right]$$
 [6]

where  $E^0$  is the equilibrium potential and  $k_0$  is the reaction rate constant. This equation suggests that the peak potential  $E_p$  changes



**Figure 5.** Peak current densities observed in LSV studies of HT oxidation (10 mM HT) in ethaline medium indicate reversible behavior because of agreement with the Randles-Sevcik equation. The slope provides  $D_{\rm HT} = 2.4 \times 10^{-7} \, {\rm cm}^2 \, {\rm s}^{-1}$  consistent with known diffusivities of HT in this viscous medium.<sup>18,23</sup>

with the scan rate  $\nu$ , as confirmed experimentally in Figs. 3c and 3d. So, if  $E_p$  is plotted as a function of ln ( $\nu$ ) for HT oxidation in an aqueous medium, a linear relationship with a slope of  $RT/2\alpha_a F$  is expected. This is confirmed in Fig. 6b. A linear best-fit to data in Fig. 6b yields a slope of 14.46 mV, from which  $\alpha_a$  can be calculated as 0.89. This value is consistent with the previously measured effective charge transfer coefficient for HT oxidation (the high value of apparent  $\alpha_a$  is due to adsorption phenomena accompanying HT oxidation as discussed elsewhere<sup>18,23</sup>).



Figure 6. (a) Peak current density from LSV for HT oxidation (10 mM HT) in an aqueous medium (0.5 M NaCl) showing irreversible behavior, i.e., agreement with the Nicholson-Shain equation for  $D_{\rm HT} = 6 \times 10^{-6} \, {\rm cm}^2 \, {\rm s}^{-1}$ . (b) Peak potentials show a scan rate dependence, further suggesting irreversible behavior. Slope  $RT/2\alpha_a F = 14.46 \, {\rm mV}$  provides anodic charge transfer coefficient  $\alpha_a = 0.89$  also in agreement with previously reported kinetics data.<sup>18,23</sup>

#### Conclusions

Meso-scale electrode chips of the type depicted in Fig. 1 are shown to have unique advantages in enabling precise measurements of the diffusion and electrochemical reaction properties in viscous (non-aqueous) and non-viscous (aqueous) media. These electrodes offer uniform current distribution on account of their small  $(\sim 0.1 \text{ cm})$  size. Also, when optimally-placed reference probes are incorporated, these electrodes minimize the ohmic drop at practically-relevant current densities thereby negating the need for "live"  $IR_{\Omega}$  compensation in transient measurements such as LSV or CV. Finally, such electrodes are cheap and are compatible with smallvolume electrolytes, which is advantageous in high-throughput screening of newly-synthesized redox-active compounds that may be available only in small proportions. This study provides a methodical approach to applying such meso-scale electrodes in voltammetry experiments leading to reliable measurements of diffusion-reaction properties of a model redox-active compound. i.e., 4-Hydroxy-TEMPO, in viscous DES and aqueous media.

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