Electronic Supporting Information

Liquid-Liquid and Gas-Liquid Dispersions in Electrochemistry: Concepts, Applications and Perspectives

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FIGURE CAPTIONS

Fig S1. Schematic diagrams of (a) autoclave and glass cell (one-compartment). (b) H-type cell (two-compartment).

Fig S2. i/E curves for O_2 reduction. Supporting electrolyte: (a) without (c) with CMC of A336; (b and d) expanded voltammograms. Supporting electrolyte: O_2 saturated 0.1 mol L^{-1} K_2SO_4.[S1] Figures a-d adapted from reference [S1] with permission from Elsevier, copyright 2007. Angular velocity of electrode rotation $\omega_{1/2}$ vs. current plot of (e) PF-decalin/PF-tributylamine, 0.1 m NaOH. (f) PF-methyldecalin, 0.1 m NaOH.[S2] Images adapted with permission from Elsevier. Figures e-f adapted from reference [S2] with permission from Elsevier, copyright 2000.

Fig S3. List of saturated alcohols obtained by ECH of limonene and carvone on a Raney Nickel electrode in aqueous micellar and emulsified solutions stabilised by different surfactants.[S3]

Fig S4. FDCA yield (blue), HMF conversion (red) and cell voltage (orange) as a function of (a) organic/water volume ratio of the biphasic model electrolyte, and (b) the influence of current density at 1:2 organic/water volume ratio at a flow rate of 500 mL min^{-1}.[S4]

Fig S5. CV plots of (a) 10 mM of chloroacetonitrile (CAN) and (b) 9-bromoanthracene (9-BAN). Nomenclature: Red, 12 mM [DDMIM][Cl] with supporting electrolyte 0.1 M phosphate buffer pH 7; Black, 12 mM [DDMIM][Cl] with supporting electrolyte 0.1 M phosphate buffer pH 7; and blue, 0.1 M phosphate buffer pH 7. Insert in (a): DMF with 0.1 M TBAP as supporting electrolyte. The electrolytic solutions were continuously fed with a stream of CO_2.[S5] Images adapted from reference [S5] with permission from RSC, copyright 2021.

Fig S6. (a) Voltammograms of 1.2 mM $Ru(NH_3)_6^{3+}$ reduction in 0.1 M KCl solution. Curves: **a**, silent conditions; **b**, 110 W cm^{-2} ultrasound; and **c**, 190 W cm^{-2} ultrasound. (b) Yield of decane *vs.* charge plot. Reaction conditions: 15 mmol of hexanoic acid in 1.0 M NaOH, 190 W cm^{-2} of 20 kHz ultrasound, 7 mm electrode to horn distance, 0.18 A cm^{-2} current density at a 12 mm diameter Pt disc electrode.[S6] Images adapted from reference [S6] with permission from Elsevier, copyright 2001.

Fig S7. (a) CV plots of 72 mM MEPBr + 0.5 M K_2SO_4 at pH 5.1 (red line) and 72 mM KBr + 0.5 M K_2SO_4 solution at pH 5.1 (black line). (b) CA plots for a Pt UME showing the droplets' collision time with the electrode.[S7] Images adapted from reference [S7] with permission from Elsevier, copyright 2017.
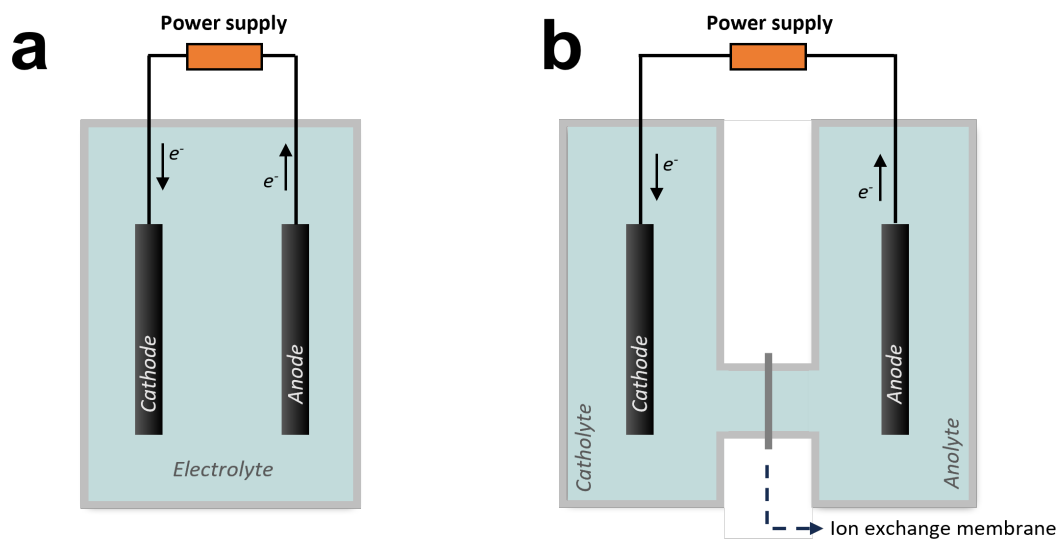
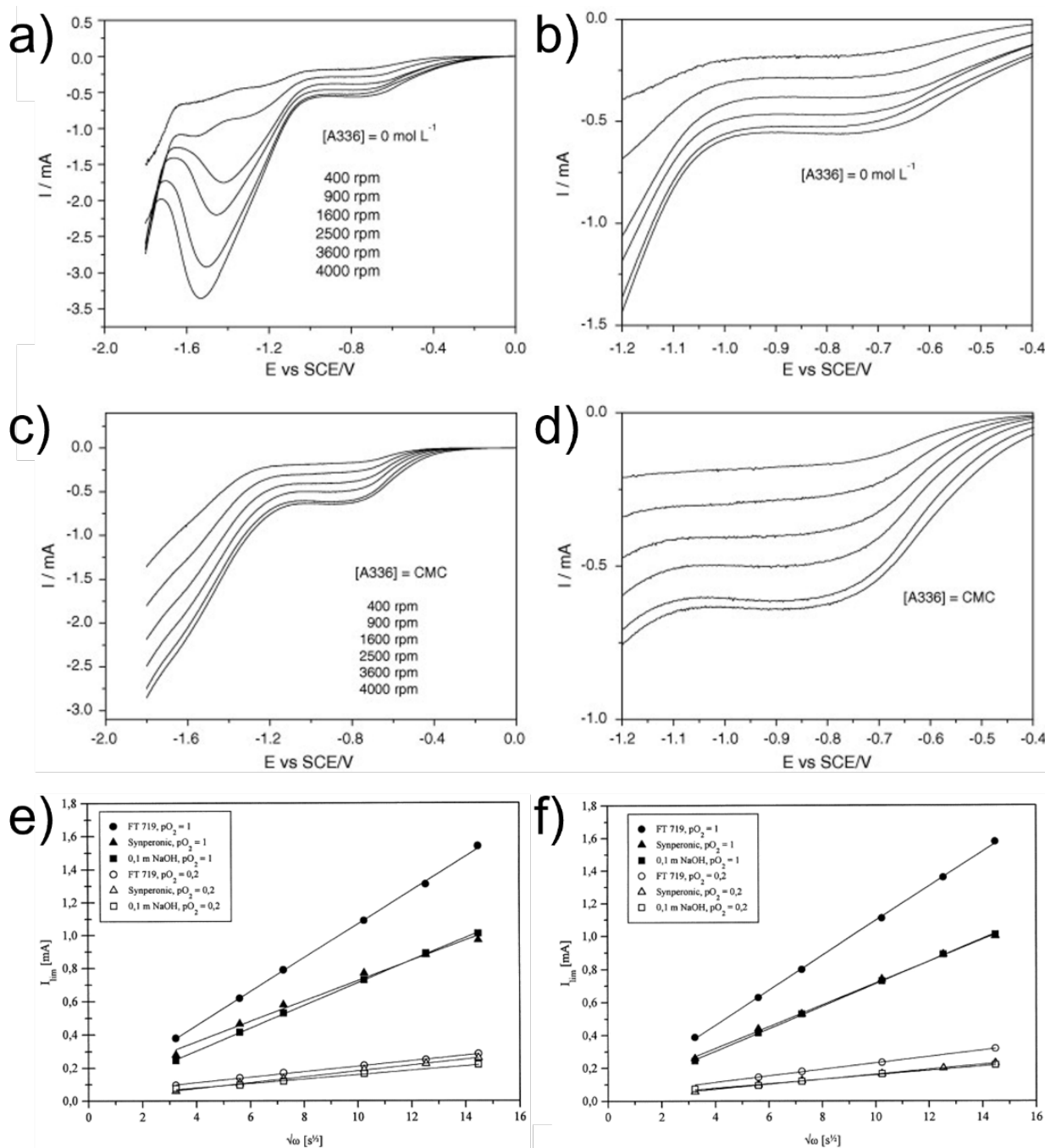**Fig S1.** Schematic diagrams of (a) autoclave and glass cell (one-compartment). (b) H-type cell (two-compartment).

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In **Fig S2a&b**, the second reduction peak (-1.4 V to -1.6 V) indicate A336 inhibits H_2O_2 reduction to H_2O. Meanwhile, the half-wave potential shifts to more negative potentials in the presence of A336, which means A336 affects the thermodynamic properties of ORR. In **Fig S2e&f**, the presence of FT 719 enhances the current due to a more favoured O_2 transfer from the organic phase to the electrode surface using a fluorinated surfactant.

1 D-Limonene   2 (+)p-Menthene   3 p-Menthane (c+t)

4 (-)-Carvone   5 Dihydrocarvone(c+t)   6 Carvotanacetone

7 Carvomenthone (c+t)   8 Neocarvomenthol   9 Carvomenthol

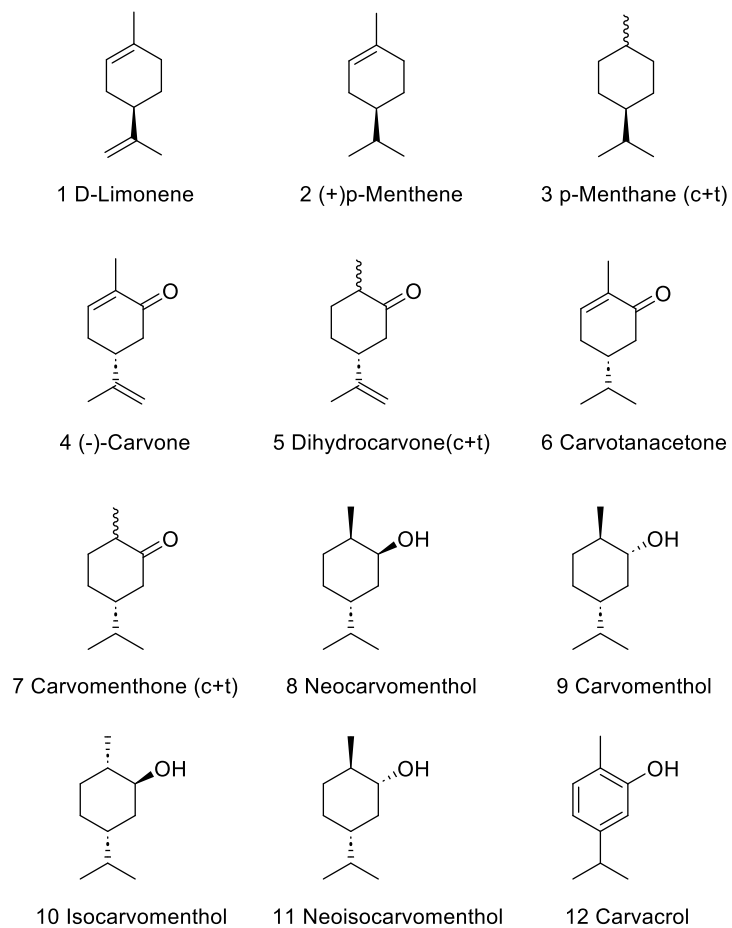10 Isocarvomenthol   11 Neoisocarvomenthol   12 Carvacrol

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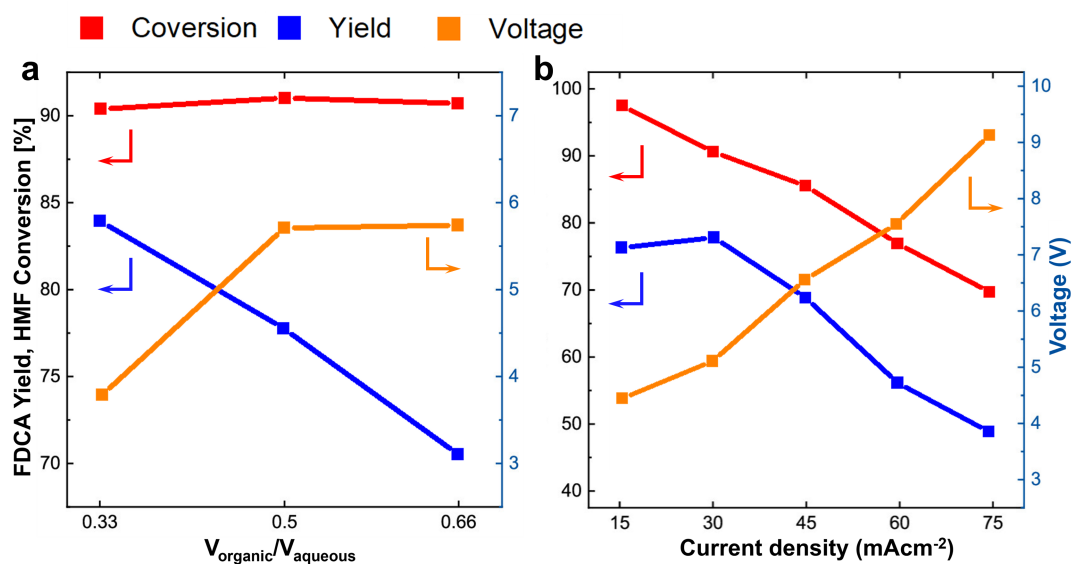
Fig S4. FDCA yield (blue), HMF conversion (red) and cell voltage (orange) as a function of (a) organic/water volume ratio of the biphasic model electrolyte, and (b) the influence of current density at 1:2 organic/water volume ratio at a flow rate of 500 mL min^{-1}.[S4]

The results show a high FDCA yield by feeding a HMF-rich organic phase to the electrode, while HMF was extracted into the aqueous phase and oxidized to FDCA.
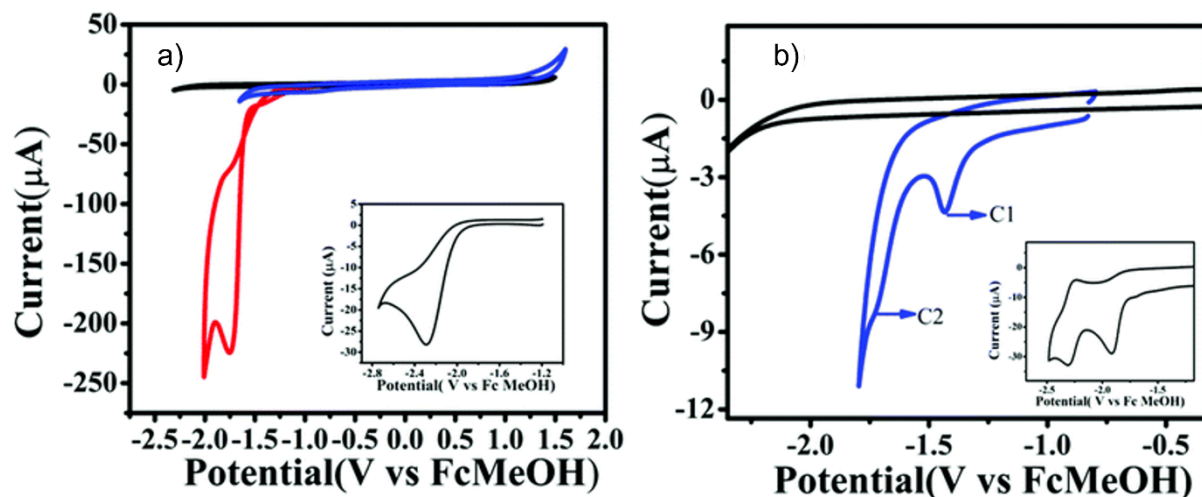
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Compared to the CV plots reported for CAN and 9-BAN at similar conditions without SAIL micelles, the reduction peaks appear at lower overpotential due to an enhanced mass transfer.
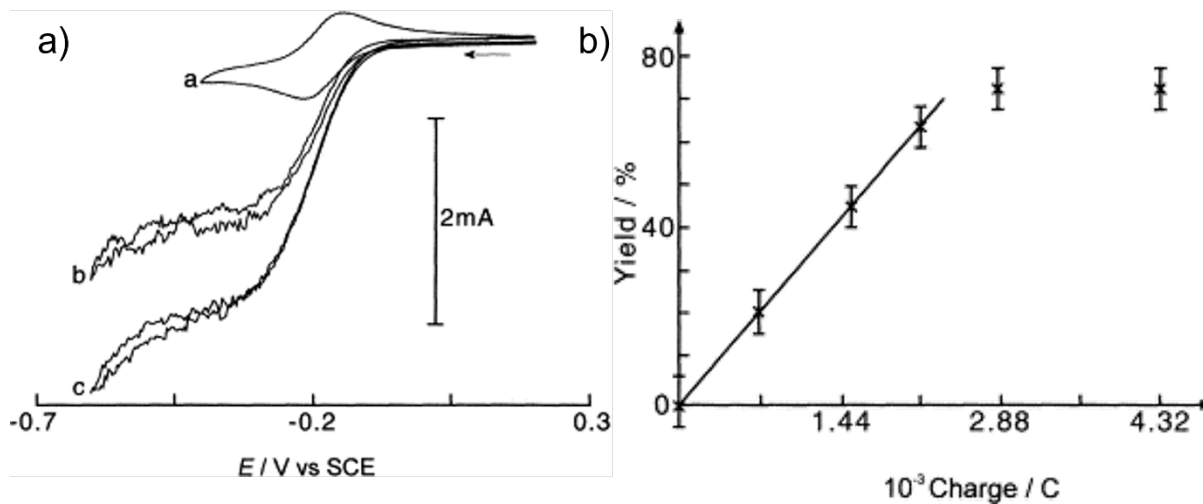
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Fig S6a shows the effect of ultrasound for biphasic Kolbe coupling processes. A considerable current increase in the presence of ultrasound is clearly visible. Under sono-emulsion conditions, there is enough electrode surface to enable the redox process. **Fig S6b** plots the decane yield in the presence of ultrasound reaching 75%.
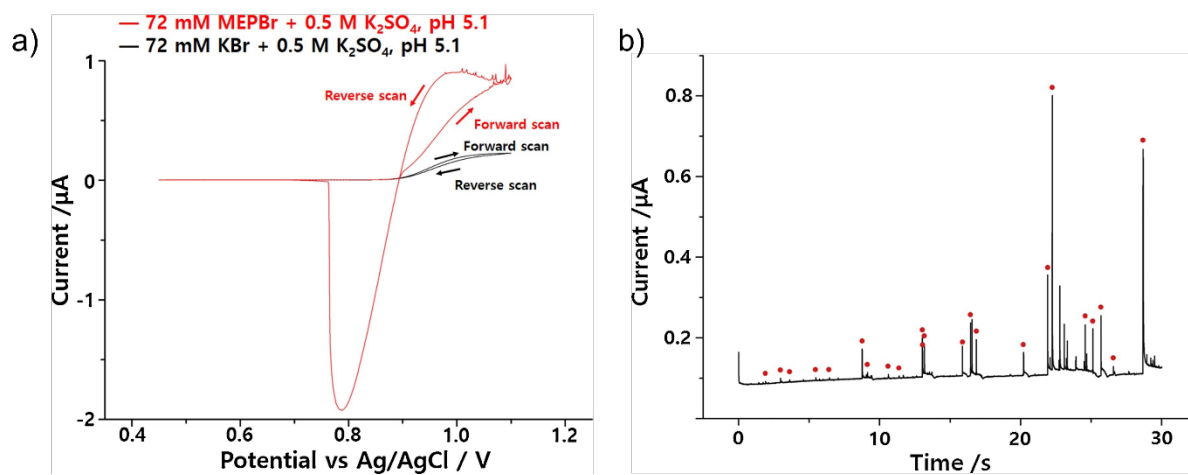
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Fig S7a shows that MEPBr$^+$ starts oxidation at *ca*. 0.85 V and reaches a diffusion-controlled state at >1.0 V, with a much larger current than in aqueous KBr. A reduction peak at *ca*. 0.8 V is observed that corresponds to the reduction of Br^{3-} in the droplets adsorbed on the electrode. **Fig S7b** indicates the droplets' collision time with the electrode along with an increased current due to a higher concentration of Br$^-$ after collision.

References

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