

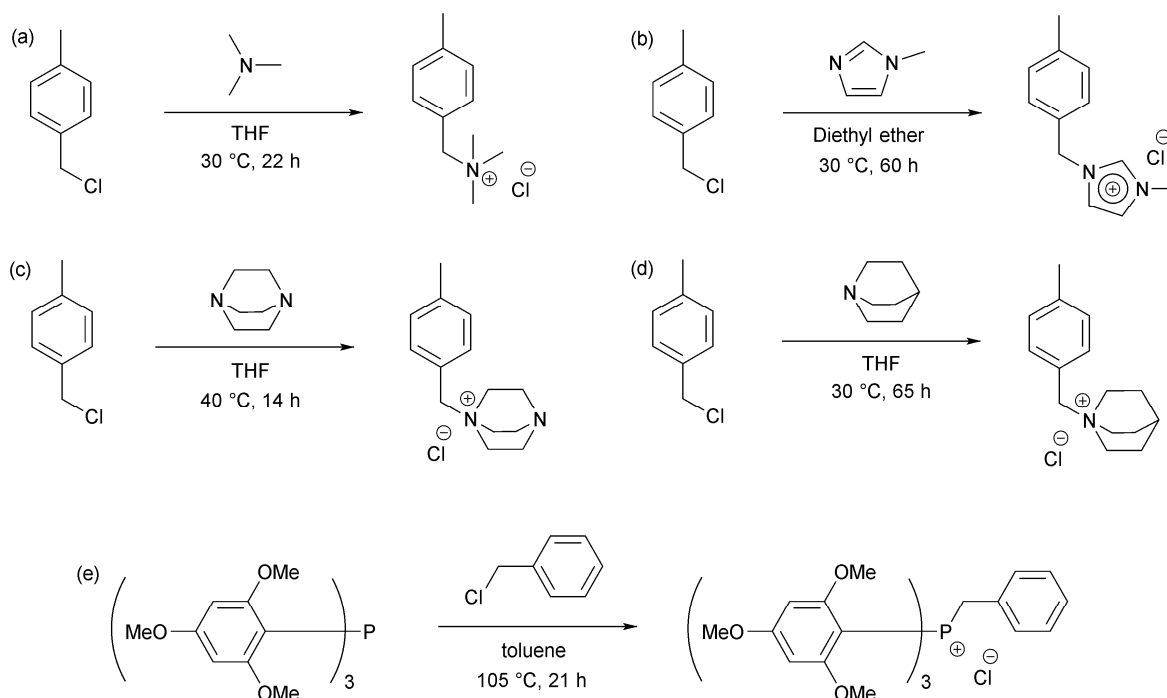
Electronic Supplemental Information (ESI)

Effect of cationic molecules on the oxygen reduction reaction on fuel cell grade Pt/C(20 wt%) catalyst in potassium hydroxide (aq, 1 mol dm⁻³)

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Synthetic Schemes

6-(benzyloxy)-N,N,N-trimethylhexan-1-aminium chloride (BOTMHA) and 1-benzyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (BAABCO) were synthesised as previously reported.¹ 1-(4-methylbenzyl)trimethylammonium chloride (MBTMA), 1-(4-methylbenzyl)-3-methylimidazolium chloride (MBMI), 1-(4-methylbenzyl)-4-aza-1-azoniabicyclo[2.2.2]octane chloride (MBAABCO), 1-(4-methylbenzyl)-1-azoniabicyclo[2.2.2]octane chloride (MBABCO), and benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride (BTTMPP) were synthesised as shown in Scheme ESII.



Scheme ESII The synthesis of: (a) 1-(4-methylbenzyl)trimethylammonium chloride (MBTMA), (b) 1-(4-methylbenzyl)-3-methylimidazolium chloride (MBMI), (c) 1-(4-methylbenzyl)-4-aza-1-azoniabicyclo[2.2.2]octane chloride (MBAABCO), (d) 1-(4-methylbenzyl)-1-azoniabicyclo[2.2.2]octane chloride (MBABCO), and (e) benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride (BTTMPP)

General Experimental

Starting materials, reagents and solvents for reactions were reagent grade and, unless otherwise stated, used as purchased. Toluene was distilled from sodium benzophenone ketyl under nitrogen. Infra-red (IR) spectra were recorded in the range 600-4000 cm⁻¹ using an Agilent Clary 600 FTIR spectrometer fitted with a MKII Golden Gate Single Reflection ATR System. Peaks for contaminant water, absorbed due to the hygroscopic nature of the compounds, have not been noted. NMR spectra were obtained on either a Bruker 500 MHz or Bruker 300 MHz spectrometer. ¹H NMR spectra were referenced to TMS at 0 ppm. The data is given as follows: chemical shift (δ) in ppm, integration, multiplicity, coupling constants (J , accurate to 0.3 Hz). ¹³C spectra were referenced to TMS at 0 ppm. The data is given as follows: chemical shift (δ) in ppm, multiplicity. ³¹P spectra were referenced to phosphoric acid at 0 ppm. The data is given as follows: chemical shift (δ) in ppm, multiplicity. Mass spectrometry (MS) used electrospray ionisation (ESI) and was carried out on either a Waters TOF MS; LCT Classic (Waters) or a Micromass Quattro Ultima Triple Quadrupole Mass Spectrometer (Micromass). The data is given as follows: m/z , % peak height, assignment.

(a) 1-(4-methylbenzyl)trimethylammonium chloride (MBTMA)

To 4-methylbenzyl chloride (2.655 g, 18.9 mmol) was added 100 mL of THF. This mixture was stirred at 30 °C, and an outlet from the vessel was attached to a bath of dilute hydrochloric acid. Trimethylamine gas was bubbled through the mixture over 2 h, and then the vessel was sealed and left for a further 20 h. [The trimethylamine gas was generated by dropping aqueous trimethylamine (45 wt. %) solution onto solid sodium hydroxide, using flowing nitrogen to carry it to the reaction vessel and then into the dilute acid.] The precipitate was washed with THF (2 × 25 mL) then with diethyl ether (2 × 25 mL). The solid was then dried under vacuum (3.06 g, 81%); IR (cm⁻¹) 3027, 2962, 2923, 1635, 1616, 1478; ¹H-NMR (d₆-DMSO) 7.50 (2 H, d, *J*=8.0 Hz), 7.39 (2 H, d, *J*=8.0 Hz), 4.59 (2 H, s), 3.09 (9 H, s), 2.43 (3 H, s); ¹³C NMR (d₆-DMSO) 139.8, 132.7, 129.3, 125.7, 67.0, 51.4, 20.8; MS (Micromass, ESI+) *m/z* = 365 (2%, [M₂³⁷Cl]⁺), 363 (5%, [M₂³⁵Cl]⁺), 165 (11%), 164 (87%, M⁺), 105 (100%, MeC₆H₄CH₂⁺). ¹H NMR data correlate approximately with those given in the literature in a different solvent (CDCl₃).²

(b) 1-(4-methylbenzyl)-3-methylimidazolium chloride (MBMI)

To 1-methylimidazole (5.99 g, 73.0 mmol) was added 25 mL of diethyl ether, and 4-methylbenzyl chloride (8.50 g, 60.4 mmol). The mixture was stirred at 30 °C for 60 h, then cooled over ice and filtered. The solid was washed with diethyl ether (2 × 25 mL), and then dried under vacuum. The solid was recrystallized from THF /i>PrOH to give white crystals (4.72 g, 35%); IR (cm⁻¹) 3131, 3080, 3015, 2985, 2950, 1562, 1517, 1445; ¹H-NMR (d₆-DMSO) ¹H-NMR (d₆-DMSO) 9.57 (1 H, s), 7.88 (1 H, s), 7.78 (1 H, s), 7.38 (2 H, d, *J*=8.0 Hz), 7.21 (2 H, d, *J*=8.0 Hz), 5.44 (2 H, s), 3.88, (3 H, s), 2.29 (3 H, s); ¹³C NMR (d₆-DMSO) 138.1, 136.7, 132.1, 129.4, 128.5, 123.8, 122.2, 51.4, 35.8, 20.7; MS (Micromass, ESI+) *m/z* = 188 (12%), 187 (100%, M⁺), 105 (83%, MeC₆H₄CH₂⁺).

(c) 1-(4-methylbenzyl)-4-aza-1-azoniabicyclo[2.2.2]octane chloride (MBAABCO)

To diazobicyclo[2.2.2]octane (5.09 g, 45.4 mmol) was added 20 mL of THF. This was heated to 40 °C and then a mixture of 4-methylbenzyl chloride (5.31 g, 37.8 mmol) and 25 mL of THF was added over 2 h. The mixture was then left for a further 12 h. The solid was filtered and washed with THF (2 × 25 mL) and diethyl ether (2 × 25 mL). The solid was then dried under vacuum (7.54 g, 79%); IR (cm⁻¹) 3047, 3003, 2968, 2887, 1618, 1574, 1515, 1468, 1457; ¹H-NMR (d₆-DMSO) 7.45 (2 H, d, *J*=7.5 Hz), 7.31 (2 H, d, *J*=7.5 Hz), 4.63 (2 H, s), 3.38 (6 H, t, *J*=7.5 Hz), 3.01 (6 H, t, *J*=7.5 Hz), 2.35 (2.35, s); ¹³C NMR (d₆-DMSO) 139.7, 133.1, 129.4, 124.4, 65.9, 51.3, 44.7, 20.8; MS (Micromass, ESI+) *m/z* = 471 (1%, [M₂³⁷Cl]⁺), 469 (3%, [M₂³⁵Cl]⁺), 218 (28%), 217 (100%, M⁺), 105 (7%, MeC₆H₄CH₂⁺). ¹H and ¹³C NMR data correlate approximately with those given in the literature in a different solvent (CDCl₃).³

(d) 1-(4-methylbenzyl)-1-azoniabicyclo[2.2.2]octane chloride (MBABCO)

To 1-azobicyclo[2.2.2]octane (0.301 g, 2.71 mmol), was added 10 mL of THF, and 4-methylbenzyl chloride (0.425 g, 3.02 mmol). This mixture was stirred at 30 °C for 65 hours. The solid was then washed and filtered with cold diethyl ether (4 x 10 mL), then dried under vacuum (0.559 g, 82.0%). ¹H-NMR (d₆-DMSO) 7.40 (2 H, d, *J*=8.0 Hz), 7.31 (2 H, d, *J*=8.0 Hz), 4.40 (2 H, s) 3.41-3.38 (6 H, m), 2.35 (3 H, s), 2.05-2.01 (1 H, sep, *J*=3.2 Hz), 1.85-1.82 (6 H, m); ¹³C NMR (d₆-DMSO), 139.7, 132.9, 129.4, 124.8, 66.0, 53.5, 23.3, 20.8, 19.5. IR (cm⁻¹) 2992, 2968, 2952, 2904, 2878, 1604, 1513, 1469, 1454; MS (Micromass, ESI) *m/z* = 217 (27%), 216 (100%, M⁺). ¹H and ¹³C NMR data correlate approximately with those given in the literature in a different solvent (CDCl₃).³

(e) Benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride⁴ (BTTMPP)

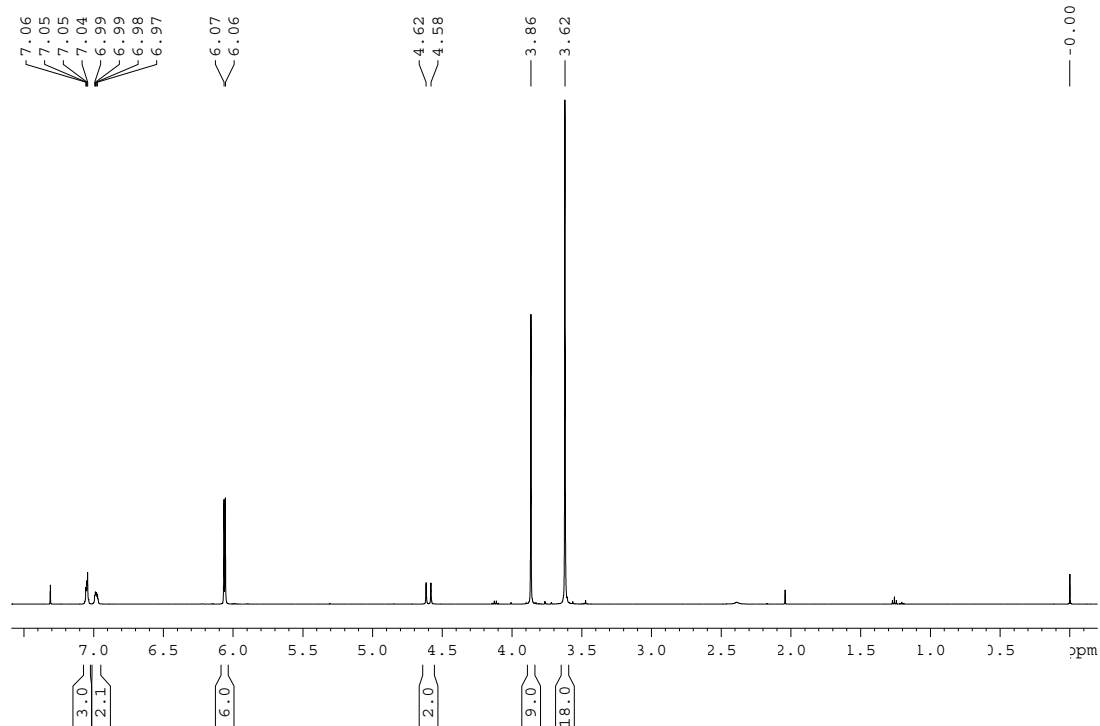
To tris(2,4,6-trimethoxyphenyl)phosphine (3.20 g, 6.36 mmol) was added dry toluene (35 mL) under N₂. Benzyl chloride (BnCl, 0.88 mL, 7.63 mmol) was added and the mixture heated at 105 °C for 21 h after which time a white precipitate formed.⁵ The mixture was allowed to cool to rt and the precipitate was removed by filtration and washed with toluene (20 mL) followed by diethyl ether (2 × 15 mL). The solid was transferred to a flask with the aid of methanol, the solvent was then evaporated and the sample dried *in vacuo*. The resultant solid was recrystallised from ethyl acetate/diethyl ether to give the title compound as white crystals (2.01 g, 50%); m.p. 218-220 °C; IR (cm⁻¹) 2979, 2841, 1594, 1575, 1454, 1413; ¹H-NMR (CDCl₃) 7.07-7.03 (3 H, m), 7.00-6.96 (2 H, m), 6.06 (6 H, d, *J*_{H-P}=4.7 Hz), 4.60 (2 H, d, *J*_{H-P}=17.3 Hz), 3.86 (9 H, s), 3.62 (18 H, s); ¹³C NMR (CDCl₃) 165.6 (d, *J*_{C-P}=1.6 Hz), 163.4 (d, *J*_{C-P}=1.2 Hz), 133.2 (d, *J*_{C-P}=6.8 Hz), 129.2 (d, *J*_{C-P}=8.7 Hz), 127.9 (d, *J*_{C-P}=1.9 Hz), 126.9 (d, *J*_{C-P}=3.1 Hz), 92.9 (s), 92.1 (s), 90.9 (d, *J*_{C-P}=7.3 Hz), 55.9 (s), 55.9 (d, *J*_{C-P}=2.8 Hz); ³¹P NMR (D₂O) 5.49 (m); MS (Waters, ESI+) *m/z* = 623 (100%, M⁺).

References to ESI

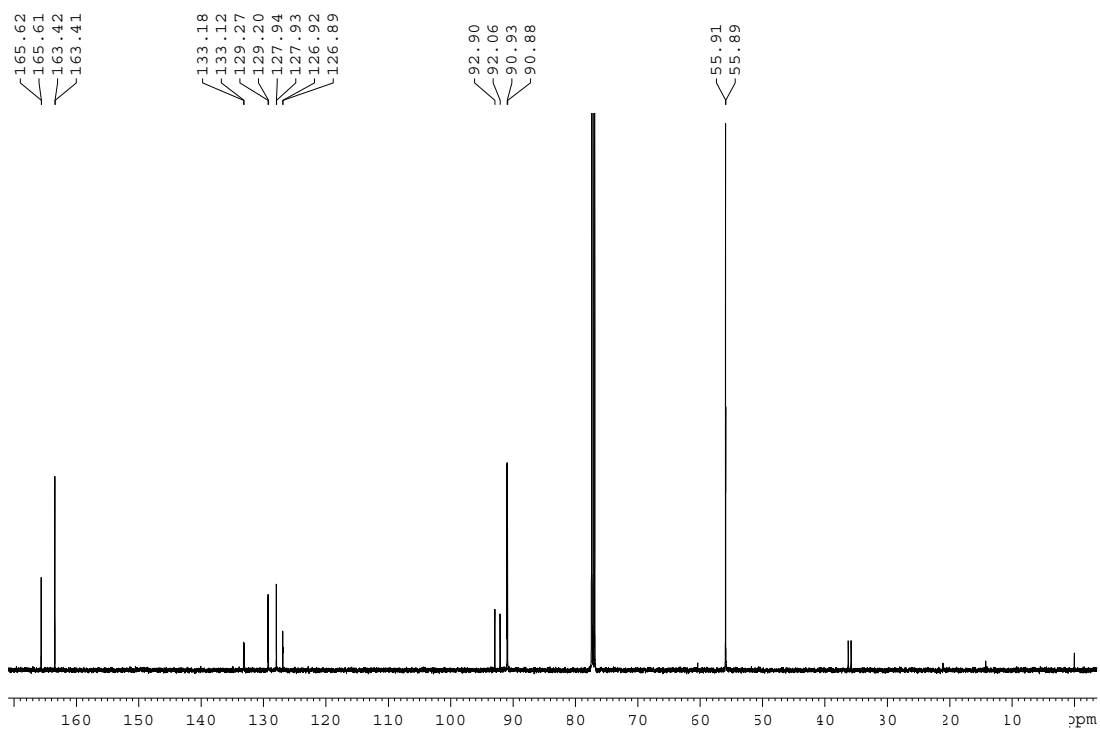
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Figure ESI2 Example NMR spectra: benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride (**BTMPP**)

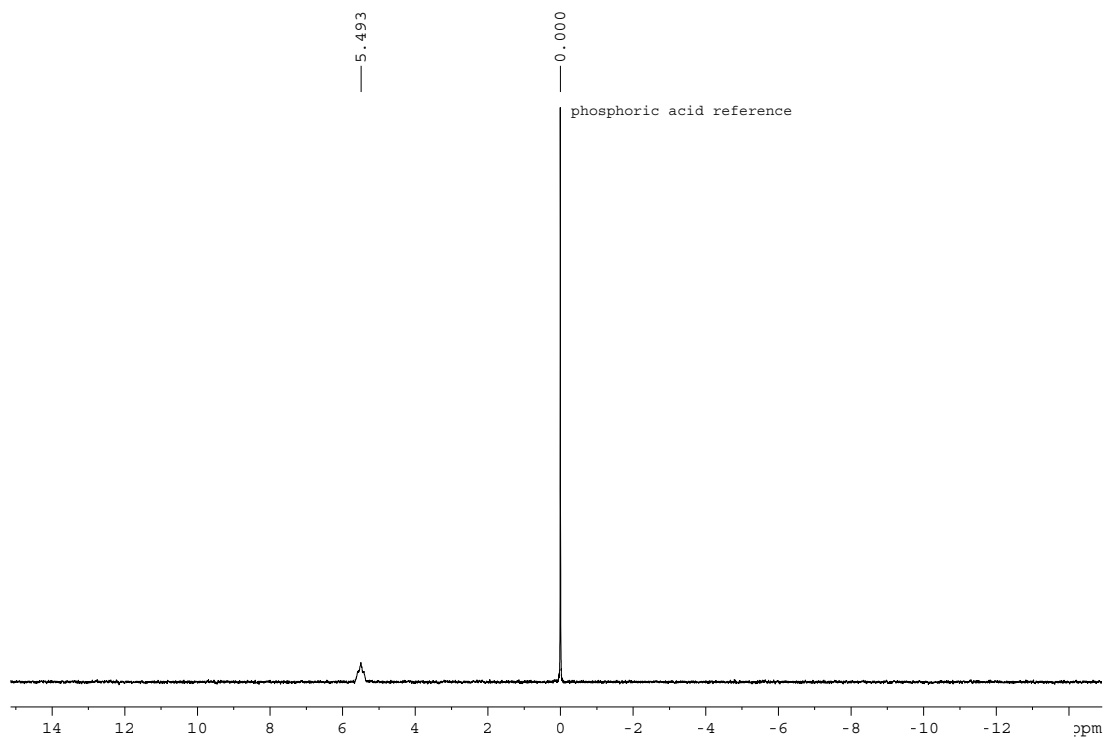
Benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride ¹H NMR (500 MHz, CDCl₃)



Benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride ¹³C NMR (125 MHz, CDCl₃)



Benzyltris(2,4,6-trimethoxyphenyl)phosphonium chloride 31P NMR (202 MHz, D2O)



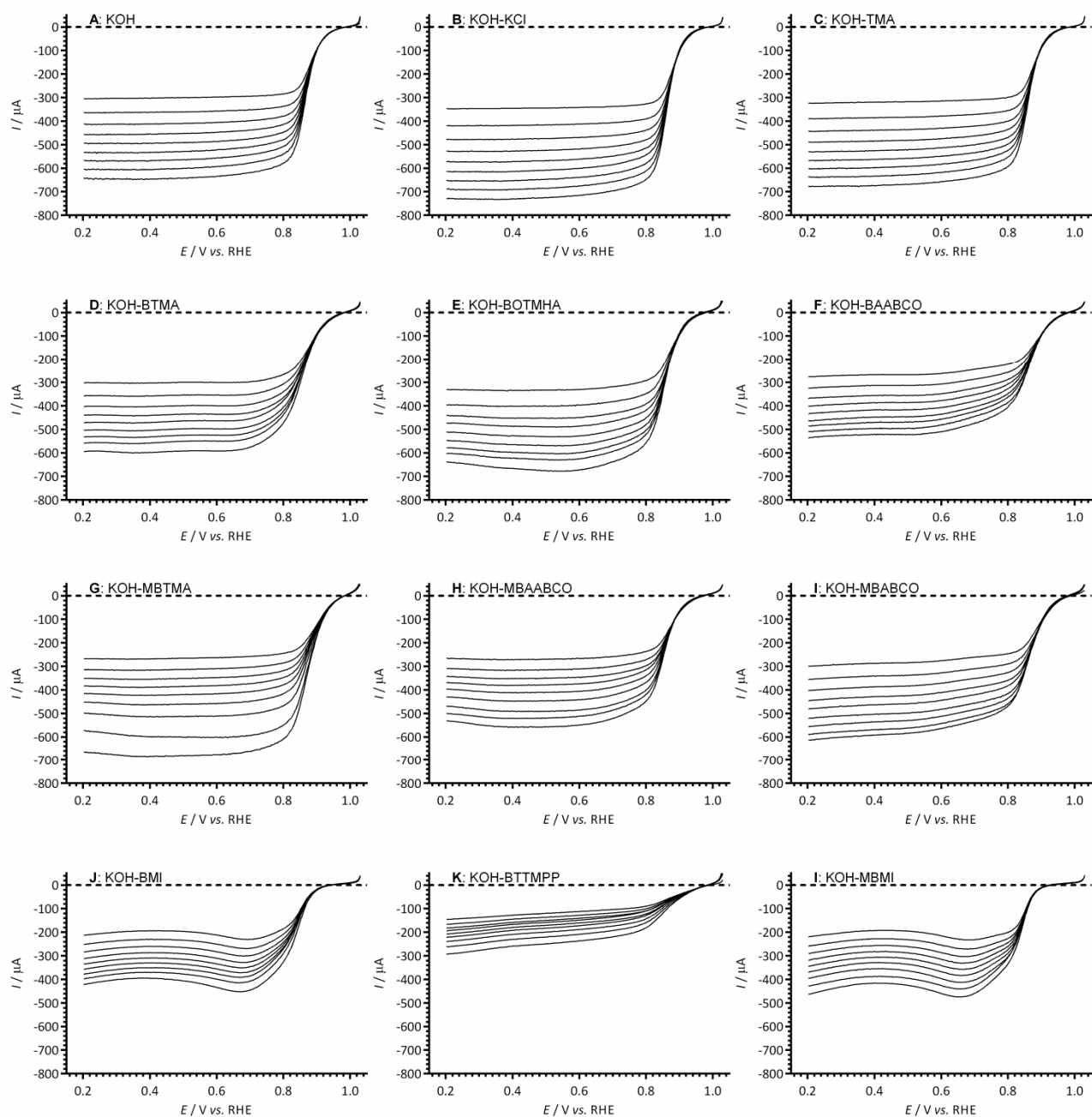


Fig. ES13 The linear sweep hydrodynamic voltammograms at 25 °C of a Pt/C-coated GC disk electrode in the O₂-saturated alkaline electrolytes with and without addition of 1 mmol dm⁻³ of KCl or the model cationic head-group molecules. Scan rate = 5 mV s⁻¹ and RDE rotation rates in the range 400 - 2000 rpm. This is the raw data linked to Figure 6 and 7 and Table 1 in the main article.

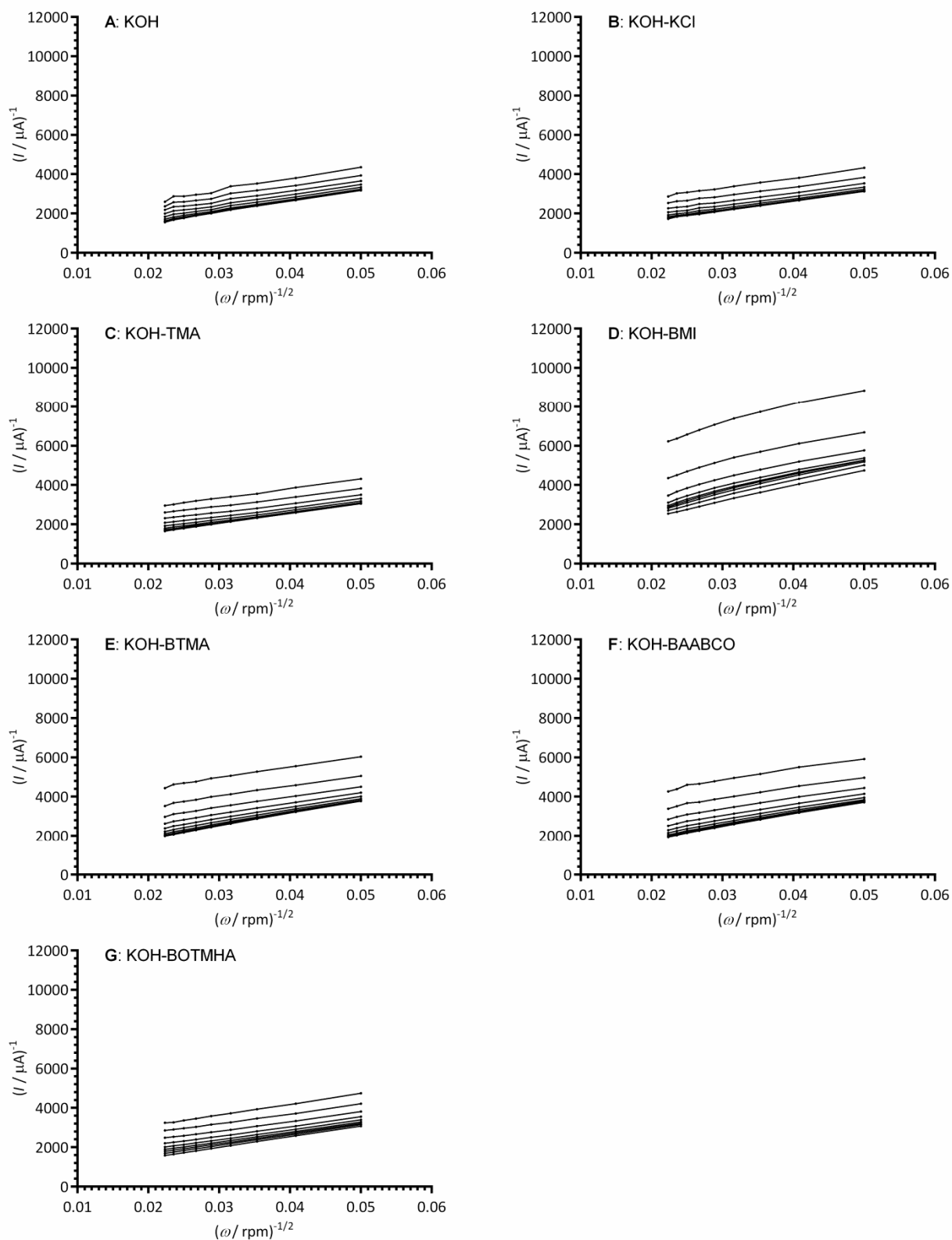


Fig. ESI4 The Koutecky - Levich plots of a Pt/C-coated GC disk electrode in the O_2 -saturated alkaline electrolytes at $25^\circ C$ with and without addition of 1 mmol dm^{-3} of KCl or the model cationic head-group molecules. Scan rate = 5 mV s^{-1} and RDE rotation rates in the range 400 - 2000 rpm. This is the raw data linked to Figures 6 and 7 and Table 1 in the main article.