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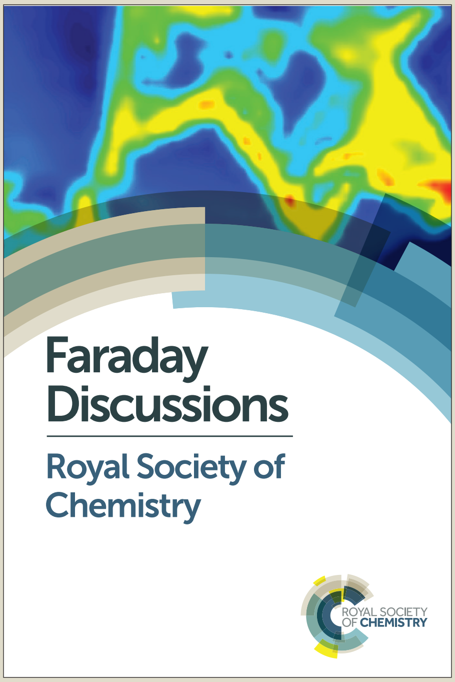

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Improving the efficiency of electrochemical CO_2 reduction using immobilized manganese complexes

James J. Walsh[‡], Charlotte L. Smith[‡], Gaia Neri, George F. S. Whitehead, Craig M. Robertson and Alexander J. Cowan*

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Abstract: Immobilization of [Mn(bpy)$(CO)_3$Br], (**1**) and [Mn(bpy(^{t}Bu)$_2$)$(CO)_3$Br] (**2**, where (bpy(^{t}Bu)$_2$) = 4,4’-di-*tert*-butyl-2,2’-bipyridine) in Nafion/multi-walled carbon nanotube films (MWCNT) on glassy carbon yielded highly active electrodes for the reduction of CO_2 to CO in aqueous solutions at pH 7. Films incorporating **2** have significantly improved selectivity towards CO_2, with CO:H_2 ~1 at -1.4 V *vs*. SCE, exceeding that for the previously reported **1**/MWCNT/Nafion electrode. Furthermore, we report the synthesis and subsequent electrochemical characterization of two new substituted Mn(I) bipyridine complexes, [Mn(bpy(COOH)$_2$)$(CO)_3$Br] (**3**) and [Mn(bpy(OH)$_2$)$(CO)_3$Br] (**4**) (where (bpy(COOH)$_2$) = 4,4’-di-carboxy-2,2’-bipyridine and (bpy(OH)$_2$) = 4,4’-di-hydroxy-2,2’-bipyridine). Both **3** and **4** were found to have some activity towards CO_2 in acetonitrile solutions, however once immobilized in Nafion membranes CO_2 reduction was found to not occur at significant levels.

1 Introduction

Carbon capture coupled with utilisation is a potentially sustainable route to useful feedstocks and fuels such as CO, HCOOH, CH_3OH and CH_4. Electrocatalytic CO_2 reduction is a particularly attractive utilisation pathway as the energetic input for CO_2 reduction can come from renewable sources of power (e.g. wind, solar), with the production of chemical fuels offering a solution to the intermittent nature of such renewables. Whilst the direct one electron reduction of CO_2 is extremely challenging, occurring at -2.15 V *vs*. SCE (pH 7),[1] the multielectron, multiproton reduction of CO_2 can be achieved at more moderate potentials ($CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$, -0.77 V *vs*. SCE, pH 7).[2] However in order to achieve high Faradaic efficiencies for CO_2 reduction a suitably selective electrocatalyst for CO_2 is required as the production of H_2 ($2H^+ + 2e^-$ $\rightarrow H_2$, -0.65 V *vs*. SCE, pH 7) often dominates in protic solvents.

Homogenous electrocatalysts based on *fac*-[M(bpy)$(CO)_3$X] (where M = Re, Mn; X = Cl^-, Br^- and bpy = 2,2'-bipyridine) have been widely studied for the reduction of CO_2 to CO due to their high selectivities and ease of synthetic modification.[3, 4] Early studies concentrated on [Re(bpy)$(CO)_3$Br] and its derivatives;[5, 6] however in 2011 it was shown that the lower cost manganese analogue, [Mn(bpy)$(CO)_3$Br] **1**, is also an excellent homogeneous electrocatalyst for the reduction of CO_2 to CO.[7] Using **1**, CO_2 reduction was reported to occur at a potential (*ca*. -1.4 V *vs*. SCE) significantly positive of that required using the analogous rhenium complex, providing that a suitable Brønsted acid such as water was present in the organic solvent (typically CH_3CN or DMF). A range of catalysts of the form [Mn^I(L)$(CO)_3$X] (L = bpy,[7] 4,4' or 6,6' -disubstituted-2,2'-bipyridine)[8, 9] have since been reported with the aim of improving both the turnover frequency (TOF) and overpotential for CO_2 catalysis using **1** and amongst the most active is [Mn(bpy(^{t}Bu)$_2$)$(CO)_3$Br] (**2**, where (bpy(^{t}Bu)$_2$ = 4,4'-di-*tert*-butyl-bipyridine). **2** has been reported to have a TOF of 340 s^{-1} at -2.2 V *vs*. SCE for CO production in the presence of 1.4 M 2,2,2-trifluoroethanol (TFE), approximately 300 times higher than that of complex **1**, although it should be noted that the onset for catalysis is *ca*. 200 mV cathodic of **1**.[8] Detailed electrochemical, spectroscopic and theoretical studies have identified several key aspects of the mechanism of CO_2 reduction using **1** and **2**.[8, 10, 11, 12] It is known that upon initial one-electron reduction, bromide loss and dimerization with another reduced moiety to yield [Mn(bpy)$(CO)_3$]$_2$ rapidly occurs. Reduction of the dimer then leads to the formation of the primary active catalyst, [Mn(bpy)$(CO)_3$]$^-$.[7] Using 2D-EPR measurements it has also been shown that with a closely related complex, [Mn(bpy(Me)$_2$)$(CO)_3$Br] (where (bpy(Me)$_2$) = 4,4'-dimethyl-2,2'-bipyridine), CO_2 reduction can also occur *via* a second pathway involving direct CO_2 and H^+ addition to the dimeric species formed upon reduction.[13] Due to the propensity of the [Mn^I(L)$(CO)_3$X] complexes to dimerize upon reduction, Kubiak *et al*. developed a complex with bulky bipyridine ligands, [Mn(mesbpy)$(CO)_3$Br] (where mesbpy = 6,6'-dimesityl-2,2'-bipyridine),[9] that was too sterically hindered to undergo dimerization, with the aim of modifying the catalytic mechanism. Promisingly, such an approach led to a large enhancement in TOF (*ca.* 5000 s^{-1}, 1.4 M TFE at *ca*. -1.8 V *vs*. SCE), although no improvement in onset potential for catalysis was achieved when compared to **1**. In addition to studies on the modification of the bpy ligand, several groups have also explored the use of *N*-heterocyclic carbenes,[14, 15] nonaromatic α-diimine ligands,[16, 17] hydroxyphenol-substituted bpy[18] and pentadentate chelating[19] ligands with Mn(I) centres for use as potential CO_2 reduction catalysts with varying degrees of success.

To date, studies on $[Mn^I(L)(CO)_3X]$ derivatives have concentrated on the development of the homogenous catalyst in an aprotic organic solvent doped with a proton source such as water, methanol or TFE. Here we address the development of this class of catalysts for use in an immobilized, recyclable form in aqueous solvents at pH 7. Nafion membranes have been used extensively as catalyst supports as they are chemically stable proton conductors with high permeability towards water. Previous examples of Nafion-supported molecular CO_2 reduction catalysts include $[Re(bpy)(CO)_3Br]$,[20] $[Ni(cyclam)]^{2+}$,[21] and a Cobalt tetramethylpyridoporphyrazine;[22] however the current densities reported during sustained electrolysis were typically low (< 0.1 mA cm^{-2}) due to the low electrical conductivity of the Nafion support. Recently we reported on an immobilized high surface area **1**/MWCNT/Nafion cathode (where MWCNT = multi-walled carbon nanotubes) that achieved CO and H_2 production in ratios suitable for use as syngas ($CO:H_2$ = 1:2) at greatly increased sustained current densities (0.7 mA cm^{-2}) although with a relatively high overpotential (η = 0.63 V, -1.4 V *vs*. SCE) at pH 7.[23] MWCNT have been previously used as supports in a number of elegant studies on molecular catalysts for water oxidation,[24] water reduction,[25] and CO_2 reduction[26] where the catalysts are either directly grafted to, or modified with pyrene groups to enable interaction with, the MWCNT. In contrast, we previously employed a very simple, potentially low-cost approach where MWCNT were added to a polymer/catalyst solution before drop-casting onto an electrode surface. It has been reported that a weak π-π interaction can occur between bpy ligands and MWCNT,[27, 28] and in our co-cast film FTIR spectroscopy indicated the presence of an interaction between the bipyridine ligand of **1** and the high surface area support,[23] although the exact nature of this MWCNT-**1** interaction remains under investigation. Critically the use of the high surface area report led to catalytic current densities an order of magnitude higher than could be achieved for the **1**/Nafion membrane alone. In this contribution, we report a **1**/MWCNT/Nafion electrode that operates at more than twice the current density (1.79 mA cm^{-2}, $CO:H_2$ ~ 0.3 at -1.4 V *vs*. SCE) of our previous study. We also examine a range of new $[Mn(L)(CO)_3X]$/MWCNT/Nafion films leading to an electrode with a high selectivity towards CO_2 over H^+ reduction even in aqueous solutions.

We also synthesise and study in solution two previously unreported $[Mn^I(L)(CO)_3X]$ complexes, modified at the 4,4'- position of the bipyridine ligand, $[Mn(bpy(COOH)_2)(CO)_3Br]$ (**3**) and $[Mn(bpy(OH)_2)(CO)_3Br]$ (**4**) (where $(bpy(COOH)_2)$ = 4,4'-di-carboxy-2,2'-bipyridine and $(bpy(OH)_2)$ = 4,4'-di-hydroxy-2,2'-bipyridine), see

Fig. 1. Complex **3** is of interest as a route to overcoming the relatively high overpotential for the reduction of CO_2 by **1** (η ~ 580 mV in CH_3CN/H_2O, 95:5).[29] The addition of electron-withdrawing groups (EWG) to the 4,4'- position of the bipyridine ligand has been shown previously to stabilise the first reduction of the analogous rhenium complex,[30] and it is anticipated that a similar anodic shift in the reduction potentials of **3** may occur. Conversely complex **4** was identified due to the unique ability of the 4,4'-di-hydroxy-2,2'-bipyridine to act as a "push-pull" ligand, where deprotonation of the hydroxyl group leads to the formation of an oxyanion bipyridine which has been shown with $[Ru(bpy)_2(bpy(OH)_2)]^{2+}$ to be a strong electron donor.[31] This may be a promising approach as the high catalytic activity of **2** is proposed to be related to the increased electron density at the Mn centre due to the presence of the bulky electron-donating *t*-butyl groups.[8] During the preparation of this manuscript the analogous rhenium complex, $[Re(bpy(OH)_2)(CO)_3Br]$ was reported to have comparable activity to $[Re(bpy(^tBu)_2)(CO)_3Br]$ for the production of CO.[32] Following homogenous studies in aprotic solvents we incorporated both the new complexes (**3**, **4**) and the current benchmark catalysts **1** and **2**, in high surface area $[Mn(L)(CO)_3X]$/MWCNT/Nafion films, leading to the report of both a new **1**/MWCNT/Nafion electrode that operates at improved current densities (1.79 mA cm^{-2}, $CO:H_2$ ~ 0.3 at -1.4 V *vs*. SCE) and a **2**/MWCNT/Nafion electrode with improved selectivity for CO_2 reduction ($CO:H_2$ ~ 1 at -1.4 V *vs*. SCE), compared to our previous report.[23]

2. Experimental

Materials and methods

Bromopentacarbonylmanganese(I), 2,2'-bipyridine, 4,4'-di-hydroxy-2,2'-bipyridine, 4,4'-di-carboxy-2,2'-bipyridine and 4,4'-di-*tert*-butyl-2,2'-bipyridine were purchased from Sigma-Aldrich and used as received. Nafion (5 % w/w in lower alcohols, Sigma-Aldrich), sodium phosphate monobasic (≥ 99 %, Sigma-Aldrich), sodium phosphate dibasic (≥ 99 %, Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (TBA PF_6, 99 %, electrochemical grade) and multi-walled carbon nanotubes (MWCNT > 98 % carbon, 6 - 13 nm × 2.5 - 20 µm, Sigma-Aldrich) were used as received. Acetonitrile (chromatographic grade, Sigma-Aldrich) was dried over molecular sieves (3 Å) prior to use and stored under argon. Milli-Q water (18.2 MΩ) was used for all aqueous solutions. CO_2 and argon (CP and pureshield grade respectively) were purchased from BOC.

Synthesis of complexes

All syntheses were carried on in the dark and under an atmosphere of Ar. [Mn(bpy)$(CO)_3$Br] and [Mn(bpy(^{t}Bu)$_2$)$(CO)_3$Br] were synthesized and characterized according to literature methods (details in ESI).

[Mn(bpy(COOH)$_2$)(CO)$_3$Br], 3: A solution of 4,4'-dicarboxy-2,2'-bipyridine (180 mg, 0.74 mmol) in 8 ml of methanol was added to a solution of $Mn(CO)_5Br$ (200 mg, 0.72 mmol) in toluene (20 ml). The mixture was refluxed for 90 minutes at 60°C, then kept in the fridge overnight. The orange-red precipitate that formed was filtered off and washed with cold diethyl ether, and the resulting red solution was rotary evaporated to dryness to yield a bright red powder. The final product was recrystallized from hot acetone and hexane, and dried *in vacuo* for 48 hours. Crystals of suitable quality for diffraction studies were grown by slow vapour diffusion of *n*-hexane into concentrated THF solutions of the complex. Yield = 46.84 %; ^{1}H-NMR (300 MHz, DMSO-d_6): δ ppm 7.17 (br. d, *J* = 1.00 Hz, 2 H) 8.09 (br. s, 2 H) 9.41 (br. s, 2 H) 9.68 (m, 1 H); FTIR (CH_3CN/H_2O, 95:5): 2030, 1940, 1931 cm^{-1}; Anal. calcd. for $C_{15}H_8BrMnN_2O_7\cdot H_2O$: C, 37.45; H, 2.10; N, 5.82. Found: C, 37.30; H, 1.81; N, 5.57. m/z (ESI); 415 ([M-Br$^-$ + HOMe]$^+$), 383 ([M-Br$^-$]$^+$).

[Mn(bpy(OH)$_2$)(CO)$_3$Br], 4: A solution of 4,4'-dihydroxy-2,2'-bipyridine (140 mg, 0.74 mmol) in 8 ml of methanol was added to a solution of $Mn(CO)_5Br$ (200 mg, 0.72 mmol) in toluene (20 ml). The mixture was refluxed for 90 minutes at 60°C, and then placed in the fridge overnight. The orange-red precipitate that formed was filtered off and washed with cold diethyl ether, and the resulting yellow solution was rotary evaporated to dryness to yield a yellow powder. The final product was recrystallized from hot acetone and hexane, and dried *in vacuo* for 48 hours. Crystals of suitable quality for diffraction studies were grown by slow vapour diffusion of *n*-hexane into concentrated acetone solutions of the complex. Yield = 50 %; ^{1}H-NMR (300 MHz, CD_3OD): δ ppm 7.05 (dd, *J* = 1.00 Hz, 2 H) 7.70 (dd, *J* = 1.00 Hz, 2 H) 8.86 (dd, *J* = 1.00 Hz, 2 H); FTIR (CH_3CN): 2024, 1930, 1915 cm^{-1}; Anal. calcd. for $C_{13}H_8BrMnN_2O_5$:C, 38.36; H, 1.98; N, 6.88. Found: C, 38.20; H, 1.97; N, 6.78. m/z (ESI); 359 ([M-Br$^-$ + HOMe]$^+$), 327 ([M-Br$^-$]$^+$).

Electrochemical measurements: A PalmSens^3 potentiostat, glassy carbon disc (A = 0.0717 cm^2, BASi) working electrode and a Pt basket counter electrode were used in all experiments. An Ag/AgCl (3 M KCl, BASi) or a freshly cleaned Ag wire, calibrated *vs.* Fc/Fc$^+$, was used as the reference electrode in water or organic electrolytes, respectively. Bulk electrolysis measurements were carried out in a custom glass H-Cell with the Pt counter electrode separated from the working and reference electrodes by a fine glass frit. All samples were thoroughly purged with either Ar or CO_2 for 30 minutes prior to use, and kept in the dark throughout the experiments. Gas chromatography (GC) was performed using an Agilent 6890N employing N6.0 He (BOC) as the carrier gas (5 ml min^{-1}). A 5 Å molecular sieve column (ValcoPLOT, 30 m length, 0.53 mm ID) and a pulsed discharge detector (D-3-I-HP, Valco Vici) were employed. CO and H_2 peak areas were quantified by comparison to multiple calibrant gas injections (500 ppm H_2 and 200 ppm CO in helium (STG)). NMR spectra were recorded on a Bruker Advance 400 NMR spectrometer operating at 400 MHz (^{1}H) or 101 MHz (^{13}C) or on a Bruker Advance 300 NMR spectrometer operating at 300 MHz (^{1}H) using an amber NMR tube. ESI-MS and elemental analyses were performed by the University of Liverpool analytical services. UV-Vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer using 1 cm or 1 mm pathlength quartz cuvettes. FTIR spectra were recorded on a Bruker Vertex instruments either in solution, cast on a CaF_2 plate, or using a diamond ATR crystal (Pike). Spectroelectrochemistry (SEC) was carried out using a liquid IR-SEC cell with a pathlength of approximately 0.2 mm that has been reported elsewhere.[33] The working and counter electrodes were Pt minigrids and a silver wire was used as the pseudo-reference. The concentration of complex was approximately 0.1 mM in dry CH_3CN containing 0.1 M TBA PF_6 electrolyte, which was recrystallized from absolute ethanol and dried overnight on a Schlenk line at 70ºC prior to use.

Preparation of membrane supported catalyst electrodes: The membrane was prepared from a sample of complex **1-4** dissolved in 0.5 ml of acetonitrile, mixed with 0.5 ml of a Nafion/alcohol solution (5.0 % w/w) in a 1:1 volume ratio in the dark to make up a 1.4 x 10^{-2} M solution. In a typical experiment 5 µl of this yellow solution, corresponding to 70 nmol of complex in 2.5 % Nafion/CH_3CN 1:1, was transferred onto a polished glassy carbon electrode using an autopipette and left to dry in air in the dark for at least 2 hours at a constant temperature (maintained at 25^{o}C), yielding a continuous pale yellow polymer film that completely coated the working area. It has been observed that the temperature control is critical in obtaining highly active films (full discussion in the ESI). Casting solutions for MWCNT/Nafion/complex films were prepared as above with the addition of MWCNT in a 1:1 mass ratio with the complex to the casting solution, followed by sonication in the dark for 15 minutes. 5 µl of this darkly coloured casting solution was then transferred onto a polished glassy carbon electrode using an autopipette and left to dry in air in the dark for at least 2 hours. Following bulk electrolysis experiments the aqueous electrolyte was studied using UV/Vis spectroscopy to confirm that complex leaching from the membrane into the electrolyte had not occurred. Morphological characterization was performed on films cast on glass slides using an Ambios Technology XP200 profilometer.

3. Results and Discussion

Synthesis and Characterisation: Complexes **3** and **4** are readily prepared by modification of the existing synthetic route of **1**.[7] It is noted that complex **3** is particularly light sensitive, undergoing rapid decomposition within minutes in solution under ambient light, therefore all electrochemical experiments are carried out in the dark. Both **3** and **4** have been characterised using FTIR spectroscopy which shows three *ν*(CO) bands corresponding to *fac*-tricarbonyl species (Table 1) in line with the single crystal structures, Fig. 1.

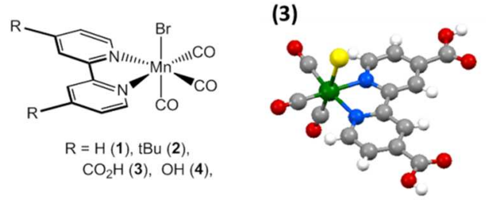

Fig. 1: [Mn^I(L)(CO)$_3$X] complexes under study, and single crystal X-ray structures of **(3)** [Mn(bpy(COOH)$_2$)(CO)$_3$Br] and **(4)** [Mn(bpy(OH)$_2$)(CO)$_3$Br], with solvent atoms omitted for clarity (details in ESI).

Due to the limited solubility of **3** in acetonitrile all experiments using this complex are carried out in the presence of 5 % water. We observe ν(CO) bands at 2030, 1940 and 1931 cm^{-1} for **3** in CH_3CN/H_2O (95:5), with the increase in the ν(CO) frequencies compared to complex **1** indicating decreased electron density at the Mn centre due to the introduction of the electron withdrawing carboxylic acid group at the 4,4' position of the bipyridine ligand.[30] In neat acetonitrile complex **4** has ν(CO) bands at 2024, 1930 and 1915 cm^{-1}, with the decrease in frequency of the stretches versus **1** indicating that the introduction of the hydroxyl groups to the bipyridine ligand has increased the electron density at the metal centre in **4**. The magnitude of the shift of the ν(CO) bands in **4** is very similar to that previously observed, and reproduced here also, for **2**.[8] Solvolysis of the Mn-Br bonds in the case of **4** occurs rapidly in the dark leading to the formation of the solvent complex [Mn(bpy(OH)$_2$)(CO)$_3$(CH$_3$CN)]$^+$ (ν(CO) 2045, 1955 and 1944 cm^{-1}, Fig. S3), which has been seen previously for this class of complex.[15, 34] It has been previously reported that *fac*-[Mn(bpy)(CO)$_3$Br] can undergo photochemical transformation to *mer*-[Mn(bpy)$(CO)_3$Br], which has ν(CO) at 2043 (vw), 1948 (s) and 1903 (m) in THF.[35] We rule out the formation of *mer* complexes of **4** due to the relative intensities of the three new ν(CO) stretches formed upon solvation, which are all of similar intensity, indicating the presence of a *fac*-tricarbonyl species.

Complex	*E* 1st (V *vs*. SCE)	*E* 2nd (V *vs*. SCE)	ν(CO) (cm^{-1})			Solvent
1	-1.24	-1.46	2027	1933	1924	CH_3CN
2	-1.39	-1.57	2025	1930	1921	CH_3CN
3	-1.07	-1.41	2030	1940	1931	CH_3CN/H_2O
4	-1.38^a	-1.73^a	2024	1930	1915	CH_3CN

Table 1: Infrared carbonyl stretching frequencies and reduction potentials for complexes **1-4** in CH_3CN, and reduction potentials of complexes **1-4** in CH_3CN or CH_3CN/H_2O (95:5) containing 0.1 M TBA PF_6 electrolyte. *a*: The first reductions of **4** are proposed to be primarily based on the bpy ligand (see Figs. 3 and 4).

Electrochemical characterisation of complex 3: The electrochemistry of **1** and **2** in CH_3CN has been reported previously,[7, 8] but the cyclic voltammetry of **1** is also shown in Fig. 2 (a) to allow comparison to the previously unreported complex **3**, Fig. 2(b). Initial reduction of **1** at -1.24 V in anhydrous CH_3CN results in bromide loss followed by fast dimerization to form $[Mn(bpy)(CO)_3]_2$ which is reduced at -1.46 V to form the catalytically active species, $[Mn(bpy)(CO)_3]^-$. In anhydrous CH_3CN, oxidation of $[Mn(bpy)(CO)_3]^-$ can occur at -1.08 V leading to dimer formation, which is oxidised at -0.21 V.[7] In the presence of water, solvolysis of the Mn-Br bond occurs and the reduction of $[Mn(bpy)(CO)_3(S)]^+$ to form the dimer is also observed at -1.11 V.

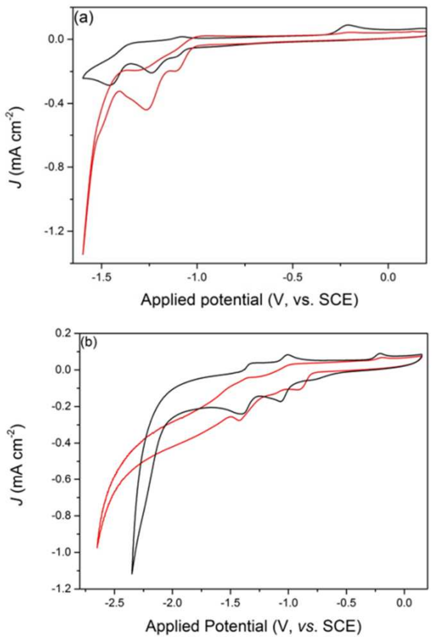

Fig. 2 (a): Solution phase CVs of the parent complex **1** under Ar (black) and CO_2 (red). (b) CVs of complex **3** under Ar (black) and CO_2 (red). Supporting electrolyte was 0.1 M TBA PF_6 in CH_3CN/H_2O (95:5), *v* = 100 mV/s.

Spectroelectrochemical measurements which would be required to confirm the chemical nature of the species produced in analogous experiments with **3** were not possible due to excessive H_2 production occurring in the spectroelectrochemical cell (5 % H_2O in CH_3CN is required to solubilise **3**). The similarities in the cyclic voltammograms of **1** and **3** allow the following tentative assignments to be made by analogy (Fig. 2 (b)). Under argon, the reduction at -1.07 V is assigned to complex **3**, with the shoulder at *ca*. -0.8 V *vs*. SCE in CH_3CN/H_2O due to $[Mn(bpy(COOH)_2)(CO)_3(Solv)]^+$, Fig. 2 (b). The significant anodic shift of the reduction potentials of both the cationic solvent complex (-0.80 V) and the bromide complex (-1.07 V) of **3** compared to **1** indicates that the electron withdrawing carboxylic acid groups are able to stabilise the reduced complex as hypothesised. In light of the precedent for similar $[Mn^I(L)(CO)_3X]$ complexes to dimerize following initial reduction, it is proposed that the two-electron reduction of the dimer $[Mn(bpy(COOH)_2)(CO)_3]_2$ occurs at -1.41 V to form $2[Mn(bpy(COOH)_2)(CO)_3]^-$, with re-oxidation of $[Mn(bpy\text{-}COOH)(CO)_3]^-$ and the subsequently formed dimer occurring at -1.00 and -0.21 V, respectively. Our assignment of the formation of the proposed active catalyst $[Mn(bpy(COOH)_2)(CO)_3]^-$ by dimer cleavage at -1.41 V is supported by the enhanced current in the presence of CO_2, which is particularly pronounced at slower scan rates (Fig. S8). However we are unable to definitively rule out other assignments, including the direct reduction of $[Mn(bpy(COOH)_2)(CO)_3]$ in the absence of dimerization, or the reduction of a manganese hydride species as has been previously proposed by Gobetto *et al.* for a $[Mn^I(L)(CO)_3X]$ complex containing hydroxyl groups.[36] It is notable that, although present, the current enhancement achieved under CO_2 with **3** in solution is small compared to that seen for **1** (Fig. 2), indicating a low catalytic TOF.[8] $[Re(bpy(COOH)_2)(CO)_3Cl]$ has previously been explored as a potential CO_2 reduction electrocatalyst, but no current enhancement in the presence of CO_2 was observed,[30] and it is likely that the reduced nucleophilic nature of the active complex here formed upon reduction of **3**, due to the presence of the EWG, is also a significant factor in decreasing the activity towards CO_2 reduction. Nonetheless, despite the reduced activity the promising anodic shift in reduction potentials of **4** warrants the study of the complex in a polymer supported electrode.

Electrochemical characterisation of complex 4: The cyclic voltammetry of **4** in anhydrous CH_3CN under argon at 100 mV s^{-1} is not typical of that observed for other $[Mn(L)(CO)_3Br]$ complexes.[7, 8] The CVs in Fig. 3 show the presence of reductions at -1.38, -2.01 and -2.20 V *vs*. SCE (labelled processes I, III and IV in Fig. 3), in addition to a scan rate dependent feature at -1.73 V *vs*. SCE (II), which becomes increasingly prominent at higher scan rates (Fig. S6).

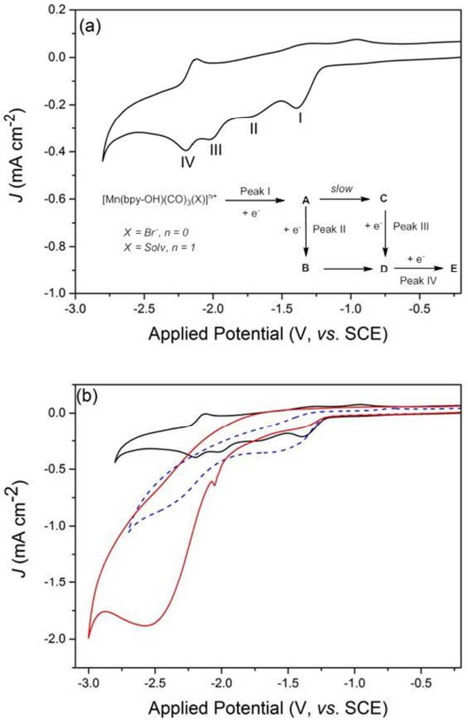

Fig. 3 (a): Cyclic voltammetry of **4** (~ 1 mM) in Ar-purged CH_3CN. Inset shows the proposed electrochemical scheme. (b) Cyclic voltammetry of **4** (~ 1 mM) in CH_3CN /Ar (black), CH_3CN/CO_2 (red) and CH_3CN/H_2O (95:5)/CO_2 (blue). All scan rates were 100 mV/s, supporting electrolyte was 0.1 M TBA PF_6.

Whilst this manuscript was under preparation an IR-SEC study of the related complex [Re(bpy(OH)$_2$)(CO)$_3$Cl] was reported, with the modified bpy ligand being able to undergo two reductive deprotonation steps to form [Re(bpy(OH)(O$^-$)(CO)$_3$Cl]$^-$ and [Re(bpy(O$^-$)$_2$)(CO)$_3$]$^-$, with assignments based upon DFT calculations and IR analysis of chemically deprotonated complexes.[32] IR-SEC indicates that the behaviour of the equivalent Mn complex (**4**) is also similar, Fig. 4. At open circuit potential (OCP), ν(CO) corresponding to both complex **4** (2024, 1930 and 1915 cm^{-1}) and the solvent complex (2044, 1955, 1944 cm^{-1}) are observed (Fig. 4 (a), multi-Lorentzian fittings Fig. S9). Upon initial reduction (peak I) the IR difference spectrum shows the loss of **4** and its related solvent complex and the growth of a new species with ν(CO) that heavily overlap with the starting materials, Fig. 4 (b). Multi-Lorentzian curve fitting (Fig. S10) demonstrates that the product formed upon initial reduction has ν(CO) at 2039, 1944 and 1932 cm^{-1} in addition to weaker IR modes assigned to the bipyridine ligand at 1640 and 1610 cm^{-1}. By analogy to the reported spectrum of [Re(bpy(OH)(O$^-$))(CO)$_3$Cl]$^-$, which has bpy modes at *ca*. 1630 and 1590 cm^{-1} and ν(CO) at 2012, 1900 and 1881 cm^{-1} corresponding to a shift of -7 to -12 cm^{-1} *vs*. the parent [Re(bpy(OH)$_2$)Cl] complex,[32] we assign the complex formed during IR-SEC to the singly reductively deprotonated species [Mn(bpy(OH)(O$^-$))(CO)$_3$(Solv)]. Given the timescales required for bulk reduction, the process labelled II in Fig. 3 (a) was not identified during IR-SEC. Further reduction of [Mn(bpy(OH)(O$^-$))(CO)$_3$(Solv)] (peak III) leads to the formation of a complex with ν(CO) at 2024, 1927 and 1903 cm^{-1}, in addition to a strong ligand mode at 1607 cm^{-1} (Figs. 4 (c), S11). This is assigned to the doubly reduced, doubly deprotonated complex [Mn(bpy(O$^-$)$_2$)(CO)$_3$(Solv)]$^-$, due to the excellent agreement with the reported IR frequencies of [Re(bpy(OH)(O$^-$)$_2$)(CO)$_3$]$^-$ (2002, 1886, 1865 and 1605 cm^{-1} (*str.*)).[32] Applying increasingly negative potentials leads to the formation of two new ν(CO) at 1807 cm^{-1} and 1889 cm^{-1}, Fig. 4 (d), with the higher frequency ν(CO) again masked by the bleaching of the starting material. The related Mn^0 complex [Mn(bpy(^{t}Bu)$_2$)(CO)$_3$]$^-$, formed at *ca.* -1.6 V *vs*. SCE,[8] has ν(CO) at 1907 and 1807 cm^{-1} and here we tentatively assign the complex with ν(CO) at 1889 cm^{-1} and 1807 cm^{-1} to either [Mn(bpy(OH)(O$^-$))(CO)$_3$]$^-$ or [Mn(bpy(O$^-$)$_2$)(CO)$_3$]$^{2-}$.

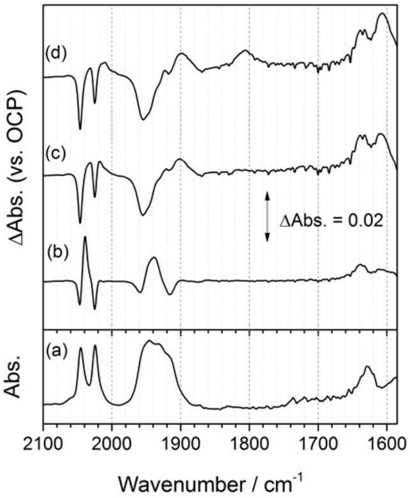

Fig. 4: IR-SEC of **4** in dry CH$_3$CN/0.1 M TBA PF$_6$. (a) at OCP, difference spectrum versus OCP and (b) at reduction (I), (c) reduction III and (d) reduction IV.

In anhydrous acetonitrile a large current enhancement is seen in the cyclic voltammetry of **4** in the presence of CO$_2$, with the enhancement onsetting at potentials cathodic of -

1.79 V *vs*. SCE (Fig. 3 (b)). In contrast to other [Mn(L)$(CO)_3$Br] complexes where the addition of a proton donor aids CO_2 reduction, here we find that the addition of 5 % water actually decreases the current density during CV. Gobetto *et al*. have reported CO_2 reduction using a hydroxyl-substituted Mn(bpy) complex in the absence of an additional proton source, but do not comment on the role of added water in the process.[36] Bulk electrolysis of 0.2 mM **4** in anhydrous CH_3CN under CO_2 at -2.1 V *vs*. SCE led to CO production with a Faradaic efficiency (FE) of 89 % and a turnover number (TON) of 0.6, with no H_2 production detected in the first four hours. Sustained electrolysis (19.5 hrs) however led to complex degradation and the FE dropped to 5 % for CO. In the presence of water (5 %) bulk electrolysis of **4** at -2.1 V shows that primarily H_2 (FE = 45 %) is produced, with only low levels of CO (FE = 6 %). It is therefore apparent that although complex **4** is a poor CO_2 reduction catalyst in CH_3CN it displays markedly different electrochemical behaviour in differing solvent environments, making it of interest to study in the highly acidic environment of the Nafion film.

Polymer Supported Electrocatalytic Reduction of CO_2 in water

To compare the catalytic behaviour of both new complexes (**3** and **4**) and the known benchmark catalysts (**1** and **2**) in a polymer support for use in aqueous electrolyte, complexes **1-4** were cast in Nafion films mixed with MWCNT onto a glassy carbon working electrode and allowed to dry in the dark. We have reported on CO_2 electrocatalysis using **1**/MWCNT/Nafion previously.[23] We have optimised the drying conditions and found that the highest current densities occur when the films are dried at 25ºC and the role of drying temperature is discussed further in the ESI and Figs. S14 and S15. In brief, there is a broad reduction at approximately -1.2 V *vs*. SCE which has been shown previously to be two overlapping processes: dimer formation followed by dimer reduction, Figs. 5 (a), 5 (b). Dimer formation may seem surprising given that **1** is immobilized, but we have shown previously that clustering on the MWCNT surfaces is likely to enable the formation of bimetallic complexes.[23] The dimer reoxidation peak is observed at -0.4 V. In the presence of CO_2 there is a significant current enhancement for **1** at potentials negative of -1.2 V, indicative of CO_2 reduction (Fig. 5). Due to the optimisation of the film drying conditions we report a large improvement in sustained current densities during CPE measurements (1.8 mA cm^{-2}, *vs*. 0.7 mA cm^{-2} previously reported at -1.4 V),[23] albeit with a slight loss in selectivity towards CO_2 (here 0.28, previous 0.47), Table 1.

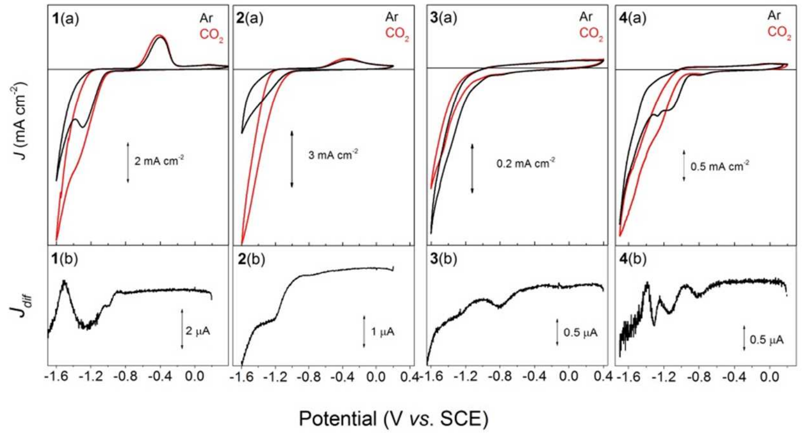

Fig. 5: Cyclic voltammograms (a) and square wave voltammograms (SWV) (b) for complexes **1-4** cast in Nafion/MWCNT on glassy carbon electrodes. Scan rates were 10 mV/s *vs*. SCE in a 0.1 M phosphate buffer electrolyte. For comparison, CVs of all four complexes in solution are overlaid in Fig. S7.

In contrast to electrodes of **1**/MWCNT/Nafion, equivalent experiments using complex **3** showed no significant enhancement in current density under CO_2. Squarewave voltammetry of a **3**/MWCNT/Nafion electrode under argon did show the presence of two reductions at *ca.* -0.8 and -1.25 V (Fig. 5(b)). The reduction at -0.8 V is present in films of MWCNT/Nafion without complexes **1-4** indicating that it is MWCNT-based. The reduction at -1.25 V is assigned to the reduction of a solvated $[Mn(bpy(COOH)_2)(CO)_3(Solv)]^+$ complex (Solv = CH_3CN, H_2O or Nafion) indicating that a concentration of **3** was electrochemically active within the polymer. However despite the promising solution electrochemical behaviour of **3**, prolonged electrolysis of a **3**/MWCNT/Nafion electrode under CO_2 at -1.4 V in aqueous solutions at pH 7 lead exclusively to H_2 production. In a similar manner **4**/MWCNT/Nafion electrodes under argon in aqueous solutions at pH 7 showed electrochemical behaviour in line with the solution studies in acetonitrile outlined above with two clear complex reductions assigned to the reduction of the solvated complex of **4** $[Mn(bpy(OH)_2(CO)_3(Solv)]^+$ at -1.15 V and of **4** at $[Mn(bpy(OH)_2(CO)_3(Br)]$ at -1.3 V, in addition to the MWCNT-based reduction at -0.8 V. In the presence of CO_2 a notable current increase was observed at potentials cathodic of -1.2 V, however prolonged electrolysis at -1.4 V under CO_2 indicated that the primary product formed was H_2, Table 2.

Catalyst	E (V, *vs.* SCE)	J_{avg} (mA cm^{-2})	Time (h)	TON$_{CO}$ total	CO:H_2	FE H_2, CO (%)
(1)/Nafion/MWCNT	-1.4	1.79	4	18.7	0.28	50, 14
(1)/Nafion/MWCNT	-1.5	4.38	4	35.9	0.21	52, 11
(2)/Nafion/MWCNT	-1.4	0.2	4	7.3	1.04	44, 46
(2)/Nafion/MWCNT^{a}	-1.5	2.65	4	46.1	0.32	71, 23
(2)/Nafion/MWCNT	-1.5	1.14	2	10.6	0.33	75, 24
(4)/Nafion/MWCNT	-1.4	0.83	4	0.3	0.02	40, 1

Table 2: CPE data for Nafion/MWCNT films containing **1**, **2** or **4**. *a*: Cell repurged every hour.

Electrochemical studies of **2**/MWCNT/Nafion electrodes are however very promising. Reductions visible by SWV at -1.28 and -1.53 V (Fig. 5 (b)) are assigned to those observed in solution for the initial reduction of **2** and its subsequently formed dimer at -1.27 and -1.48 V *vs*. SCE in CH_3CN, Fig. S12. A dimer reoxidation peak is also visible on the return sweep of the **2**/MWCNT/Nafion electrode at *ca*. -0.4 V, Fig. 5. Under CO_2 a large increase in current density is measured relative to under argon (-8.8 mA cm^{-2} *vs*. -3.2 mA cm^{-2} at -1.6 V) that onsets at approximately -1.3 V. Bulk electrolysis measurements carried out at -1.4 V demonstrate that **2**/MWCNT/Nafion electrodes are active for CO_2 reduction in pH 7 electrolyte with CO being produced with a selectivity (CO:H_2 ~1.04) exceeding that achieved with complex **1** (CO:H_2 ~0.28) under the same conditions. Based on analysis of the solution phase electrocatalysis of **2**, we postulated that films of **2**/MWCNT/Nafion would operate efficiently at more negative potentials whilst maintaining high selectivity for CO_2 reduction. CPE of **1**/MWCNT/Nafion at -1.5 V yielded CO with an average current density (J_{avg}) of *ca*. 4.38 mA cm^{-2} and a TON$_{CO}$ of 35.9 after 4 hours, with a decreased selectivity (CO:H_2 = 0.21). Surprisingly CPE at -1.5 V using **2**/MWCNT/Nafion for 2 hours resulted in lower average current densities (1.14 mA cm^{-2}) than for **1**, and after 2 hours the current density decreased dramatically. Accompanying this drop in current density was a concurrent loss in selectivity for CO_2 reduction, which may suggest that the **2**/MWCNT/Nafion electrode is being limited by the available CO_2 concentration. Indeed, re-purging with CO_2 each hour led to recovery of the activity of this system, yielding an improved J_{avg} (2.65 mA cm^{-2}), without a loss in selectivity (CO:H_2 = 0.33) over 4 hours and a total TON$_{CO}$ of over 45 at -1.5 V (Fig. S13). It is therefore apparent the **2**/MWCNT/Nafion electrode is likely to be limited by the available CO_2 concentration under typical operating conditions. Future work will explore the use of both alternative polymeric materials and electrode configurations to enhance the available CO_2 concentration at the catalytic sites. Recent examples using gas diffusion electrodes coupled to immobilized catalysts have demonstrated marked improvements in catalytic current densities.[26] The relatively weak interaction between the MWCNT and complexes is also likely to be a significant limiting factor and the development of similar complexes with aromatic functionalities better suited to π-stacking on MWCNT, such as pyrene groups, is also likely to yield further improvements in current densities.[37]

Conclusions

Two novel Mn complexes incorporating substituted bipyridine ligands, $[Mn(bpy(COOH)_2)(CO)_3Br]$ (**3**) and $[Mn(bpy(OH)_2)(CO)_3Br]$ (**4**), have been synthesized and characterized with the aim of utilisation in a high surface area $[Mn(L)(CO)_3X]$/MWCNT/Nafion electrode for CO_2 reduction. Detailed electrochemical studies of **3** and **4** were carried out and both complexes were found to have some activity towards CO_2 reduction in acetonitrile solutions; however when immobilized for use in aqueous conditions CO_2 reduction to CO was not found to occur in significant quantities. In contrast, immobilization of the benchmark catalyst **2** as an **2**/MWCNT/Nafion electrode was found to be a highly effective approach for enabling CO_2 reduction to CO in aqueous solvents at neutral pH values, with a J_{avg} of 2.65 mA cm^{-2} at -1.5 V and a selectivity towards CO_2 ($CO:H_2 = 0.33$) being achieved.

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Department of Chemistry, Stephenson Institute for Renewable Energy, The University of Liverpool, L69 7ZD, Liverpool, UK. E-mail: a.j.cowan@liverpool.ac.uk

† Electronic Supplementary Information (ESI) available: X-ray diffraction details and data, scan rate dependence of **3** and **4** in solution, FTIR spectra showing solvolysis, deconvoluted FTIR-SEC data, the effects of hourly gas re-purging on CPE of **2**/Nafion/MWCNT and temperature dependence on drop drying. See DOI: 10.1039/b000000x/

‡ These authors share equal contribution.

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