



Cite this: *Chem. Commun.*, 2014, 50, 12698

Received 14th August 2014,
Accepted 2nd September 2014

DOI: 10.1039/c4cc06404f

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[Mn(bpy)(CO)₃Br] cast in a Nafion membrane is an active heterogeneous electrocatalyst with good selectivity for CO₂ reduction to CO in neutral aqueous electrolyte. Addition of multi-walled carbon nanotubes (MWCNT) leads to a ~10 fold current enhancement and stable CO : H₂ yields (1 : 2) at –1.4 V vs. Ag/AgCl at pH 7.

The electrochemical reduction of CO₂ to products such as methanol, formic acid and CO offers an environmentally benign route to the production of high value fuels from a waste feedstock. The production of syngas (CO : H₂ ~ 0.5) from CO₂ and water is of particular interest as it can be used to make a wide range of hydrocarbon products through Fischer–Tropsch chemistry. As a result of this, significant efforts towards the development of both homogenous and supported (heterogeneous) metal complexes for CO₂ electrocatalysis are underway.^{1–3}

One of the most commonly studied homogenous CO₂ catalysts is [Re^I(bpy)(CO)₃X] (bpy = 2,2′-bipyridine and X = Cl[–], Br[–] or solvent) which has received extensive interest both as a photocatalyst and electrocatalyst due to its activity and selectivity for CO₂ reduction, often to CO.^{4–6} A limitation of [Re(bpy)(CO)₃X] is the high cost of the metal centre and the relatively high overpotential for CO production.⁴ Several recent reports have demonstrated that [Mn^I(L)(CO)₃X] (L = bpy,⁷ 4,4′ or 6,6′-disubstituted-2,2′-bipyridine^{8,9}) are highly effective precursors to catalysts for homogeneous CO₂ reduction to CO, with [Mn(bpy)(CO)₃Br] achieving quantitative selectivity for CO over H₂ at –1.35 V vs. Ag/AgCl, positive of the potential required for [Re(bpy)(CO)₃Br].⁷ Unlike [Re(bpy)(CO)₃X] which can operate,¹⁰ albeit inefficiently, in the absence of purposely added Brønsted acids, [Mn(L)(CO)₃X] requires the addition of a proton source for any activity to be observed. Studies are typically carried out in acetonitrile doped (~5%) with a protic solvent such as water or methanol. Interestingly, increased methanol

Electrocatalytic CO₂ reduction with a membrane supported manganese catalyst in aqueous solution†

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concentrations (≤5.7 M) give higher catalytic currents, as does the addition of a stronger Brønsted acid (trifluoroethanol), without a loss in selectivity towards CO₂.⁸ It is therefore interesting to further explore CO₂ reduction in proton rich environments; however solubility issues prevent the study of [Mn(bpy)(CO)₃X] for CO₂ reduction in aqueous solution.

The development of a recyclable heterogeneous electrocatalyst for CO₂ reduction in benign aqueous solutions is highly desirable. Due to its chemical and thermal stability, proton conductivity and permeability to water, Nafion membranes have been widely explored as supports for electroactive species with applications in sensing,¹¹ photocatalysis,¹² photoelectrochemistry¹³ and electrocatalysis,¹⁴ including for CO₂ reduction.^{15,16} Of particular relevance to this work are past reports on the immobilization of CO₂ reduction molecular electrocatalysts including [Re(bpy)(CO)₃Br],¹⁷ [Ni(cyclam)]²⁺,¹⁸ and a cobalt tetramethylpyridoporphyrazine.¹⁹ However Nafion supported molecular electrocatalysts have typically displayed low current densities and selectivities towards CO₂.^{17,18} For this study we postulate that the high selectivity of [Mn(bpy)(CO)₃X] for CO₂ will be advantageous in the proton rich Nafion.⁸ Furthermore we demonstrate a simple Nafion/MWCNT/[Mn(bpy)(CO)₃Br] membrane with enhanced current densities, on the mA cm^{–2} range, overcoming a major issue with Nafion supported CO₂ reduction electrocatalysts.

Full details of the catalyst preparation is given in the supporting information. Briefly, [Mn(bpy)(CO)₃Br] was dissolved in acetonitrile and mixed with a Nafion–alcohol solution. Typically 10 μl of this solution containing *ca.* 140 nmol of catalyst was cast onto a glassy carbon electrode (GCE, 0.07 cm²) and left to dry in the dark. The cyclic voltammetry (CV) (Fig. 1(a)) and square-wave voltammetry (SWV) (Fig. 1(b)) of the Nafion immobilised complex in water at pH ~ 7 under Argon shows good agreement with the reported⁷ electrochemical data for the same complex in an CH₃CN/H₂O (95 : 5) solution, also shown in Fig. S1 (ESI†). In line with the solution phase electrochemistry⁷ the reduction at –1.15 V under argon (Fig. 1(a)) is assigned to [Mn^I(bpy)(CO)₃X] reduction with subsequent rapid ligand loss and dimerization:

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† Electronic supplementary information (ESI) available: Experimental protocols, prolonged CPE and control data, FTIR and UV/vis of casting solutions. See DOI: 10.1039/c4cc06404f



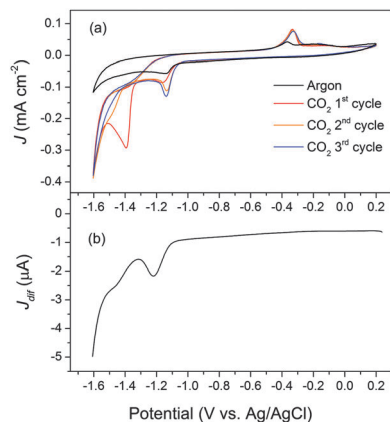
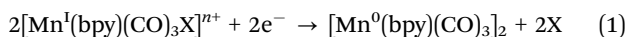
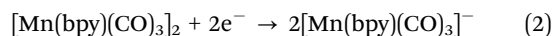


Fig. 1 (a) CV of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ cast in Nafion film on GCE in aqueous phosphate buffer (pH ~ 7 , 30 mM Na_2HPO_4 + 30 mM NaH_2PO_4) recorded at 10 mV s^{-1} under Argon (black) and CO_2 (red, gold, blue). (b) Square-wave voltammetry of the same electrode under argon at 100 mV s^{-1} .



where X can be Br^- ($n = 0$) or a solvent molecule ($n = 1$). FTIR and UV/vis analyses of the $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]-\text{CH}_3\text{CN}-\text{Nafion}$ mix (Fig. S2 and S3, ESI †) show that a significant concentration ($>55\%$ within 30 minutes of solution preparation) of $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ (Solv = CH_3CN , H_2O or n -propanol) is formed. We also observe a good agreement with the previously reported⁷ reduction potential of $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{CH}_3\text{CN})]^+$ (-1.07 V) in CH_3CN , indicating that $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ is the primary electroactive species present. Re-oxidation of the dimer to reform $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ occurs at *ca.* -0.35 V . The presence of the electrochemically generated dimer population within a Nafion membrane indicates that either (i) suitably fast complex diffusion occurs, or that (ii) electroactive $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ are localized in clusters and that they do not require diffusion for dimerization. A detailed discussion is included in the ESI † but briefly morphology studies (Fig. S9–S11, ESI †), a linear scan rate dependence of the peak current for $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ reduction (Fig. S7, ESI †) and a low electroactive concentration of catalyst, *vide infra*, leads us to propose the presence of localised $[\text{Mn}(\text{bpy})(\text{CO})_3(\text{Solv})]^+$ clusters.

A 2nd reduction at -1.47 V was clearly observed in the CH_3CN solution CV of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ (Fig. S1, ESI †). In Nafion in an aqueous solution this reduction is hard to identify in the CV at 10 mV s^{-1} under argon (Fig. 1(a)); however both higher scan rate CV (Fig. S6, ESI †) and SWV (Fig. 1(b)) clearly show a 2nd reduction at -1.45 V , assigned⁷ to the formation of $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$:



Under CO_2 a significant increase in cathodic current is observed (Fig. 1(a)) which is assigned to catalytic CO_2 reduction, with the most pronounced effect being at potentials negative of the 2nd reduction, indicating that the principle catalytically active species is $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$.^{20,21} On the first CV scan immediately after CO_2 purging a peak in the cathodic current at -1.4 V was noted, which decayed by the 3rd sweep to a steady state. This is tentatively assigned to be a result of the initially

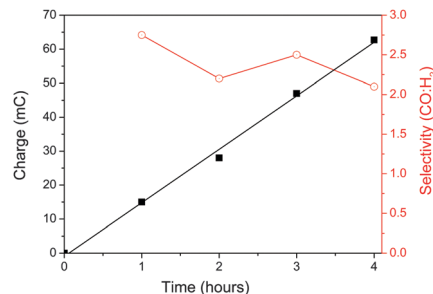


Fig. 2 Charge passed and selectivity towards CO production for Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ on GCE (0.07 cm^{-2} , *ca.* $3.5 \times 10^{-10} \text{ mol}$ of electroactive catalyst, at -1.5 V , pH ~ 7).

high CO_2 concentration in the Nafion/catalyst film, which rapidly stabilizes in subsequent sweeps.

Controlled potential electrolysis (CPE) of the Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ films at potentials between -1.3 and -1.6 V led to the production of CO and a good selectivity towards CO_2 reduction was achieved with $\text{CO}:\text{H}_2 \sim 2$, stable for >4 hours, Fig. 2. The selectivity towards CO_2 was found to be highly dependent upon the applied potential, with H_2 production, the sole product in a Nafion/GCE film in the absence of a catalyst (Fig. S20, ESI †), dominating at -1.6 V (Table 1). A total Faradaic efficiency of $\sim 75\%$ is achieved for gas phase products ($\text{CO} + \text{H}_2$) at -1.5 V . We have also considered that a low concentration of liquid phase CO_2 reduction products may be produced which would account for the small amount of missing charge. However the expected low concentrations of liquid based products, here at most $\sim \mu\text{M}$ (see ESI 1.4 †), prevents quantitative analysis by NMR.

The good stability of the current and selectivity towards CO_2 in Fig. 2 over a four hour period indicates that the CO detected is from electrocatalytic CO_2 reduction and not from ligand loss. Electrocatalysis is confirmed by the following experiments: (i) CPE at -1.5 V under Argon shows no significant CO production and a low cathodic current; when CO_2 is introduced into the cell a large increase in the current is observed and CO production is initiated, Fig. S13 (ESI †). (ii) Prolonged CPE gives total turnover numbers (TONs) based on the total amount of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$

Table 1 Controlled potential electrolysis of GCE coated with $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ in Nafion membranes in phosphate buffer (pH ~ 7)

Catalyst	V	Charge ^b (mC)	Primary products (FE%)	TON ^c (CO_2)
Mn/Nafion	-1.30	38	CO (26), H_2 (17)	150^d
Mn/Nafion	-1.40	64	CO (22), H_2 (24)	209^d
Mn/Nafion	-1.50	63	CO (51), H_2 (24)	471^d
Mn/Nafion	-1.60	389	CO (7), H_2 (81)	385^d
Mn/Nafion/CNT	-1.25	131	CO (11), H_2 (52)	9^e
Mn/Nafion/CNT	-1.40	740	CO (22), H_2 (47)	101^e
Re/Nafion ^a	-1.44	25	CO (29), HCO_2H (12), H_2 (53)	116
Re/Nafion ^a	-1.54	53	CO (17), HCO_2H (12), H_2 (78)	173

^a Literature values from ref. 17 for $[\text{Re}(\text{bpy})(\text{CO})_3\text{Br}]/\text{Nafion}$ normalised to an equivalent surface area of 0.07 cm^{-2} . ^b Charge after 4 hours CPE for this work. ^c TON calculated for CO or HCO_2H production. ^d Based on $3.5 \times 10^{-10} \text{ mol}$ (0.25% of 140 nmol). ^e Based on $8 \times 10^{-9} \text{ mol}$ (11% of 70 nmol) (Fig S8. ESI).



in the casting solution ≥ 14 well in excess of the theoretical maxima of 3 obtainable *via* ligand loss (Fig. S21 and S22, ESI[†]). The TON per electroactive catalyst is in reality even higher than this as the majority of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ deposited is electrochemically inactive. Using the electroactive quantity (*ca.* 3.5×10^{-10} mol, 0.25%) found through slow scan rate CV analysis (Fig. S7, ESI[†]) we actually achieve a TON > 450 after 4 hours for CO_2 reduction at -1.5 V with a Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ film, representing one of the highest reported TON for this class of catalyst, confirming the systems stability. Solution TONs of 13 and 23 have been previously reported for $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ at 4 and 22 hours respectively prior to any loss in activity, (ESI 3.2[†]).⁷ Repeated experiments over a 2 day period with a single film (Fig. S21, ESI[†]) also indicate that the samples have reasonable mechanical stability and that they can be recycled as we observe that the CO production rate is approximately constant in successive experiments. However over very long periods of time, although the CO production rate is maintained, the selectivity towards CO_2 does decrease due to an increase in the surface area of the bare GCE brought about by partial delamination. Furthermore, electrochemical (Fig. S14 and S15, ESI[†]) and spectroscopic (NMR and UV/vis Fig. S16 and S17, ESI[†]) analyses of post CPE electrolytes show no evidence for catalyst loss into solution.

A small, but not insignificant (x2) enhancement in the cathodic current at potentials as low as -1.15 V under CO_2 (Fig. 1(a)) and the presence of CO in CPE experiments (Table 1) at -1.3 V, slightly positive of that required for the production of $[\text{Mn}(\text{bpy})(\text{CO})_3]^-$ indicates that CO_2 reduction may also be occurring *via* a 2nd minor pathway. It has recently been shown that 4,4'-substituted dimeric complexes such as $[\text{Mn}(\text{dmb})(\text{CO})_3]_2$ are catalytically active towards CO_2 at potentials positive of that required for the formation of the monomeric anion.^{7,20,21} Here we tentatively assign the low level of CO production at ≤ -1.3 V to be occurring *via* CO_2 and H^+ addition to $[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ in Nafion. The increased activity of $[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ in Nafion towards CO_2 may be related to the enhanced proton concentration in our aqueous-Nafion system.

A limiting factor of the Nafion- $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ system is the low concentration (0.25%) of electroactive material when a planar GCE is employed. MWCNTs have an extremely large surface area, unique electrochemical properties and can be used to immobilise molecular electrocatalysts either *via* π - π interactions^{14,22} or through covalent functionalization.^{23,24} A range of high surface area molecular electrocatalytic-MWCNT systems have been reported including for water oxidation and reduction,^{23,24} and CO_2 reduction.^{22,25} MWCNT have also been used to enhance the activity of Nafion supported molecular electrocatalysts for fuel cell¹⁴ and sensing applications amongst others.^{11,26} Weak π - π interactions between bpy ligands and MWCNT have been reported previously²⁶ and here FTIR studies indicate the presence of a non-covalent interaction between the MWCNT and $[\text{Mn}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$ (Fig. S4, ESI[†]), although the hydrophobic nature of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{X}]^{n+}$ is likely to be a more significant factor in preventing catalyst leaching, Fig. S5 and S15 (ESI[†]). Incorporation of increasing concentrations of MWCNT into the Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ membrane greatly enhances the

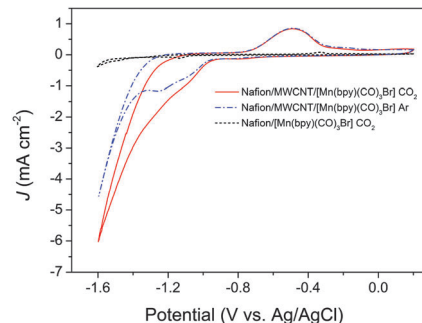


Fig. 3 CV of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ cast in Nafion film on a GCE (0.07 cm^2) with and without MWCNT. Recorded in aqueous phosphate buffer ($\text{pH} \sim 7$, $30 \text{ mM Na}_2\text{HPO}_4 + 30 \text{ mM NaH}_2\text{PO}_4$) at 10 mV s^{-1} under argon and CO_2 .

concentration of electroactive catalyst (Fig. S8 and S12, ESI[†]), with 11% active at a loading of 1:1 wt MWCNT: $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$, in contrast to 0.25% in the absence of MWCNT.

The large increase in electroactive concentration of $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ using the high surface area MWCNT support leads to a dramatic *ca.* 10 fold enhancement in current density under CO_2 at -1.4 V (3 mA cm^{-2} vs. 0.3 mA cm^{-2}) in the slow scan rate CV (10 mV s^{-1}), when compared to Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$, Fig. 3. CPE of Nafion/ $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ /MWCNT under CO_2 at -1.4 V leads to sustained CO and H_2 production in a *ca.* 1:2 ratio, ideal for use as syngas, Fig. S22 (ESI[†]). Fig. 3 also indicates a shift in the peak potentials of $[\text{Mn}(\text{bpy})(\text{CO})_3]_2$ reduction (-1.25 V) and oxidation (-0.50 V), and the onset of CO_2 reduction, upon incorporation of MWCNT, *cf.* Fig. 1. CPE experiments confirming the formation of CO at -1.25 V (Table 1), *ca.* 100 mV positive of that reported for $[\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}]$ in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$,⁷ further reinforce the promise of this membrane supported catalyst.

In conclusion we present an immobilised electrocatalyst for CO_2 reduction that operates in neutral aqueous solutions with good selectivity towards the production of CO . The low cost heterogeneous system is found to be stable and reusable in successive experiments. Addition of MWCNT to the casting solution leads to an x10 enhancement in current density, circumventing one of the key issues with Nafion immobilised electrocatalysts for CO_2 . The MWCNT system sustained CO and H_2 production at a ratio ideal for use as syngas ($\sim 1:2$). A likely limitation remains the permeability of CO_2 through the Nafion membrane and we anticipate that suitable structuring to enhance gas diffusion will lead to further improvements in catalytic activity.

AJC and JJW acknowledge the EPSRC for a fellowship (EP/K006851/1) and for financial support respectively and Prof. K. Durose and Dr R. Treharne for access to the profilometer.

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