



The influence of electrolyte identity upon the electro-reduction of CO₂



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ABSTRACT

The influence of supporting electrolyte cations on the voltammetric behaviour and product distribution in N-methylpyrrolidone-based carbon dioxide electroreduction systems is investigated. The reduction potentials associated with TBABF₄ (0.1 M) and corresponding alkali metal (M⁺) electrolytes; LiBF₄, NaBF₄ and RbBF₄ (focussing mainly on the reduction of the widely employed Li⁺ species) were established in both the presence and absence of CO₂ at polycrystalline noble metal working electrodes. *In situ* and *ex situ* Raman spectroscopy, X-ray photoelectron spectroscopy, scanning electron microscopy and qualitative element identification via flame testing were used to aid the assignment of reduction processes. It was established that CO₂ reduction products in the metal cationic systems were formed at a much less negative potential than those found with the non-metal cation (−1.5 V vs. Ferrocene, c.f. −2.2 V), however the resultant alteration of the surface environment was found to deactivate the electrode to further CO₂ reduction. The presence of CO₂ in solution was found to affect the potential required for the bulk deposition of metal from the electrolyte through the same process. Where TBA⁺ and M⁺ were employed simultaneously in the system, the resultant voltammetry shared the majority of features with the pure M⁺ system with CO₂ reduction suppressed at more negative potentials therefore supporting the conclusion that any ‘catalytic effect’ associated with TBA⁺ is in fact a lack of deactivation given by the M⁺ system, rather than any enhancement offered by the former.

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1. Introduction

The effect of electrolyte upon CO₂ reduction has been overlooked in comparison to the extensive research conducted into the influence of the electrode material. In much of the CO₂ reduction literature the supporting electrolyte is assumed to act simply as a charge carrier, despite the significant effects that the ion identity can have on the electrical double layer, on solvent properties (such as viscosity and solvating parameters), ion pairing stabilisation of radicals and ions generated, as well as specific interactions with the redox active species and the electrode surface.

Comparative studies exist exploring the link between supporting electrolyte identity, CO₂ reduction potentials and product distribution although they focus heavily upon aqueous [1–5] and methanol based systems [6–8]. The comparison of tetraalkylammonium and lithium salts in a CO₂-saturated methanol solution at a copper working electrode was reported to yield different CO₂ reduction products (at higher overpotentials for the latter): the authors concluded that CO formation from CO₂ is promoted by the tetrabutylammonium cation, TBA⁺ [7]. The mechanism for this was suggested to be stabilisation of the high energy intermediate,

CO₂^{•−}, by ion pairing with the TBA⁺. Li⁺ was reported to suppress the reduction of CO₂ however this was proposed to be linked to strong Li⁺–CO₂^{•−} ion pairing, forming a stable species in solution which was then not further reduced.

Tetraalkylammonium salts have been reported to work as effective electron mediators for CO₂ reduction by Bockris and co-workers in an aprotic solvent system [9,10].

In this work we have investigated CO₂ reduction employing N-methylpyrrolidone, NMP, as the solvent. NMP is a dipolar aprotic solvent with a large negative electrochemical window, low volatility [11] and a high selectivity for CO₂ solvation, so much so that it is employed industrially for CO₂ removal from gas streams under the process name “Purisol” [12]. The electrolytes investigated were tetrabutylammonium tetrafluoroborate, TBABF₄, and its alkali metal (M⁺ = lithium, sodium and rubidium) analogues, LiBF₄, NaBF₄ and RbBF₄, at a standard concentration of 0.1 M. Focus was placed on the lithium system due to the prominence of lithium salts in many non-aqueous systems, such as the lithium-ion and lithium-air battery [13], providing a better insight into the expected reactivity of CO₂ with lithium hydroxide and peroxides once commonly used aboard space craft to scrub CO₂ from the atmosphere [14]. The working electrode materials employed were gold and platinum (disk electrodes, 2 mm diameter and foil 1 cm²) as both offer well definable, reproducible surfaces [15,16]. The solution was saturated with

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CO₂ gas prior to measurement, with a concentration assumed to be close to the equilibrium solubility of 0.145 M [17].

2. Experimental

2.1. General

All electrochemical measurements, sample preparation and spectroscopic measurements (except X-ray photoelectron spectroscopy, XPS, and scanning electron microscopy, SEM) were performed at room temperature and pressure under either an Ar (99.998%, BOC) or CO₂ (>99.990%, BOC CO₂) atmosphere.

All of the electrochemical measurements were made (and samples prepared) in a standard three electrode cell on an Autolab Potentiostat (PGSTAT 100, Eco-Chemie) using GPES software except the *in situ* Raman measurements for which a smaller custom-made thin layer cell was employed. An Ivium potentiostat (CompactStat), with corresponding software, was employed for the *in situ* Raman spectroscopy.

N-methylpyrrolidone NMP (99.5% anhydrous, Sigma Aldrich) was found to give the cleanest solvent background when it was syringed directly from the suba sealed container in which it was supplied using a dried gas tight syringe into the cell. The aqueous H₂SO₄ (95+%, Fisher) solution employed was made using DI water (>18 MΩ cm resistivity), prepared using a Millipore reverse osmosis unit coupled to an Elga “Purelab Ultra” purification system (Veolia Water Systems). Saturation of solution with CO₂ typically took 20 min of gentle bubbling, so de-gassing was allowed to proceed for 30 min to ensure saturation was reached.

The electrolytes tetrabutylammonium tetrafluoroborate (≥99.0%, Fluka Analytical), Lithium tetrafluoroborate (98%, Sigma–Aldrich), Rubidium tetrafluoroborate (98%, Alfa Aesar) and Sodium tetrafluoroborate (98%, Janssen Chimica) were used as received. Ferrocene (Fc, 99%, Alfa Aesar) was employed as an internal calibrant added to the cell once the data from the system was gathered, and a full CV covering the Fc oxidation and previous analyte processes was recorded, allowing the calibration of potentials vs. Fc. The measurements were made vs. a flame-cleaned platinum wire pseudo-reference electrode in a glass tube filled with the corresponding electrolyte solution connected to the bulk solution by a glass frit.

This was not done for the *in situ* Raman measurements due to the limited cell space and inaccessibility of the solution once sealed, so a bare Pt wire was employed without calibration post measurement however no evidence was seen to suggest a shift in potential.

2.2. Working electrode preparation

The surface preparation of the various electrode materials tested was vital for study of UPD, as such a strict regime was adopted to allow reproducible surface conditions. The Au and Pt foil/sheet (0.25 mm and 0.5 mm thick. 99.99%, Advent Research Materials) were flame cleaned and characterised by cycling in 0.1 M H₂SO₄ in the electrochemical cell. Cyclic voltammetric scans were performed, initially at high scan rate (500 mV s⁻¹), from 0.0 V to 1.7 V and back to 0.0 V for Au, and from 0.1 V to 1.3 V then to -0.3 V for Pt, then more slowly (100 mV s⁻¹) from 0.25 V to 1.6 V to 0.25 V for Au, and 0.1 V to 1.25 V to -0.25 V for Pt until reproducible scans, showing only the anticipated features [15,16,18], were obtained. (Aqueous potentials are given vs. Ag/AgCl sat.)

Typically 10–30 scans were performed in total with potential steps employed when necessary to form bubbles and aid mechanical polishing of the surface (1.80 V and -0.1 V vs. Ag/AgCl for Au and 1.6 V and -0.3 V vs. Ag/AgCl for Pt).

2.3. Raman spectroscopy

Raman spectroscopy was performed using a 633 nm excitation wavelength (Renishaw RL633 Class 3B 20 mW HeNe laser) at 10% intensity. The Raman spectrometer was a Renishaw Mk1 System 2000 RM controlled using Wire software on a Windows 95 operating system, and fitted with an Olympus BH2 microscope.

Gold surfaces have been reported to offer significant augmentation of signals of species found at the surface over similar wavenumber regions, 300–2000 cm⁻¹, using the same HeNe laser source (λ = 633 nm). The enhancement in signal intensity from the surface enhancement effect can be up to 10¹⁰, allowing much greater sensitivity than seen in tradition Raman spectroscopy, which relies upon a relatively weak inelastic scattering effect. The mechanism by which the SERS effect occurs is complex and is dependent upon both the surface, as the name suggests, and also the metal–molecule charge transfer and an allowed molecular resonance [19].

The interpretation of SERS spectra can be challenging as the traditional selection rules for Raman activity no longer necessarily hold as the adsorption of species at the electrode surface can result in an alteration in symmetry of the molecule and different adsorption sites or applied potential on the same surface can result in different modes of chemi- or physisorption, which in turn can result in signal loss, gain and alterations in wavenumber, strength or form of the signal response [20].

2.4. XPS measurements

Measurements were made at Newcastle University using the NEXUS service on an AXIS Nova XPS Spectrometer (Kratos Analytical).

The following experimental parameters were used; XPS spectrum lens mode with field of view 1, with a survey resolution of pass energy 160 eV and acquisition time of 362 s for 3 sweeps. An aluminium anode (225 W) was employed with a step size of 1000 meV and dwell time 100 ms with the charge neutraliser off. Analysis and fitting was done using CasaXPS software Version 2.3.17dev6.2a.

2.5. SEM measurements

The secondary electron and backscattered electron imaging, as well as the energy dispersive X-ray analysis (EDAX) of selected samples, were done using a FEI Quanta 200 SEM system operated at high vacuum.

2.6. Flame tests

A previously cleaned piece of Pt or Au foil, held in clean tweezers, was put into the flame (Bunsen burner or small butane Proxon Microflame burner, respectively). Once the ‘blank’ was run the prepared, washed sample was similarly exposed and any colour change in the flame (and associated qualitative intensity of such) was recorded.

3. Results

CO₂ reduction from saturated NMP solution containing alkali metal cations, M⁺, and tetrabutylammonium, TBA⁺, as supporting cations was found to give dramatically different voltammetry as illustrated in Fig. 1.

It is immediately obvious that, over the potential range presented, there is significantly more CO₂ reductive current observable in the presence of TBA⁺ than Na⁺ from -2.2 V (vs. Fc) onward.

Each of the alkali metal electrolytes yielded a similar response to Na⁺ with a peak, or series of small peaks, prior to the point at

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