The effect of oxidation state of metal on hydrogen production electro-catalyzed by nickel complexes supported by maleonitriledithiolate ligand

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Abstract: Two molecular electro-catalysts based on nickel complexes, $[\text{Ni}(\text{mnt})_2]^{n-}$ ($n = 2$ (**1**) and 1 (**2**)) are formed by the reactions of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2(\text{mnt})$ and $[\text{BzPyN}(\text{CH}_3)_2]\text{Br}$ or $[4\text{-ClBzPyN}(\text{CH}_3)_2]\text{Br}$ ($\text{BzPyN}(\text{CH}_3)_2 = 1\text{-benzyl-4-(dimethylamino)pyridinium}$, $\text{mnt} = 2,2\text{-dicyanoethylene-1,1-dithiolate}$, and $4\text{-ClBzPyN}(\text{CH}_3)_2 = 4\text{-Cl-benzyl-4-dimethylaminopyridinium}$). Electrochemical investigations show **1** and **2** can electrocatalyze hydrogen generation both from acetic acid and aqueous buffer solution. And complexes **1** and **2** afford a turnover frequency (TOF) of 282.95 and 504.25 moles of hydrogen per mole of catalyst per hour at an overpotential (OP) of 0.848 V from a neutral buffer, respectively, indicating that the nickel(III) complex constitutes the better active catalyst than the nickel(II) species.

Keywords: Nickel(II) and nickel(III) complexes; electrocatalysts; proton and water reduction; hydrogen evolution.

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1. Introduction

In order to avoid energy crisis, people are developing new systems to get new energy. And hydrogen is of particular interest as a secondary energy carrier, its generation from water is a current topic of intensive research [1,2]. In particular, electro-catalytic method for hydrogen generation from organic acid or water have been explored as cost-effective ways of producing a carbon-neutral fuel. However, one of the key challenges for hydrogen generation by proton or water reduction is the development of efficient catalysts with low overpotential, good stability, and high turnover rate [3,4]. Therefore, a great deal of research efforts have been devoted to the development of effective catalysts based on transition metal complexes, such as manganese [5], nickel [6-9], cobalt [10-12] and copper [13-15] for the reduction of proton or water to form H₂. There are several reports about that the donor type and electronic properties of the ligands play vital roles in determining the structure and reactivity of the corresponding metal complexes [16-18]. However, few studies on catalytic properties by metal complexes with varying oxidation states. In this paper, we report the investigation on two molecular electrocatalysts based on nickel complexes, [Ni(mnt)₂]ⁿ⁻ (n= 1 or 2) with different oxidation states. Both nickel complexes exhibit electrocatalytic activity for hydrogen generation from acetic acid and aqueous buffer.

2. Experimental

2.1. Materials and physical measurements

2-Chlorobenzyl bromide, 3-chlorobenzyl bromide, 4-chlorobenzyl bromide and 4-dimethylaminopyridine were purchased from Aldrich and were used without further purification. 1-(4'-chlorobenzyl)-4-dimethylaminopyridinium bromide ($[4\text{ClBzPyN}(\text{CH}_3)_2]\text{Br}$) and disodium maleonitriledithiolate (Na_2mnt) were synthesized following the literature procedures [19,20]. $[\text{BzPyN}(\text{CH}_3)_2]_2[\text{Ni}(\text{mnt})_2]$ **1** and $[4\text{-ClBzPyN}(\text{CH}_3)_2][\text{Ni}(\text{mnt})_2]$ **2** (mnt^{2-} = maleonitriledithiolate) were prepared according to the reported methods [21,22]. Elemental analyses for C, H, and N were obtained on a Perkin-Elmer analyzer model 240. UV-Vis spectra were measured on a Hitachi U-3010 spectrometer. ESI-MS experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer by introducing samples directly into the ESI source using a syringe pump. X-ray photoelectron analysis were carried out by ESCALAB 250 Xi X-photoelectron spectroscopy with monochromatic Al K α (1486.6 eV) X-ray sources. Electrochemical measurements were conducted on a CHI-660E electrochemical analyzer under N₂ using a three-electrode cell in which a glassy carbon electrode was the working electrode, an Ag/AgNO₃ (organic media) or a saturated Ag/AgCl (aqueous media) electrode was the reference electrode, and platinum wire was the auxiliary electrode. In organic media, a ferrocene/ferrocenium (1+) couple was used as an internal standard, and 0.10 mol L⁻¹ [(n-Bu)₄N]ClO₄ was used as the supporting electrolyte. Controlled-potential electrolysis (CPE) in aqueous media was conducted using an air-tight glass double compartment cell separated by a glass frit. The working compartment was fitted with a glassy carbon plate and an Ag/AgCl reference electrode. The auxiliary compartment was fitted with a Pt gauze

electrode. The working compartment was filled with 0.050 L of 0.25 mol L⁻¹ phosphate buffer, while the auxiliary compartment was filled with 0.035 L phosphate buffer solution. After adding **1** or **2**, cyclic voltammograms were recorded. After electrolysis, a 5.0×10⁻⁴ L aliquot of the headspace was removed and replaced with 5.0×10⁻⁴ L of CH₄. The headspace sample was injected into the gas chromatograph (GC). GC experiments were carried out with an Agilent Technologies 7890A gas chromatography instrument. Gaussian 09 data package [23] were used to complete all theoretical calculations. N and C atoms were calculated by using M06-2X/6-311++G(2df, 2p), and S atoms were calculated by using M06-2X/6-311++G(3df, 3pd). AUG-cc-pVTZ was used to calculate Ni atoms. Polarized continuum model (PCM) [24], radii and non-electrostatic model (SMD) [25] were used to estimate the energy in acetonitrile. The relation of gas and liquid phase Gibbs free energy follows $\Delta G_{(aq)} \approx \Delta G_{(gas)} + \Delta(\Delta G_{(sol)})$. $\Delta G_{(aq)}$ and $\Delta G_{(gas)}$ stand for gas and liquid phase Gibbs free energy, respectively. $\Delta(\Delta G_{(sol)})$ indicates the variable of the Gibbs free energy by solvation.

3. Results and discussion

3.1. General characterization

Experimentally, the direct combination of 1:2:2 mol equiv of NiCl₂·6H₂O, Na₂mnt and 1-benzyl-4-(dimethylamino)pyridiniumbromide affords a nickel(II) complex, [BzPyN(CH₃)₂]₂[Ni(mnt)₂] **1**. In the presence of I₂, the reaction of NiCl₂·6H₂O, Na₂mnt and 1-(4'-chlorobenzyl)-4-dimethylaminopyridinium bromide at a mole ratio

of 1:2:1 provides a nickel(III) complex, $[4\text{-ClBzPyN}(\text{CH}_3)_2][\text{Ni}(\text{mnt})_2]$ **2** (Scheme 1). These results are also in agreement with the X-ray photoelectron spectroscopy (XPS) analysis (Figs. S1-S2). As shown in Fig. S1, XPS spectrum of complex **1** shows one peak at 854.5 eV, which is assigned to $\text{Ni}^{2+} 2p_{3/2}$, a typical characteristic of Ni(II) oxidation state. The Ni $2p_{3/2}$ region for complex **2** shows one peak at 855.3 eV (Fig. S2), which is assigned to $\text{Ni}^{3+} 2p_{3/2}$, indicating that the oxidation state of nickel in complex **2** is +3. These are consistent with the results reported in the literature [26].

To test properties of complexes **1** and **2** in liquid, electronic spectra were measured in both organic and aqueous media. From Fig. S3, the UV/Vis spectrum of **1** in acetonitrile shows an absorption peak at 438 nm, which corresponds to a ligand-metal-charge-transition (LMCT) between the ligands and nickel ion. And complex **2** exhibits a LMCT at 478 nm. As shown in Fig. S4, in aqueous buffer at the pH range 2.0–11.0, the intensities of the absorption bands of complex **1** at 316 and 428 nm indeed changes, but the peak position does not move, suggesting there are new components appear under these conditions, such as $[\text{H-Ni}(\text{mnt})_2]^-$ or $[\text{HO-Ni}(\text{mnt})_2]^{3-}$. From Fig. S5, the intensities of the absorption bands of complex **2** at 289 and 375 nm also changes with varying pH values, indicating there are new components appear under these conditions.

Scheme 1. Schematic representation of the synthesis of nickel complexes **1** and **2**.

In methanol, complex **1** exists in the same state as that in solid. This is in agreement with the result from ESI-MS measurement which exhibits one ion at a mass-to-charge ratio (m/z) of 340.2737, with the mass and isotope distribution pattern corresponding to that of $[\text{Ni}^{\text{II}}(\text{mnt})_2\text{H}]^-$ (Fig. S6). Similarly, in methanol, complex **2** exhibits one ion at a mass-to-charge ratio (m/z) of 340.2693, with the mass and isotope distribution pattern corresponding to that of $[\text{Ni}^{\text{III}}(\text{mnt})_2\text{H}]$ (Fig. S7).

3.2. Linear scan voltammetry

To test if these two nickel complexes can act as electrocatalysts, first we used linear scan voltammetry (LSV) to investigate their electrochemical behaviors. As shown in Fig. 1a, the potential for reduction of **1** are the same as that of the back-ground (ca. -1.55 V versus Ag/AgCl), indicating that no proton is lost during the initial reduction. Similar to that of complex **1**, no proton is lost during the initial reduction for complex **2** (Fig. 1b). According to Fig. 1, the peak current increases continually with increasing complex **1** or **2** concentration from 0.0 to $4.08 \times 10^{-4} \text{ mol L}^{-1}$, and no turning point is

found, demonstrating that **1** or **2** undergoes redox cycling during the electrochemical experiments. From Fig. S8, The catalytic current increases significantly with decrease of pH from 7.0 to 3.0, suggesting that there is a protonation step in the catalytic reaction.

3.3. Cyclic voltammetry

In CH₃CN solution at a glassy carbon electrode, complex **1** displayed a rich redox electrochemistry. No significant change was found after several scans, indicating that the catalyst is stable under these conditions (Fig. S9). As shown in Fig. 2a, the cyclic voltammogram of 5.0×10^{-4} mol L⁻¹ complex **1** shows one reversible couple at 0.25 V and one quasireversible redox couple at 0.81 V versus Ag/AgNO₃. For comparison, [BzPyN(CH₃)₂]Br displays one quasireversible redox peak at 0.80 V and one reversible redox couple at 1.26 V versus Ag/AgNO₃ (Fig. S10a). These two oxidation waves of **1**, being close to the oxidations of [BzPyN(CH₃)₂]Br, are assigned to [BzPyN(CH₃)₂]Br. Scanning to cathodic potentials reveals an irreversible redox event at a cathodic peak potential of $E_{p,c} = -0.37$ V followed by two quasireversible couples at -1.10 V and -1.91 V versus Ag/AgNO₃. The second and third redox peaks are assigned to the Ni^{II/I} and Ni^{I/0} couples, respectively. Scan rate analyses of voltammograms exhibit linear dependences in plots of current versus $v^{1/2}$ (Fig. S11), as expected for diffusional species at all observed redox events. Under the similar conditions, complex **2** also displayed a rich redox electrochemistry. No significant change was found after several scans, indicating that the catalyst is stable under these conditions (Fig. S12). From Fig. 2b, complex **2** shows one reversible couple at 0.34 V

and one quasireversible redox couple at 1.13 V versus Ag/AgNO₃. For comparison, [4Cl-BzPyN(CH₃)₂]Br displays one quasireversible redox peak at 0.85 V and one reversible redox couple at 1.23 V (Fig. S10b). These two oxidation waves of **2**, being close to the oxidations of [4Cl-BzPyN(CH₃)₂]Br, are assigned to [4ClBzPyN(CH₃)₂]Br. Scanning to cathodic potentials reveals one quasireversible couple at -1.57 V and one irreversible wave at -1.77 V versus Ag/AgNO₃, which are assigned to the couples of Ni^{III/II} and Ni^{II/I} couples, respectively. Scan rate analyses of voltammograms exhibit linear dependences in plots of current versus $v^{1/2}$ (Fig. S13), as expected for diffusional species at all observed redox events.

3.4. Electrocatalytic hydrogen from acetic acid in CH₃CN

To test if these two nickel complexes can act as electrocatalysts for hydrogen generation, we employed acetic acid as proton resource. As shown in Fig. 3a, with the addition of varied amounts of acetic acid (from 0.0 to 5.0×10⁻³ mol L⁻¹), apparent voltammetric currents emerge at -1.95 V and increase with increasing proton concentration. This indicates that hydrogen evolution electrocatalyzed by **1** requires the reduction of Ni(II) to Ni(I) and protonation. Interestingly, with the acetic acid concentration increased from 0.0 to 5.0×10⁻³ mol L⁻¹, the onset of the catalytic wave moves positive ca. 0.23 V from -1.84 to -1.61 V versus Ag/AgNO₃. Differently, the addition of varied amounts of acetic acid (from 0.0 to 5.0×10⁻³ mol L⁻¹) led to current strength increase at -1.77 V and -1.59 V versus Ag/AgNO₃ with increasing proton concentration (Fig. 3b). This indicates that hydrogen generation electrocatalyzed by **2**

requires the reductions of Ni(III) to Ni(II) and Ni(II) to Ni(I) and protonation. With the acetic acid concentration increased from 0.0 to $5.0 \times 10^{-3} \text{ mol L}^{-1}$, the onset of the catalytic wave moves positive ca. 0.17 V from -1.51 to -1.34 V versus Ag/AgNO₃.

On the basis of the above observations, analyses and literature precedents [21,22], a possible catalytic cycle for the generation of hydrogen from acid mediated by **1** is depicted in Scheme 2. One-electron reduction of $[\text{Ni}^{\text{II}}(\text{mnt})_2]^{2-}$ **1** produces a putative $[\text{Ni}^{\text{I}}(\text{mnt})_2]^{3-}$ species. Then addition of hydrogen proton (H^+) yields the $\text{Ni}^{\text{III}}\text{-H}$ species, $[\text{H-Ni}^{\text{III}}(\text{mnt})_2]^{2-}$. Another one-electron reduction of the $\text{Ni}^{\text{II}}\text{-H}$ species, $[\text{H-Ni}^{\text{II}}(\text{mnt})_2]^{3-}$. Further addition of hydrogen proton (H^+) affords H_2 , and regenerates the starting **1**. To complex **2**, a similar procedure is carried out, but there is a two-electron reduction of $[\text{Ni}^{\text{III}}(\text{mnt})_2]^-$ **2**.

Scheme 2. The possible catalytic mechanism for proton reduction by **1**.

Further investigations for the catalytic activity were carried out by bulk

electrolysis of CH₃CN solutions of **1** (3.0×10^{-6} mol L⁻¹) or **2** (3.0×10^{-6} mol L⁻¹) with 5.0×10^{-3} mol L⁻¹ acetic acid under varying applied potentials. Figs. S14a-b show the total charge of bulk electrolysis of **1** or **2** in the presence of acetic acid, where the charge increase significantly at increasingly negative potential. When an applied potential was -1.46 V versus Ag/AgCl, the maximum charge reaches 28 mC (by complex **1**) and 41 mC (by complex **2**) during 2 min of electrolysis, with accompanying evolution of a gas. Gas chromatography (GC) was also used to detect the H₂ produced after a two hour bulk electrolysis by measurement of the ratio of the concentrations of H₂ to CH₄ in the headspace of the cell. According to Figs. S15a-b, $\sim 3.0 \times 10^{-5}$ L (from complex **1**) and 1.1×10^{-4} L (from complex **2**) of H₂ are produced over an electrolysis period of 2 h, respectively. A CPE experiment under -1.45 V versus Ag/AgCl without complex **1** or **2** only gives a charge of 3 mC (Fig. S14c), showing that these two complexes do indeed serve as effective catalysts for hydrogen production under such conditions. Overpotentials are calculated by using the method of Evans et al [27] (Eq. 1). According to Eq. 2 [28], the TOFs are calculated to be 29.75 (by complex **1**) and 43.12 (by complex **2**) moles of hydrogen per mole of catalyst per hour, respectively (Eqs. S1-S2 and Figs. S16). Remarkably, complex **2** is more effective than that of complex **1**, indicating that the nickel(III) complex can constitute the better active catalyst than the nickel(II) sample. This can be attributed to that the Ni²⁺ complex is more stable than the Ni³⁺ sample. This is in agreement with the theoretical analysis that the Gibbs free energy of complexes **1** and **2** in acetonitrile are -2566.860 and -2566.675 hartree/mol (1 hartree/mol = 2625.47 kJ/mol),

respectively.

Overpotential = Applied potential - $E_{\text{HA}}^{\ominus}$

$$= \text{Applied potential} - (E_{\text{H}}^{\ominus} - (2.303RT/F)\text{p}K_{\text{aHA}}) \quad (1)$$

$$\text{TOF} = \Delta C / (F \cdot n_1 \cdot n_2 \cdot t) \quad (2)$$

Where, F is Faraday's constant, n_1 is the number of moles of electrons required to generate one mole of H_2 , n_2 is the number of moles of catalyst in solution, and t is the duration of electrolysis; ΔC is the charge from the catalyst solution minus the charge from solution without catalyst.

3.5. Catalytic hydrogen generation from aqueous buffer

The electrochemical behaviors of complexes **1** and **2** were then examined in aqueous buffer with different pH values. And Figs. 4a-b exhibit a systematic increase in i_{cat} with decreasing pH from 7.0 to 2.7 in the presence of **1** or **2**, respectively. The onset of the catalytic current is clearly influenced by the solution pH, and the reduction waves are shifted to lower potentials with increasing pH values, which is consistent with a catalytic process [29]. As shown in Figs. S17a-b, in the absence of **1** or **2**, a catalytic current is not apparent until a potential of -1.52 V versus Ag/AgCl is attained. Interestingly, upon addition of **1** or **2**, the onset of the catalytic wave remains almost constant at ca. -1.52 V versus Ag/AgCl, and the current strength increases significantly with increasing concentrations of **1** or **2** from 7.05×10^{-6} to 3.27×10^{-5} mol L^{-1} .

The electro-catalytic activities were also evaluated by bulk electrolysis of

$3.0 \times 10^{-6} \text{ mol L}^{-1}$ **1** or **2** in 0.25 mol L^{-1} buffer and the total charge of bulk electrolysis from a neutral buffer (pH 7.0) with and without **1** and **2** were listed in Fig. 5. At an applied potential of -1.46 V versus Ag/AgCl, the buffer solution gives only 35 mC during 2 min of electrolysis in the absence of **1** or **2** (Fig. 5a). Under the same conditions, the charge reaches 409 mC and 519 mC with the addition of **1** or **2** (Figs. 5b-c), respectively, and a large number of gas bubbles appeared, which are tested to be H_2 by gas chromatography. According to Figs. S18a-b, the activities are estimated to be $3.96 \times 10^{-3} \text{ L}$ (complex **1**) and $9.19 \times 10^{-3} \text{ L}$ (complex **2**) of H_2 during a 1 h electrolysis with a Faradaic efficiency of 92% (complex **1**) and 86% (complex **2**) for dihydrogen, respectively (Figs. S19a-b). According to Eqs (2) and (3) [30], TOFs for electrocatalytic hydrogen production by complexes **1** and **2** are calculated to be 282.95 and 504.25 moles of hydrogen per mole of catalyst per hour at an OP of 0.848 V, respectively (Eqs. S3-S4 and Figs. S20).

$$\text{Overpotential} = \text{Applied potential} - E(\text{pH}) = \text{Applied potential} - (-0.059\text{pH}) \quad (3)$$

From Fig. S20, the TOF of 504.25 moles of hydrogen per mole of catalyst per hour at an OP of 0.848 V produced by complex **2** is higher than that of other molecular nickel catalysts reported in the literature for electrochemical hydrogen production from neutral water. For instance, a dinickel complex supported by macrocyclic ligand that exhibits a TOF of 160 moles of H_2 per mole of catalyst per hour at an OP of 820 mV [31], and a nickel complex with 2,3-bis(2-hydroxybenzylideneimino)-2,3-butenedinitrile ion that achieves a TOF of

436 moles of H₂ per mole of catalyst per hour at an OP of 837.6 mV [7]. Similar to that in organic media, complex **2** also shows higher efficiency for hydrogen production than that of complex **1** in aqueous media. From a 72 h CPE of a natural buffer solution (pH 7.0) in the presence of complex **1** or **2**, we also can find that catalyst **2** is a more active species than **1**. As shown in Fig. S21a, a total of 715 C is accumulated during the electrolysis catalyzed by complex **1**, and in the presence of complex **2**, 1068 C is passed during a 72 h electrolysis (Fig. S21b).

*3.6. Investigation of the stability and durability of complexes **1** and **2***

In order to test whether **1** or **2** retains activity for water reduction for a long time, two 72 h CPE experiments were performed in a neutral buffer solution with 3.0×10^{-6} mol L⁻¹ complexes **1** and **2** under -1.45 V versus Ag/AgCl, respectively. According to Fig. S21a, a total of 715 C was passed during a 72 h electrolysis, and complex **1** gives a charge build-up over time, with no substantial loss in activity over the course of 30 h. After a 72 h electrolysis period, pH increased by 4.3 units (from 7.0 to 11.3), consistent with accumulation of OH⁻ by water reduction, $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. From Fig. S22a, the catalytic current remains almost constant for at least 72 h, indicating this catalyst is stable under these conditions. For complex **2**, a 72 h electrolysis from complex **2** afforded 1068 C of charge with no substantial loss in activity over the course of 72 h (Fig. S21b), which is consistent with the catalytic current experiment. From Fig. S22b, the catalytic activity was sustained for at least 72 h. After a 72 h electrolysis period, pH increased by 4.6 units (from 7.0 to 11.6), consistent with accumulation of OH⁻ by water reduction.

To prove complex **1** or **2** acts as a homogeneous electrocatalyst, we checked dependence of the catalytic current on concentration of complexes **1** and **2**. According to Fig. S17, the observation of the catalytic current being dependent on concentration of **1** or **2** could indicate both **1** and **2** are homogeneous catalysts. And the following pieces of evidence also suggest that complexes **1** and **2** are homogeneous electrocatalysts: a) The catalytic current did not increase after several cycle CV scans (Fig. S9 and Fig. S12) [32]. b) No precipitations were found in the solution and the color of the solution did not change during cyclic voltammetry or bulk electrolysis of complexes **1** and **2**.

4. Summary

In this paper, we have studied the effect of the oxidation state of metal center on hydrogen production electro-catalyzed by nickel complexes supported by maleonitriledithiolate ligand via electrochemical methods, including linear scan voltammetry and cyclic voltammetry. Electrochemical studies show that $[\text{Ni}^{\text{III}}(\text{mnt})_2]^-$ and $[\text{Ni}^{\text{II}}(\text{mnt})_2]^{2-}$ afford a TOF of 282.95 and 504.25 moles of hydrogen per mole of catalyst per hour at a OP of 0.848 V from a neutral buffer solution, respectively, indicating that the nickel(III) electrocatalyst is more active than the nickel(II) species. This can be attributed to that the nickel(II) complex is more stable than Ni^{3+} sample.

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Fig. 1. Linear scan voltammetrys (LSVs) of a neutral buffer solution (pH 7.0) without and with complexes **1** (a) and **2** (b). Conditions: Glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference electrode, scan rate 0.10 V/s.

Fig. 2. CVs of $5.0 \times 10^{-4} \text{ mol L}^{-1}$ complexes **1** (a) and **2** (b) in CH_3CN with 0.10 mol L^{-1} of $[\text{n-Bu}_4\text{N}]\text{ClO}_4$. Ferrocene internal standard (*). Glassy carbon working electrode ($1.0 \times 10^{-2} \text{ m}$ diameter), Pt counter electrode, Ag/AgNO_3 reference electrode, scan rate 0.10 V/s .

Fig. 3. CVs of a $5.0 \times 10^{-4} \text{ mol L}^{-1}$ solution of complex **1** (a) and complex **2** (b) in CH_3CN with varying concentrations of acetic acid. Glassy carbon working electrode ($1.0 \times 10^{-2} \text{ m}$ diameter), Pt counter electrode, Ag/AgNO_3 reference electrode, scan rate 0.10 V/s .

Fig. 4. (a) CVs of 5.0×10^{-4} mol L⁻¹ complexes **1** (a) and **2** (b) in buffer with varying pH values (scan rate: 0.10 V/s).

Figure(s)

Fig. 5. (a) Charge buildup versus time from electrolysis of a 0.25 mol L⁻¹ buffer solution (pH 7.0) under -1.46 V versus Ag/AgCl. Charge buildup versus time from electrolysis of 3.0×10⁻⁶ mol L⁻¹ **1** (b) or **2** (c) under various applied potentials at pH 7.0. All data have been deducted blank.