Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Yu-Jen Shih^{a,1}, Yao-Hui Huang^a, C.P. Huang^{b,*}

^a Department of Chemical Engineering, National Cheng-Kung University, Tainan 701, Taiwan
^b Department of Civil and Environmental Engineering, University of Delaware, Newark, DE 19716, USA

ARTICLE INFO

ABSTRACT

Article history: Received 8 August 2017 Received in revised form 22 September 2017 Accepted 9 October 2017 Available online 10 October 2017

Keywords: Graphite Lead oxide Pseudocapacitance Ammonia oxidation Nitrogen selectivity Constant potential

1. Introduction

Ammonia nitrogen (NH₃/NH₄⁺) is one of the main nutrients of eutrophication process. In particular, ammonia, even in dilute concentration, may lead to severe toxicity in fishes and plants [1]. Domestic, agricultural, and industrial wastewaters are major anthropogenic sources of ammonia in water [2]. Recently, ammonia has emerged as a promising fuel for electricity generation in solid oxide fuel cells (SOFCs) due to low cost, low carbon footprint, and relatively high safety [3]. With extensive uses in high-tech industry, the management of ammonia pollution has become an important issue for protecting natural environments. Anammox[®] process is presently the most appealing biological technology for the elimination of ammonia nitrogen from sewage, but it takes time for the conversion of ammonia to nitrogen gas per the nitrification-denitrification sequential microbial metabolisms [4,5]. Indirect electro-oxidation involving chloride electrolysis in breakpoint chlorination can rapidly decompose ammonia to nitrogen at a specific Cl_2 to NH_3 molar ratio [6,7]:

$$2Cl^{-} \rightarrow Cl_{2} + 2e^{-} \text{ (on the anode)}$$
(1)

$$Cl_2 + H_2O = HOCl + H^+ + Cl^-, K_a = 3.94 \times 10^{-4}$$
 (2)

© 2017 Elsevier Ltd. All rights reserved.

Graphite-supported α - and β -PbO₂ electrodes (PbO₂@G) were prepared by electrochemical deposition at

appropriate potentials with regard to Pb(II)/PbO₂ redox couple under alkaline and acidic conditions,

respectively, for studying the direct electro-oxidation of ammonia in aqueous solutions. Results of surface

characterization including scanning electron microscopy (SEM), X-ray diffractometer (XRD) and X-ray photoelectron spectroscopy (XPS) indicated the presence of polymorphs of PbO₂@G. Cyclic voltammetry

(CV) of the electrolyte containing NH₃ indicated mediation of electron transfer by PbO₂. At the onset

potential of ca. +1.0 to +1.45 V (vs. Hg/HgO), a pathway of NH₃ oxidation to nitrogen byproducts, namely,

N₂, NO₂⁻, and NO₃⁻ was proposed. The removal efficiency and selective conversion of ammonia (0.1 M

Na₂SO₄, pH 11, 25 °C) on PbO₂@G was determined based on controlled potential experiments.

$$3HOCl + NH_3 \rightarrow N_2 + 3H_2O + 3H^+ + 3Cl^-$$
 (3)

$$4HOCl + NH_4^+ \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^-$$
(4)

However, high chloride salt concentration was normally required to compensate for the low chlorine evolution activity over the anode [8], which potentially led to the formation of chloramine intermediates of rather toxic disinfection by-products (DBPs), i.e., NH₂Cl, NHCl₂, and NCl₃.

The electrochemical oxidation (EO) is an attractive method, particularly, for the treatment of wastewaters. EO is an eco-friendly approach, as it requires only electricity and electron is a clean and effective reagent per sec. Electrolysis renders specific pollutants oxidized or reduced thereby reducing the toxicity. Boron-doped diamond (BDD), tin oxide (SnO₂), and lead oxide (PbO₂) are among the typical non-active anodes that have a high oxygen overpotential (OER), which can completely oxidize hydrocarbons (R) with total mineralization. Anodes with high oxygen overpotential can *in-situ* produce strong oxidants such as hydroxyl radicals (HO•), which are strong oxidation agents [9]:

$$MO_x + H_2O \rightarrow MO_x - H_2O_{(ads)}$$
(5)

https://doi.org/10.1016/j.electacta.2017.10.060 0013-4686/© 2017 Elsevier Ltd. All rights reserved.



Research paper





E-mail address: huang@udel.edu (C.P. Huang).

¹ Current address: Institute of Environmental Engineering, National Sun Yat-sen University, Kaohsiung 804, Taiwan.

$$MO_x - H_2O_{(ads)} = MO_x - HO^{\bullet}_{(ads)} + H^+ + e^-$$
 (6)

$$MO_x - HO^{\bullet}_{(ads)}) + R \rightarrow MO_x + CO_2 + H_2O$$
(7)

where MO_x denotes the electroactive sites of metal oxides. Among the non-active materials, PbO_2 was an effective anode for wastewater treatment due to high electrical conductivity, good stability, low cost, and long service life [10]. Over the past decade, PbO_2 electrode has been widely studied for the treatment of organic wastewaters [11–13], mainly focused on the indirect EO mode involving the generation of hydroxyl radicals. On the other hand, activated electrodes such as carbon, graphite, iridium oxide (IrO₂), ruthenium oxide (RuO₂), and platinum (Pt) only mediate partial oxidation of organic compounds [14].

There were studies on the direct EO of ammonia for energy generation. Among all electrodes, Pt was one of the most commonly studied [15,16]. Nonetheless, the cost of Pt remains a main constrain of its wide applications. To date, there is no comprehensive investigation on the mechanism of direct EO of ammonia over PbO₂ electrode in dilute aqueous solutions. This has prompted us to synthesize an anode by depositing PbO₂ onto graphite support (PbO2@G) using a potential sweep method in alkaline and acidic solutions, separately. The electron transfer process over PbO₂@G, i.e., the working electrode, was characterized by cyclic voltammetry in ammonia containing electrolyte. Batch constant-potential experiments (amperometry) were conducted to verify the efficacy of the PbO₂ electrode in electrooxidation of ammonia and its selectivity measured in terms of nitrogen species including nitrite, nitrate, and nitrogen molecule, in dilute aqueous solutions.

2. Materials and Methods

2.1. Chemicals

Lead sulfate (PbSO₄), and lead nitrate (Pb(NO₃)₂), provided by Sigma-Aldrich Co., USA, and Merck KGaA, Germany, respectively, were used to synthesize PbO₂@G electrode. The ammonia solution was prepared by dissolving a given amount of ammonium sulfate, ((NH₄)₂SO₄, J.T. Baker, USA) in the supporting electrolyte of sodium sulfate, (Na₂SO₄, Sigma-Aldrich Co., USA). The solution pH was controlled by sodium hydroxide, (NaOH, Merck KGaA, Germany) and sulfuric acid (H₂SO₄, 95%, Sigma-Aldrich Co., USA). Chemicals for the analysis of nitrogen species namely, sodium nitrite (NaNO₂), sodium hypochlorite (NaClO), *N*-(1-Naphthyl) ethylenediamine dihydrochloride (C₁₀H₇NHCH₂CH₂NH₂•2HCl), sulfanilamide (H₂NC₆H₄SO₂NH₂), and sodium phenoxide (NaOC₆H₅•3H₂O) were purchased from Sigma-Aldrich Co., USA. Potassium nitrate (KNO₃) and sodium nitroprusside (Na₂[Fe(CN)₅NO]) were purchased from Riedel-deHaën AG, Germany. ethylenediaminetetraacetic acid disodium salt dihydrate (C₁₀H₁₄N₂Na₂O₈•2H₂O, EDTA-Na₂) was purchased from U&I Bio-Tech, Inc., USA. All reagents were of analytical grade and used without purification.

2.2. PbO₂@G synthesis

The raw graphite was polished with an ultrafine sandpaper (P400, 3 M), followed by acid etching in 1 M of H_2SO_4 for 30 min, then rinsing in acetone for 10 min and in deionized water for another 10 min in a ultrasonic bath to remove any adhesive and grease. Cyclic voltammetry (CV) was conducted using graphite (plate) electrode in two lead electrolytes, (i) $Pb(NO_3)_2$ in 0.5 M HNO_3 (vs. Ag/AgCl/3 M KCl, $E^0 = 0.21$ V vs. NHE, RE-1B, ALS Co. Ltd., JAPAN) and (ii) PbSO4 in 2 M NaOH (vs. Hg/HgO/1 M NaOH, E⁰=0.14 V vs. NHE, RE-61AP, ALS Co. Ltd., JAPAN) using a potentiostat (CHI611C, CH Instruments, Inc., USA). IrO₂ coated titanium (effective area = $1.5 \times 2 \text{ cm}^2$) was the counter electrode [17]. PbO₂@G electrodes were finally synthesized (on the working graphite electrode) by sweeping the Pb^{II}/PbO₂ redox couple (50 mV s⁻¹) at 85 °C for 2 h in acidic solution or basic solution (Supporting Information shows the diagram of sweeping potential). The electrochemical stability of obtained PbO2@G electrodes were tested by scanning the potential window for between +0.40 and +1.40 mV for 400 cycles using voltammetric method as shown in Fig. S2. Results showed insignificant voltammetric changes of both the PbO2/G electrodes.

2.3. Characterization of the PbO₂@G electrode

The chemical state of PbO₂@G electrode was characterized by Xray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, Physical Electronics, Inc., USA) with a monochromatic Al K α Xray source (1487 eV). A scanning electron microscopy (SEM, JSM-6700F, JEOL Ltd., Japan) was used to observe the micromorphology of electrode before and after electrochemical



Fig. 1. Cyclic voltammetry of graphite electrode in the electrolytes containing (a) $2 \text{ M NaOH} + 0 \sim 0.015 \text{ M PbSO}_4$, and (b) $0.5 \text{ M HNO}_3 + 0 \sim 0.15 \text{ M Pb(NO}_3)_2$. (Sweeping rate = 10 mV s^{-1} , counter electrode = IrO_2 coated titanium).

experiments. The crystallographic structure was analyzed by X-ray diffraction (XRD, DX III, Rigaku Co., Japan) operated with Cu K α source (λ = 1.5406 Å) at a scan rate of 0.06°-s⁻¹ in the incidence angle range of 20–85° (2 θ).

2.4. Ammonia oxidation experiments

The ammonia nitrogen redox characteristics on PbO@G, i.e., the working electrode (effective area = 3 cm^2) were conducted at constant voltage (CV) in 0.1 M of Na₂SO₄ as supporting electrolyte. IrO₂/Ti was the counter electrode. The reference electrode was Hg/ HgO. The *i-E* response of voltammetry in the presence of 0–10 mM NH₃ was recorded by scanning potential in a range of +0.35 to +1.5 V (vs. Hg/HgO) at specific rate (*v*, V/s). A three-electrode potentiostat system was used to carry out batch ammonia oxidation experiments under constant potential (amperometry) at pH 11 and 25 °C (working electrode = PbO₂@G rod, counter electrode = stainless steel mesh, reference electrode = Hg/HgO/1 M NaOH, A = 80 cm²). The configuration of the reactor is as provided in the Supporting Information.

A flow injection analyzer (FIA, Lachat's Quik Chem 8500 Series 2, USA) was used to analyze the concentration of aqueous nitrogen species (NH₃-N, NO₃⁻-N, NO₂⁻-N). Ammonia was analyzed by the indophenol method (at 630 nm) based on the Berthelot reaction, which involves reaction among phenolate, hypochlorite, and ammonia, with nitroprusside as catalyst [18]. The total oxidized nitrogen (NO_x) was determined by reducing nitrate to nitrite (in a copperized cadmium column) prior to diazotization of nitrite with sulfanilamide followed by coupling with N-(1-naphthyl)-ethyl-enediamine dihydrochloride (NED). Concentration of the pink azo dye produced was then calibrated spectrophotometrically at 540 nm [19]. Nitrate concentration was the difference between NO_x and nitrite, which was determined separately. The limit of detection was $0.2 \mu g/L$ for NH₃-N, and $0.25 \mu g/L$ for NO₂⁻-N and NO₃⁻-N.

3. Results and Discussion

3.1. Electrodeposition and characterization of PbO₂ on graphite

The cyclic voltammetry (CV) was used to assess the electrochemical behavior of Pb^{II} ions on the graphite. As shown in Fig. 1, the potential window of -0.2 to +0.8 V and +0.4 to +1.7 V was selected for characterizing the redox behavior of PbSO₄ and Pb (NO₃)₂, respectively, according to the variable formal potentials of Pb^{II}/PbO₂ couples in base and acid electrolytes [20], i.e.,

$$PbO_{2(s)} + 2e^{-} + 2H_2O = Pb(OH)_3^{-} + OH$$

$$E = 0.209 - 0.03pOH + 0.03pPb(II) + 0.03 \times p\alpha_{Pb(OH)_{3}} \quad (V \text{ vs. SHE})$$
(8)

$$PbO_{2(s)} + 4H^{+} + 2e^{-} = Pb^{2+} + 2H_{2}O$$

$$E = 1.46 - 0.12pH + 0.03pPb(II) + 0.03p\alpha_{pb^{2+}} \quad (V vs. SHE) \qquad (9)$$

Where Pb(II), $\alpha_{Pb(OH)_3^-}$, and $\alpha_{Pb^{2+}}$ are total lead concentration, fraction of $Pb(OH)_3^-$ and fraction of Pb^{2+} species, respectively. Pb^{II}/ PbO₂ redox reaction has a pair of peak potentials, O₁ and R₁, which peak currents increased with Pb(II) concentrations. The redox peaks were at 533 and 38 mV (vs. Hg/HgO) in 2 M of NaOH electrolyte; when scanned in the positive and negative directions in 0.5 M of HNO₃, the redox peaks were at 1610 and 1184 mV (vs.

Ag/AgCl). At higher potential, oxygen evolution reaction (OER) occurred (O₂). Since the *i*-*E* response of Pb^{II}/PbO₂ in CV has been known to vary with the type of electrolyte, a layer of PbO₂ would accumulate onto the graphite by sweeping the potential window at which more Pb^{II} was oxidized and less PbO₂ was reduced. Thus, the potentials that were applied to synthesize PbO₂@G were cyclically scanned at +0.2 to +0.8 V and +1.2 to 1.8 V for 2 h in base and acid electrolytes, respectively (Fig. S1).

Results of XRD analysis (Fig. 2) revealed that the mineral phases of PbO₂ electrochemically deposited on the graphite in NaOH and HNO₃ were scrutinyite (α -type) and plattnerite (β -type), respectively, based on JCPDF reference (#45-1416 and #41-1492). β -PbO₂@G has higher crystallinity than α -PbO₂@G due to its well-defined diffraction peaks. The grain size of PbO₂ was estimated by the Debye-Scherrer relationship, $d = (K\lambda)/(B\cos\theta)$, where *d* is the size of primary grain in the crystal, λ the X-ray wavelength (CuK α 1, 1.541 Å), B is the full width at half maximum of a specific diffraction peak (FWHM), K a shape factor of crystallite, typically is 0.89, and θ is the diffraction angle. The average size of α -PbO₂@G and β -PbO₂@G were 3.2 and 36 nm, respectively, according to the corresponding FWHM of (111) plane (at $2\theta = 28.6^{\circ}$ and 36.3°, Fig. 2a and c). The crystal size of β -PbO₂ was close to that of PbO₂ electrodeposited in nitric acid solution reported in the literature [21,22], while the much smaller size of α -PbO₂ indicated the presence of much disordered structure lattice."

It is clearly seen from SEM that the loose and porous grains of α -PbO₂@G is comprised of nano-sized strips (Fig. 3a, b), and β -PbO₂@G is regularly crystallized in pyramidal shape (Fig. 3d, e). After cycling voltammetry experiment in 10 mM NH₃ (pH 11,



Fig. 2. XRD patterns of PbO₂@G prepared in (a) 2 M NaOH before and (b) after electrolytic ammonia oxidation; PbO₂@G prepared (c) in 0.5 M HNO₃ before and (d) after electrolytic ammonia oxidation (electrolytic conditions: 10 mM NH₃, +0.35 to +1.5 V, scanned by 50 mV s⁻¹ for 100 loops).



Fig. 3. SEM images of α -PbO₂@G (a) 3,000 × and (b) 20,000 × before and (c) after oxidizing ammonia (60,000 ×); β -PbO₂@G (d) 3,000 × and (e) 15,000 × before and (f) after oxidizing ammonia (15,000 ×) (electrolytic conditions: NH₃ = 10 mM, potential window = +0.35 to +1.5 V, scan rate = 50 mV s⁻¹, 100 loops).

50 mV/s for 100 loops), the crystals of β -PbO₂@G became rectangular and the strips morphology of α -PbO₂@G disappeared, implying that PbO₂ might participate at chemical ammonia redox reaction at the electrode surface (Fig. 3c and f). The modification of structure was consistent with that of XRD analysis. During electrolysis, α -PbO₂ underwent phase transition to β -PbO₂ and the lattice defect of lead vacancy could be derived from β -PbO₂ in the presence of ammonia (Fig. 2b and d).

Normally, lead dioxide polymorphs were not fully stoichiometric, resulting in high conductivity [23]. The chemical composition may be more correctly represented by $(Pb^{IV})_{1-x-v}(Pb^{II})_vO_{2-4x-v}$ $_{2v}(OH)_{4x+2y}$ where the cationic vacancies clustered together and acted as interfaces in crystallographically ordered regions and served as hosts for Pb²⁺ ions. In other words, the surface Pb from +IV oxidation state in PbO₂ changed moderately to +II as PbO. Fig. 4 shows the core level spectra of the Pb 4f spin orbit doublet and O1s level. The Pb 4f spectra of either α - or β -PbO₂@G comprised of Pb^{II} bands $(4f_{7/2} \text{ and } 4f_{5/2})$, which were observed at 138.1 eV and 142.9 eV, respectively, suggesting the presence of PbO or Pb₃O₄ compounds on the surface layer of the electrode [24]. On the other hand, the peaks characterizing Pb^{IV} were at 137.2 eV and 142 eV [25]. From the XPS analysis the atomic ratio of Pb^{IV} to Pb^{II} was around 1.0 for both of PbO2@G electrodes and increased to 1.4 for β -type and approximately around 1.2 for α -type after CV scanning in 10 mM NH₃. The O 1 s spectral components in lattices of PbO₂ and PbO were at 529 and 530 eV, respectively, while those at 531 and 532 eV were attributed to hydroxide and adsorbed oxygen, respectively [26]. The —OH signal in α -PbO₂@G was rather intense as compared to β -PbO₂@G (Fig. 4b and d), restated, Pb^{II} electrodeposited in alkaline solution was present as a majority of hydroxide. After voltammetry in NH₃-containing solutions, the number of surface -OH groups decreased. Deprotonation occurred on the hydrous oxide surface that led to electrochemical evolution of oxygen on the lead dioxide electrode [27]. The XPS data appropriately explained the changes in XRD analysis and morphology of PbO₂ by electrochemical reactions that modified the oxidation state of Pb and the amount of elemental oxygen content in the surface region.



Fig. 4. XPS spectra of α -PbO₂@G in the regions of (a) Pb 4f and (b) O 1s and β -PbO₂@G in the regions of (c) Pb 4f and (d) O 1s without and with electrochemical oxidation of ammonia (electrolytic conditions: NH₃ = 10 mM, potential window = +0.35 to +1.5 V, scan rate = 50 mV s⁻¹, 100 loops).

3.2. Electroanalytical ammonia oxidation over the PbO₂@G electrodes

The voltammograms of PbO₂@G electrodes in the supporting electrolyte (0.1 M Na₂SO₄, pH 11) were demonstrated in Fig. 5. Both α - and β -phase electrodes exhibited increase in capacitive charging current (i_C) with increase in sweep speed within the potential range of PbO_x/PbO₂ redox (0.3-1.5 V, vs. Hg/HgO). Such inherent redox process and electrostatically non-faradaic charge were the origin of pseudocapacitance [28].

 $PbO_2 + (4-2x)H^+ + (4-2x)e^- = PbO_x + (2-x)H_2O x = 1 \sim 2$ (faradaic reaction) (10)

 $PbO_x(OH)_y + \delta H^+ + \delta e^- = PbO_{(x-\delta)}(OH)_{y+\delta}$ (capacitive chargingdischarging) (11)

Nevertheless, the capacitance of α -PbO₂@G was substantially greater than β -PbO₂@G. Since the potential was continuously charging during voltammetry, the i_c , which decayed under controlled potential kept flowing [29]. The differential capacitance C_d can be obtained by linearly regressing currents *i* of the electrode against the sweep rate *v* on the CV curves as follows [30,31], that is:

$$i_{\rm C} = \frac{d\sigma}{dt} = \frac{d\sigma}{dE} \times \frac{dE}{dt} = C_{\rm d} \times \nu \tag{12}$$

Where σ and E was the charge density and the overpotential, respectively. From the slope of i_c vs. v plot, the minimal capacitance, E_{pzc} , of α -PbO₂@G was 34 mF cm⁻² at pH_{pzc} 8.5, which remarkably was higher than the graphite substrate, 9 mF cm⁻² at pH_{pzc} 6. The minimal capacitance of β -PbO₂@G was 4 mF cm⁻² at pH_{pzc} 10 as shown in the Supporting Information (Fig. S3). Due to the huge difference between non-faradiac charging (*i.e.* C_d) of the two crystal phases, the peak current of reversible oxidation/ reduction of lead dioxide (Eq. (10)), which had an onset potential around +1.0 V (vs. Hg/HgO) for β -PbO₂@G (Fig. 5b), however, was masked by the high capacitance behavior for α -PbO₂@G (Fig. 5a).

The faradiac current was measured with respect to the baseline of capacitive current by changing the applied potential on the working electrode. The large pseudocapacitance of α -PbO₂@G might restrict the accuracy of the current measurement (i_p) during ammonia redox reaction, particularly at high sweep rate when the magnitude of i_C and i_p were a function of v and $v^{1/2}$, respectively [32]. Thus, in the following voltammetry studies, β -PbO₂@G electrode was used to assess the degradation of nitrogen compounds on the basis of similar potential range for ammonia oxidation exhibited by both electrodes (Fig. S4). Fig. 6 shows the polarization curves, i.e., log *i* versus *E*. as a function of pH in the potential range where PbO_x/PbO₂ transformation occurred. The decrease in formal potential of Pb^{II} to Pb^{IV} with increasing pH was anticipated per the Nernst equation since the proton was involved (Eq. (10)). On the other hand, note that the Tafel slope **b** was a function of transfer coefficient (α) and electron number (**n**) of concern, where b=2.303/(1- α)nf (f=nF/RT). In the presence of ammonia, the Tafel slope b decreased from 193 mV dec⁻¹ at pH 4 to 96.8 mV dec⁻¹ at pH 11, verifying that the number of electron involved with PbO_x to PbO₂ doubled by increasing pH from 4.0 to 11.0. The speciation of aqueous NH₄⁺ and NH₃ is pH-dependent



Fig. 6. Tafel analysis of the voltammetric feature of β -PbO₂@G swept from an onset potential of PbO_x/PbO₂ to the limiting current region (0.5 mV s⁻¹) at various pH in the electrolyte of 0.1 M Na₂SO₄ and 0.01 M NH₃.



Fig. 5. Cyclic voltammetry of (a) α -PbO₂@G and (b) β -PbO₂@G as a working electrode. (supporting electrolyte = 0.1 M Na₂SO₄, pH 11, counter electrode: IrO₂/Ti, effective area = 3 cm²).

with an equilibrium constant of pK_a = 9.25, and NH₃ is a dominant species at pH > 10 (NH₃/N_T > 85%). Hence, it was expected that direct electro-oxidation of NH₃-N simply occurred in the electrical double-layer structure of PbO₂ electrode.

Fig. 7 demonstrates the voltammetry of β -PbO₂@G electrode in the electrolyte containing Na₂SO₄ and NH₃. When the potential was increased to above +0.95 V, the peak current of PbO_x/PbO₂ couple was a specific function of the scan rate (v) and bulk concentration of NH₃ (C^{*}), indicating that the faradaic reactions ascribed to the electron transfer between the electrode surface and nitrogen species were diffusion-controlled. Note that in order to improve the resolution of the CV curves, The total current (Fig. 7a and c) was subtracted from the background current to obtain the net current as a function of applied voltage (Fig. 7b and d). Fig. 7b and d) give the net redox current of NH₃ oxidation as a function of $v^{1/2}$ and C^{*}. The deconvolution of current profile in a potential window of +0.8 to +1.4 V was therefore conducted using an Origin Pro. Software. Fig. 8a shows the fitting result of sweeping rate at 10 mV s⁻¹ (0.001 M NH₃, pH 11) could be used to identify four anodic potential peaks, namely, E_{p1} , E_{p2} , E_{p3} , and E_{p4} , at +1.0, +1.07, +1.16 and +1.25 V, respectively. (Owing to the electrode kinetics, E_p should vary with ν and C^{*} as shown in Fig. S5.) According to the Nicholson and Shain equation $(i_p = 2.99 \times 10^5 n(\alpha n_\alpha)^{1/2} A D^{1/2} C^* v^{1/2})$ peak currents (i_p) of faradaic reactions on CV diagrams aere related to ν (V s⁻¹) and C^{*} (mol cm⁻³) [33–35], where **n** is the number of electron transferred, **A** is the effective area (3 cm^2) , and **D** is the diffusion coefficient (e.g., 1.64×10^{-5} cm² s⁻¹ for NH₃). The term of αn_{α} is the transfer coefficient times the number of electron involved in the rate-limiting step, from the relationship: $|E_p - E_{p/2}| = 47.7 / \alpha n_{\alpha}(mV)$, at 298 K; where $E_{p/2}$ is the potential at the current $I_{p/2}$. Voltammetry results under various ν and C^{*} in Fig. 7b and d were used to secure the information of the corresponding electrochemical processes. The species of anodic oxidation was quantitatively rationalized with electrode kinetics, and the value of α reflected the symmetry of free energies (of reactant and product) and the magnitude of the activation barrier [36]: at $\alpha < 0.5$ and $\alpha > 0.5$, the reaction coordinate favored reduction and oxidation, respectively. Fig. 8b exhibits αn_{α} of the four peaks at different NH₃ concentrations, which were all larger than 0.5 and followed the increasing order of $E_{p2} > E_{p4} \sim E_{p3} > E_{p1}$. Based on the above results, one could conclude that ammonia and nitrogen intermediates were oxidized preferably on the PbO₂ electrode, whereas the first step of electron transfer was relatively slow.

The slopes of i_p against $(\nu \times \alpha n_{\alpha})^{1/2}$ plots were proportional to ammonia concentration, thus obtaining the factor of electron



Fig. 7. Voltammetry of β -PbO₂@G electrode at various (a) scan rate (0.01 M NH₃) and (c) ammonia concentration (ν = 10 mV s⁻¹); net current of ammonia oxidation from (b) 0.01 M NH₃ and (d) scan rate of 10 mV s⁻¹.



Fig. 8. (a) Deconvolution of current of ammonia at PbO@G from conditions of 10 mV s⁻¹, 1 mM NH₃ and pH11. (b) Effect of NH₃ concentration on the transfer coefficient as a function of scan rate. (c) Linear regression of $I_P/(\nu \times \alpha n_{\alpha})^{1/2}$ versus ammonia concentration.

number, n (Fig. 8c), (the fittings are as shown in Fig. S6). As a result, the corresponding n value for anodic peaks of E_{p1} , E_{p2} , E_{p3} and E_{p4} were 1.2, 1.5, 2.1 and 2, respectively. The pathway of electrochemical oxidation of ammonia on platinized Pt has been proposed. The general scheme with stepwise dehydrogenation was the key reaction of electro-oxidation of NH₃ [37,38]. In the present research, since the current of the PbO_x/PbO₂ couple was enhanced in the presence of NH₃, that is, the electron transfer step of NH₃ oxidation initiated coincidently at a potential of around that of the PbO_x to PbO₂ pair, the electrons to deprotonate ammonia were

thought to be directly taken by PbO₂.

$$PbO_2 + NH_3 \leftrightarrow PbO_2 \equiv NH_{3(ad)} \rightarrow Pb^{4+}O_2 \equiv NH_{3(ad)}$$
(13)

$$Pb^{4+}O_2 \equiv NH_{3(ad)} \rightarrow Pb^{2x+}O_x \equiv NH_{(2x-1)(ad)} + (2-x)H_2O_{(ad)}$$

$$\to Pb^{3+}O_{3/2} \equiv NH_{2(ad)} + 1/2H_2O_{(ad)}$$
(14)



Fig. 9. Concentration profile of nitrogen species at constant potentials $1.0V \sim 1.45 V$ (vs. Hg/HgO) over the α -PbO₂@G for (a) ammonia oxidation, (b) nitrite, (c) nitrate and (d) nitrogen gas evolution. (NH₃-N = 20 ppm, pH 11, electrolyte = 10 mM Na₂SO₄, counter = stainless steel, A = 80 cm²).

The electron transfer was responsible for the oxidation of PbO_x , so that $PbO_2@G$ catalytically mediated the dehydrogenation of NH_3 .

$$Pb^{3+}O_{3/2} + 1/2H_2O_{(ad)} \to Pb^{4+}O_2 + H^+ + e^-$$
 (15)

The deprotonated surface ammonia, NH_x , dimerized on the electrode surface, yielding N_2H_2 , N_2H_3 , N_2H_4 species, which were intermediates of nitrogen evolution [39].

$$N_2H_x + xOH^- \rightarrow N_2 + xH_2O + xe^- \tag{16}$$

In addition, adsorbed NH_x could be readily oxidized to N atom, which were precursors of oxygenated nitrogen produced at high overpotentials.

$$NH_x + xOH^- \rightarrow N + xH_2O + xe^- \tag{17}$$

Reactions of Eq. (16) & (17) were corresponding to the above polarization at anodic E_{p2} . The increase in oxidation state of nitrogen from ammonia to zero-valent nitrogen (N₂ or N) requires three electrons transferred, which was close to the 2.7 obtained by voltammetry. Furthermore, the chemical reaction between the adsorbed hydroxyl ions and oxygenated intermediates that could be resulted from E_{p3} and E_{p4} presumably led to the formation of nitrite and nitrate ions.

$$N + 2xOH^{-} \rightarrow NO_{x} + xH_{2}O + 2xe^{-} (1 < x < 2)$$
(18)

From the deconvolution of net anodic current in Fig. 8a, therefore, the onsets of E_{p3} and E_{p4} were at around 1.05 and 1.15 V (vs. Hg/HgO), respectively, implying that the selectivity would move toward the oxidation of $N_{(ads)}$ in parallel to N_2 evolution.

3.3. Batch oxidation of ammonia on PbO₂@G using amperometry

Results of voltammetric analysis revealed that the reversible redox of surface Pb^{II}O/Pb^{IV}O oxides (Eq. (10)) took place at sweeping potential of ca. $+1.0 \sim +1.1$ V (vs. Hg/HgO) (Fig. 5b). At a constant potential range of +1.0, +1.15, +1.3, and +1.45 V, therefore,

amperomertry in the presence of 20 ppm NH₃ (pH 11, 0.1 M Na₂SO₄) was carried out to evaluate the capability of PbO₂@G electrodes to treat ammonia solution. Figs. 9 and 10 indicate the percent ammonia removal and concentration profiles of nitrogen byproducts, including N₂, NO₂⁻ and NO₃⁻, using α - and β -PbO₂@G working electrode, respectively. By increasing the electrode potential from +1.0 to +1.45 V, the ammonia removal percentage increased from 13 to 76% for α -PbO₂, and from 30 to 68% for β -PbO₂ in 7 h. As expected, the low effectiveness of α -phase on ammonia oxidation could be attributable to its high adsorptive pseudocapacitance behavior (C_d , eq. (12)); namely, the current was predominated by the charging of chemisorbed species with potential-dependent coverage [40]. With increasing potential, nevertheless, ammonia oxidation reached the region of limiting current and α -phase showed better efficiency because of its larger number of surface site than β -phase (based on micromorphology in Fig. 3). Fig. 11 summarizes the distribution of pertinent nitrogen species as a function of applied potential: relatively low nitrate ions and high nitrogen gas yielded over β -PbO₂@G at low applied potential (< 1.15 V) was observed. Meanwhile, the nitrite concentration was almost negligible (< 0.15 ppm) for both electrodes at low applied potential, but increased to reach a plateau with increase in potential (> 1.3 V) (Figs. 9b and 10b). The electrodes were evaluated in terms of ammonia removal efficiency (NH_{3r}, %) and nitrogen conversion with respect to ammonia removal $(S_N, \%)$ according to the following equations, respectively:

$$NH_{3r}(\%) = \frac{[NH_3]_0 - [NH_3]_t}{[NH_3]_0} \times 100$$
(19)

$$S_{N_i} = \frac{[N_i]}{[NH_3]_0 - [NH_3]_t} \times 100$$
⁽²⁰⁾

where $[N_i]$ was $[N_2]$, $[NO_3^-]$, or $[NO_2^-]$. As shown in Fig. 11b and e, S_{N_2} varied inversely with S_{NO_3} and there were crossover between them at ca. 1.2 V for α - and β -PbO₂, at which N₂ evolution



Fig. 10. Concentration profile of nitrogen species at constant potentials $1.0V \sim 1.45 V (vs. Hg/HgO)$ over the β -PbO₂@G for (a) ammonia oxidation, (b) nitrite, (c) nitrate and (d) nitrogen gas evolution. (NH₃-N = 20 ppm, pH 11, electrolyte = 10 mM Na₂SO₄, counter = stainless steel, A = 80 cm²).



Fig. 11. Speciation, selectivity and current efficiency of converting ammonia to nitrogen byproducts at (a), (b), (c) α-PbO₂@G and (c), (d), (e) β-PbO₂@G electrodes.

accounted for half of 55% ammonia removed. The high selectivity for converting ammonia to nitrogen gas at 1.15 V was 60% for α -phase and 80% for β -phase, which was in agreement with voltammetric results and verified according to the proposed oxidation pathway (eqs. (13)–(16)). To evaluate the current efficiency (η , %) of ammonia conversion, the total charge, Q_{total}, at various constant potentials was obtained by integrating the electric current profiles of α - and β -PbO₂ (Fig. S7) over reaction time. η is defined as,

$$\eta(\%) = \frac{nF[N_i]V}{\int I(t)dt} \times 100 = \frac{nF[N_i]V}{Q_{total}} \times 100$$
(21)

where [N_i] is the levels of NO₃⁻ or NO₂⁻ or N₂ (*M*) created after 7 h electrolysis, F is the faradaic constant (96,485C eq⁻¹) and V is the reaction volume (*L*). The electron number n involved in the production of NO₃⁻, NO₂⁻ and N₂ is 8, 6 and 6, respectively. As can be seen in Fig. 11c and 11f, the current efficiency of NH₃ conversion ($\eta_{NO3} + \eta_{NO2} + \eta_{N2}$) was less than 30% on α -PbO₂; whereas, β -PbO₂ exhibited a current efficiency of *ca*. 50%, particularly at high voltage (1.3 V and 1.45 V). A significant portion of current was consumed by pseudocapacitive charging of α -phase (*i.e.* reversible redox couple of electrode material), thus reducing the current efficiency in the electron transfer of nitrogen molecules.

The kinetics of electro-oxidation of ammonia over PbO₂@G electrodes was assessed by the steady-state approximation, based on the following assumptions. First, the chemical reactions only occurred heterogeneously on active surface sites of electro-catalysts; second, the nitrogen species in the bulk solution were in equilibrium with their corresponding surface species via the adsorption/desorption reaction. Thus, the surface coverage by adsorbed entities was low and almost constant, including θ_{NH3} , θ_{NH2} , θ_{N} , θ_{N2H4} , θ_{N2} , θ_{N02} , and θ_{N03} . The following diagram shows the general reaction scheme of ammonia oxidation with corresponding rate and equilibrium constants:

$$\begin{array}{c|c} < 1.2 \text{ V} &> 1.2 \text{ V} \\ \hline &> 1.2 \text{ V} \\ \\ &> 1.2 \text{ V} \\ \hline &= 1.2 \text{ V} \\ \hline &$$

Rate equations of NH₃, N₂, NO₂⁻ and NO₃⁻ in solution were described in terms of surface coverage, i.e., $-\frac{d[NH_3]}{dt} = k_2\theta_{NH3}\theta_{OH}$, $\frac{d[N_2]}{dt} = k_4\theta_{OH}^4\theta_{N2H4}$, $\frac{d[NO_2]}{dt} = k_6\theta_{NH2}\theta_{OH} - k_9\theta_{NO2}\theta_{OH}^2$, and $\frac{d[NO_2]}{dt} = k_8\theta_{OH}^2\theta_{OH}\theta_{NO2}$, and the global ammonia oxidation rate is $r_{NH_3} = 2r_{N_2} + r_{NO_2} + r_{NO_3}$, whilst $[NH_3]_0 = [NH_3]_t + [N_2]_t + [NO_2^-]_t + [NO_3^-]_t$. By integrating the above rate equations, the corresponding reaction rate constants were calculated by fitting the nitrogen species with the rate expressions. (The Supporting Information gives details of the kinetic derivations.)

$$C_{NH3} = C_{NH3,0} e^{-k_a t} \tag{23}$$

$$C_{N2} = K_c C_{NH3,0} (1 - e^{-k_a t})$$
(24)

$$C_{NO2} = \frac{k_a K_d (1 - K_c)}{k_b - k_a} C_{NH3,0} (e^{-k_a t} - e^{-k_b t})$$
(25)

$$C_{NO3} = \frac{(1 - K_c)(k_b K_e - k_a K_e + k_b K_d)}{k_b - k_a} C_{NH3,0} (1 - e^{-k_a t}) - \frac{k_a K_d (1 - K_c)}{k_b - k_a} C_{NH3,0}$$
(16)

where
$$k_a = \frac{k_B^+ k_2 \theta \theta_{0H}}{k_1 + k_2 \theta_{0H}}$$
, $k_b = \frac{k_B^+ k_2 \theta \theta_{0H}^2}{k_B \theta_{0H}^2 + k_B^+}$, $K_c = \frac{k_B^+ k_d \theta_{0H}^2}{k_4 k_3^+ \theta_{0H}^2 + k_5 k_6 + k_4 k_6 \theta_{0H}^4}$, $K_d = \frac{k_B^+ \theta_{0H}^2}{k_B \theta_{0H}^2 + k_B^+}$, which are functions of rate constants of ammonia adsorption (k_1^+) and deprotonation (k_2) , NH₂ combination (k_3^+) , NO₂⁻ desorption/adsorption (k_8^+/k_8^-) and oxidation (k_9) , respectively. Table 1 lists the rate constants, k_a and k_b , and equilibrium constants, K_c , K_d and K_e , at different applied potentials. The efficiency of ammonia depletion was influenced by deprotonation, which was enhanced with increasing the overpotential. The equilibrium constant, K_c of NH₂ combination, restated, at low overpotential the formation of N₂H₄ affects the evolution of nitrogen gas. The major difference was that k_b of the β -phase electrode was significantly higher than that of the α -phase. In other words, the larger amount of nitrate ions generated from α -phase electrode was due to the greater nitrite ion adsorption capacity compared to the β -phase electrode. Obviously, the nanoporous morphology of α -PbO₂@G contributed reactive sites that retained charged nitrogen intermediates, such as NO₂⁻ on the electrode surface, which were easily oxidized to the highest oxidation state at higher overpotential.

4. Conclusions

Ammonia oxidation occurred readily over PbO₂@G electrodes. The formal potential of Pb^{II}/PbO_2 redox couple was determined by voltammetry and used to synthesize α and β -PbO₂; α - (scrutinyite) and β -PbO₂ (plattnerite), polymorphs of lead dioxide, were electrochemically formed over graphite electrode in alkaline and acid solutions, respectively. Because α -phase lead dioxide had a porous structure, in contrast to the well-crystalline β -phase, the pseudocapacitance of α -PbO₂ was almost ten times that of β -PbO₂. There was pH-dependent enhancement in the onset current of surface PbO_x at ca. +1.0 V (Hg/HgO), which indicated that PbO_2 mediated the electron transfer. The pathway of NH₃ oxidation to nitrogen species (N₂, NO₂⁻ and NO₃⁻) was evaluated based on the corresponding peak potential behaviors on CV curves. Results of batch experiments at controlled potentials (amperometry test) in the range of +1.0 to +1.45 V. showed that β -PbO₂ had high nitrogen gas evolution at low overpotential (< 1.15 V), attributed to its relatively low capacitance. However, α -PbO₂ was capable of removing a greater amount of ammonia at high overpotential $(NH_{3r} = 76\% \text{ at } 1.45 \text{ V})$ because of its larger number of active sites.

Acknowledgements

The authors wish to thank The Ministry of Science and Technology (MST) – Taiwan, for financial support of this research under Contract No. 104-2218-E-006 –020 –MY3. Additional support was provided by US NSF IOA (grand no. 1632899).

Table 1 Rate constants involved in ammonia oxidation over α - and β -PbO₂@G electrodes.

E, vs. Hg/HgO	$k_a (h^{-1})$	$k_{b} (h^{-1})$	K _c (a.u.)	K _d (a.u.)	K _e (a.u.)
	α-PbO ₂ @G				
1.00 V	0.015	0.35	0.45	0.65	0.35
1.15 V	0.085	1.50	0.25	0.25	0.75
1.30 V	0.105	1.35	0.18	0.15	0.85
1.45 V	0.190	1.20	0.19	0.11	0.95
	β -PbO ₂ @G				
1.00 V	0.055	0.75	0.45	0.65	0.35
1.15 V	0.085	1.5	0.38	0.3	0.7
1.30 V	0.135	4.0	0.18	0.25	0.75
1.45 V	0.160	5.0	0.19	0.25	0.75

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.electacta.2017. 10.060.

References

- [1] R. Esteban, I. Ariz, C. Cruzb, J.F. Moran, Review: Mechanisms of ammonium toxicity and the quest for tolerance, Plant Sci. 248 (2016) 92–101.
- [2] W.T. Mook, M.H. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam, M.A. Abu Hassan, Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: A review, Desalination 285 (2012) 1–13.
- [3] A. Afif, N. Radenahmad, Q. Cheok, S. Shams, J.H. Kim, A.K. Azad, Ammonia-fed fuel cells: a comprehensive review, Renew. Sust. Energ. Rev. 60 (2016) 822– 845
- [4] B. Ma, S. Wang, S. Cao, Y. Miao, F. Jia, R. Du, Y. Peng, Biological nitrogen removal from sewage via anammox: Recent advances, Bioresource Technol. 200 (2016) 981–990.
- [5] G. Moussavi, M. Mahdavianpour, The selective direct oxidation of ammonium in the contaminated water to nitrogen gas using the chemical-less VUV photochemical continuous-flow reactor, Chem. Eng. J. 295 (2016) 57–63.
- [6] H. Zhang, H. Liu, X. Zhao, J. Qu, M. Fan, Formation of disinfection by-products in the chlorination of ammonia-containing effluents: Significance of Cl₂/N ratios and the DOM fractions, J. Hazard. Mater. 190 (2011) 645–651.
- [7] X. Zhang, W. Li, E.R. Blatchley, X. Wang, P. Ren, UV/chlorine process for ammonia removal and disinfection by-product reduction: Comparison with chlorination, Water Res 68 (2015) 804–811.
- [8] Y. Gendel, O. Lahav, Revealing the mechanism of indirect ammonia electrooxidation, Electrochim. Acta 63 (2012) 209–219.
- [9] J. Chen, Y. Xia, Q. Dai, Electrochemical degradation of chloramphenicol with a novel Al doped PbO₂ electrode: Performance, kinetics and degradation mechanism, Electrochim. Acta 165 (2015) 277–287.
- [10] Q. Zhang, X. Guo, X. Cao, D. Wang, J. Wei, Facile preparation of a Ti/α-PbO₂/ β-PbO₂ electrode for the electrochemical degradation of 2-chlorophenol, Chinese J. Catal. 36 (2015) 975–981.
- [11] D. Shao, J. Liang, X. Cui, H. Xu, W. Yan, Electrochemical oxidation of lignin by two typical electrodes: Ti/Sb/SnO₂ and Ti/PbO₂, Chem. Eng. J. 244 (2014) 288– 295.
- [12] H. Särkkä, A. Bhatnagar, M. Sillanpää, Recent developments of electrooxidation in water treatment – A review, J. Electroanal. Chem. 754 (2015) 46– 56.
- [13] Q. Dai, J. Zhou, M. Weng, X. Luo, D. Feng, J. Chen, Electrochemical oxidation metronidazole with Co modified PbO₂ electrode: Degradation and mechanism, Sep. Purif. Technol. 166 (2016) 109–116.
- [14] E. Sogaard, Chemistry of Advanced Environmental Purification Processes of Water Ch. 3-Electrochemical Oxidation – A Versatile Technique for Aqueous Organic Contaminant Degradation, Elsevier B.V., 2014, pp. 75–134.
- [15] M.H.M.T. Assumpção, R.M. Piasentin, P. Hammer, R.F.B. De Souza, G.S. Buzzo, M. C. Santos, E.V. Spinacé, A.O. Neto, J.C.M. Silva, Oxidation of ammonia using PtRh/C electrocatalysts: Fuel cell and electrochemical evaluation, Appl. Catal. B Environ. 174–175 (174) (2015) 136–144.
- [16] J.C.M. Silva, R.M. Piasentin, E.V. Spinacé, A.O. Neto, E.A. Baranova, The effect of antimony-tin and indium-tin oxide supports on the catalytic activity of Pt nanoparticles for ammonia electro-oxidation, Mater. Chem. Phys. 180 (2016) 97–103.
- [17] M.H. Tahmasebi, A. Vicenzo, M. Hashempour, M. Bestetti, M.A. Golozar, K. Raeissi, Nanosized Mn-Ni oxide thin films via anodic electrodeposition: a study of the correlations between morphology, structure and capacitive behavior, Electrochim. Acta 206 (2016) 143–154.
- [18] B.M. Stewart, Effect of temperature on the formation of indophenol blue in a spectrophotometric method for the determination of ammonia, Water Res. 19 (1985) 1443–1445.
- [19] B.S. Gentle, P.S. Ellis, M.R. Grace, I.D. McKelvie, Flow analysis methods for the direct ultra-violet spectrophotometric measurement of nitrate and total nitrogen in freshwaters, Anal. Chim. Acta 704 (2011) 116–122.
- [20] S.G. Bratsch, Standard electrode potentials and temperature coefficients in water at 298.15K, J. Phys. Chem. Ref. Data 18 (1989) 1–21.
- [21] Y. Chen, H. Li, W. Liu, Y. Tu, Y. Zhang, W. Han, L. Wang, Electrochemical degradation of nitrobenzene by anodic oxidation on the constructed TiO₂-NTs/ SnO₂-Sb/PbO₂ electrode, Chemosphere 113 (2014) 48–55.
- [22] C. Wang, F. Wang, M. Xu, C.G. Zhu, W. Fang, Y. Wei, Electrocatalytic degradation of methylene blue on Co doped Ti/TiO₂ nanotube/PbO₂ anodes prepared by pulse electrodeposition, J. Electroanal. Chem. 759 (2015) 158–166.
- [23] X. Li, D. Pletcher, F.C. Walsh, Electrodeposited lead dioxide coatings, Chem. Soc. Rev. 40 (2011) 3879–3894.
- [24] G. Li, H.Y. Yip, K.H. Wong, C. Hu, J. Qu, P.K. Wong, Photoelectrochemical degradation of Methylene Blue with β-PbO₂ electrodes driven by visible light irradiation, J. Environ. Sci. 23 (2011) 998–1003.
- [25] G. Li, L. Jiang, B. Zhang, Q. Jiang, D.S. Su, G. Sun, A highly active porous Pt-PbO_x/ C catalyst toward alcohol electro-oxidation in alkaline electrolyte, Int. J. Hydrogen Energ. 38 (2013) 12767-12773.

- [26] J.M. Thomas, M.J. Tricker, Electronic structure of the oxides of lead. Part 2. An XPS study of bulk rhombic PbO, tetragonal PbO, β-PbO₂ and Pb₃O₄, J. Chem. Soc. Faraday Trans. 2 (71) (1975) 329–336.
- [27] O. Shmychkova, T. Luk'yanenko, R. Amadelli, A. Velichenko, Physico-chemical properties of PbO₂-anodes doped with Sn⁴⁺ and complex ions, J. Electroanal. Chem. 717–718 (2014) 196–201.
- [28] B.E. Conway, W.G. Pell, Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices, J.Solid State Electrochem. 7 (2003) 637–644.
- [29] L.R. Bard, Electrochemical Methods, Fundamentals and Applications, second ed., John Wiley & Sons, New York, 2001.
- [30] S. Kumagai, M. Sato, D. Tashima, Electrical double-layer capacitance of microand mesoporous activated carbon prepared from rice husk and beet sugar, Electrochim. Acta 114 (2013) 617–626.
- [31] Y. Liu, D.Y. Kim, Enhancement of capacitance by electrochemical oxidation of nanodiamond derived carbon nano-onions, Electrochim. Acta 139 (2014) 82– 87.
- [32] J. Tu, W. Cai, X. Shao, Direct separation of faradaic and double layer charging current in potential step voltammetry, Talanta 116 (2013) 575–580.
- [33] B. Liu, S. Zheng, S. Wang, Y. Zhang, A. Ortega, N.S. Kim, K. Hand, H. Du, The redox behavior of vanadium in alkaline solutions by cyclic voltammetry method, Electrochim. Acta 76 (2012) 262–269.

- [34] L.A. Diaz, A. Valenzuela-Muniz, M. Muthuvel, G.G. Botte, Analysis of ammonia electro-oxidation kinetics using a rotating disk electrode, Electrochim. Acta 89 (2013) 413–421.
- [35] M. Melashvili, D. Dreisinger, Y. Choi, Cyclic voltammetry responses of gold electrodes in thiosulphate electrolyte, Miner. Eng. 92 (2016) 134–140.
- [36] R. Guidelli, R.G. Compton, J.M. Feliu, E. Gileadi, J. Lipkowski, W. Schmickler, S. Trasatti, Defining the transfer coefficient in electrochemistry: An assessment (IUPAC Technical Report), Pure Appl. Chem. 86 (2) (2014) 245–258.
- [37] F.J. Vidal-Iglesias, N. Garcia-Araez, V. Montiel, J.M. Feliu, A. Aldaz, Selective electrocatalysis of ammonia oxidation on Pt(1 0 0) sites in alkaline medium, Electrochem. Commun. 5 (2003) 22–26.
- [38] V. Rosca, M.T.M. Koper, Electrocatalytic oxidation of ammonia on Pt(111) and Pt(100) surfaces, Phys. Chem. Chem. Phys. 8 (2006) 2513–2524.
- [39] P. Li, R. Zhang, N. Liu, S. Royer, Efficiency of Cu and Pd substitution in Fe-based perovskites to promote N₂ formation during NH3 selective catalytic oxidation (NH₃-SCO), Appl. Catal. B-Environ. 203 (2017) 174–188.
- [40] J.C.K. Ho, G.T. Filho, R. Simpraga, B.E. Conway, Structure influence on electrocatalysis and adsorption of intermediates in the anodic O_2 evolution at dimorphic α and β -PbO₂, J. Electroanal. Chem. 366 (1994) 147–162.