A re-evaluation of Sn(II) phthalocyanine as a catalyst for the electrosynthesis of ammonia

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Abstract: The electrosynthesis of ammonia from nitrogen and water is a topic of considerable interest in the quest for sustainable and decentralized NH_3 production. Tin(II) phthalocyanine complexes have been proposed as electrocatalysts for nitrogen reduction to ammonia in aqueous solution, with Faradaic yields approaching 2% having been reported. Herein, however, we show that such complexes are not electrocatalysts for this transformation, with the amount of ammonia detected being essentially the same under N_2 and under Ar. Instead, we suggest that apparent ammonia generation could arise either through contaminants in the as-prepared tin(II) phthalocyanine complexes, or by the electro-decomposition of these complexes under cathodic bias.

Keywords: Nitrogen reduction, Ammonia synthesis, Electrocatalysis, Electrosynthesis, phthalocyanine

1. Introduction

Ammonia is a key commodity chemical, essential for fertilisers, detergents, plastics and explosives. In 2016, total worldwide NH_3 production exceeded 140 million tons, and demand for ammonia continues to grow [1]. The industrial production of ammonia is currently achieved almost exclusively *via* the Haber Bosch process. This process reacts gaseous N_2 and H_2 together at high temperatures and pressures and has revolutionised the chemical industry [2]. However, because the hydrogen used in the Haber Bosch process is normally obtained from fossil fuels, there have been increasing efforts in recent years to develop more sustainable procedures for the synthesis of ammonia. One of the most attractive of these alternative methodologies is electrochemistry, and the state-of-the-art regarding the electrosynthesis of ammonia has been reviewed recently by ourselves [3] and others [4-6].

Of the various electrochemical approaches that can be envisioned, the one that most appealed to us from a sustainability point of view was the direct electroreduction of nitrogen to ammonia at room temperature, using water as the source of the required protons and electrons. Such systems have been reported previously with various cathodes, including studies by Sclafani and co-workers (Fe) [7], Kordali *et al*. (Ru/C) [8], Wessling and co-workers (Ru and Rh) [9], Lan *et al.* (Pt/C) [10,11], Kim *et al.* (Ni) [12] Yan and co-workers (Au) [13], Wang and co-workers (polymer cathodes) [14] and Chen *et al.* (Fe-carbon nanotubes) [15]. Generation of ammonia by nitridation of lithium (at elevated temperature) followed by hydrolysis (at room temperature) has also been reported recently [16].

However, the approach that most intrigued us was the use of metal-phthalocyanine complexes (especially those based on Sn) as nitrogen reduction electrocatalysts, as reported by Furuya and Yoshiba in two communications some years ago [17,18]. Their results suggested that Sn(II) phthalocyanine complexes were capable of the direct electroreduction

of nitrogen to ammonia in 1 M KOH at modest potentials, with a Faradaic efficiency of nearly 2%. However, the only electrochemical technique used in these papers to establish catalytic activity was bulk electrolysis. This, coupled to the lack of reports reproducing this data, suggested to us that a more thorough investigation of this system could yield insights into the mechanism of activity and hence allow improvements to be obtained in the rate and yield of ammonia production.

Herein, however, we show that more in-depth study of the Furuya-Yoshiba system fails to support the claims that these complexes are acting as nitrogen reduction electrocatalysts. We find no evidence for electrocatalysis by cyclic voltammetry, nor do bulk electrolysis experiments under a nitrogen atmosphere produce more ammonia than manifests under an argon atmosphere. Instead, we show that not only is the as-purchased Sn(II) phthalocyanine contaminated with ammonium salts (or other species that decompose to release ammonia), but also that the Sn(II) phthalocyanine itself seems to decompose under cathodic bias. It is thus to these non-electrocatalytic sources of NH_3 that we attribute the presence of the small amounts of ammonia that we do detect.

2. Materials and Methods

2.1 Materials: Sulfuric acid (95%) was purchased from Fisher. Potassium hydroxide (90%), sodium hydroxide (98-100.5%), phenol (99%), ammonium chloride (99.5%+) and sodium phosphate dibasic (98.5%) were purchased from Sigma Aldrich. Sodium citrate tribasic (99%), tin(II) phthalocyanine, and sodium pentacyanonitrosylferrate(II) (98%) were purchased from Alfa Aesar. Ethanol (100%) and acetone (99%) were purchased from VWR. Propan-2-ol was purchased from Honeywell. All chemical reagents were used as purchased, except for Sn(II) phthalocyanine (see washing procedure below). All aqueous solutions were

prepared with ultrapure grade water (18.2 MΩ-cm resistivity), obtained from a Sartorius Arium Comfort combined water system. pH determinations were made with a Hanna HI 9124 waterproof pH meter. Glassy carbon foil substrates (Carbon-Vitreous 3000C (C) foil, 1.0 mm thickness) were obtained from GoodFellow. All other materials were obtained as stated in the text.

2.2 Ammonia determination: Ammonia was determined colorimetrically using Scheiner's indophenol protocol [19]. Briefly, a 2.5 mL sample of electrolyte was placed in a clean glass sample vial. 1 mL of phenol-nitroprusside buffer and 1.5 mL of alkaline hypochlorite solution were promptly added, the mixture shaken and left in a dark place to develop. After 45 minutes, a UV-vis spectrum was taken, with the value of the absorbance at 635 nm noted. A calibration curve was also established by this procedure, using ammonium chloride diluted to various concentrations over the range 0.04 - 0.20 mg L^{-1} in 1 M KOH (giving a range of 0.02 – 0.10 mg L^{-1} after being further diluted by the indophenol test reagents: see Figure 1). UV-Vis spectra were collected in solution using quartz cuvettes on a JASCO V-670 spectrophotometer, unless otherwise noted. The cuvettes were washed successively with acetone and deionized water prior to use. The Sn(II) phthalocyanine complex is essentially insoluble in 1 M KOH, and suspensions of Sn(II) phthalocyanine in 1 M KOH at the loadings we report here do not produce significant absorption at 635 nm.

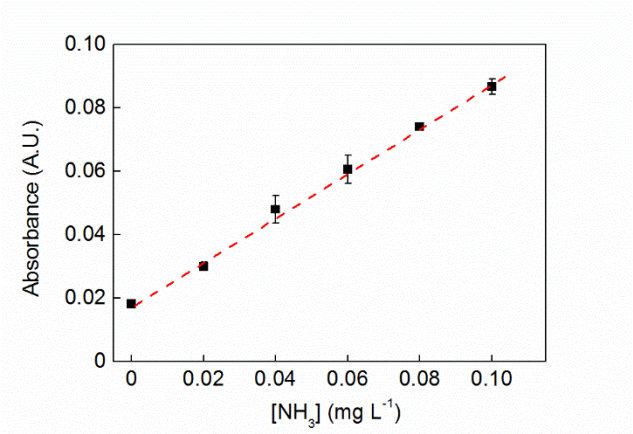

Figure 1: Calibration curve used to determine ammonia concentrations in solution. Values for the number of moles of ammonia produced in a given experiment were taken from the amount measured in the electrolyte post electrolysis minus that determined to be in solution prior to electrolysis. Pre-electrolysis values were typically around 0.015 mg L^{-1} in indophenol test samples (and therefore around 0.03 mg L^{-1} in the electrolyte). Each point in the calibration curve is the average of three separate determinations and the error bars are standard deviations.

2.3 Electrochemical methods: Electrochemical studies were performed in a three-electrode configuration using a CH Instruments CHI760D potentiostat. Platinum wire was used as the counter electrode and was washed with acetone and deionized water and then sonicated in ultrapure water before each experiment. An Hg/HgO reference electrode (1 M NaOH, CH Instruments) was used. A glassy carbon foil electrode (2 × 1 cm) was used as the working electrode. The working electrode was polished with 0.5 µm diamond polishing solution and washed with ultrapure water and propan-2-ol prior to use. Three-electrode potentials were converted to the RHE reference scale using E(RHE) = E(Hg/HgO) + 0.140 V + (0.059 × pH) [20].

2.3.1 Cyclic voltammetry: Cyclic voltammograms were collected in a single chamber cell at room temperature (20 °C) using a scan rate of 100 mV/s in 1 M KOH. Measurements were compensated for the *i*R drop and conducted without stirring. The *i*R test function available on the CH potentiostats uses the general method developed by He and Faulkner [21].

2.3.2 Bulk electrolysis: Bulk electrolyses were performed in a three-electrode configuration in single compartment electrochemical cells. Solutions were agitated by gas bubbling (either with nitrogen or argon), at equivalent rates of bubbling through the solutions. Bulk electrolyses were conducted without considering any resistive losses; solution resistances were measured using the *i*R test function (as for cyclic voltammetry) and were found to be on average 3.7 Ω for a bare 2 × 1 cm carbon foil electrode, and 5.0 Ω for a 2 × 1 cm carbon foil electrode with Sn(II) phthalocyanine deposited on it (see procedure below). At the currents typically passing in these experiments, voltage drops caused by this uncompensated resistance were thus on the order of 1 - 5 mV, and could be neglected.

2.4 Washing procedure for the Sn(II) phthalocyanine: 50 mg of Sn(II) phthalocyanine was suspended in 10 mL ultrapure-grade water, and the Sn(II) phthalocyanine then pelleted from this suspension by centrifugation. The supernatant was then decanted and the pellet re-suspended in 10 mL fresh ultrapure-grade water. This process was repeated five times with each 50 mg batch of Sn(II) phthalocyanine. The supernatant solution after each centrifugation was subjected to the indophenol test, giving approximate ammonia concentrations of 0.08 mg L^{-1} in the first wash supernatant and an average of 0.006 mg L^{-1} in the supernatant after 3-5 washes. After the fifth wash, the pelleted material was suspended in acetone and re-pelleted by centrifugation (to help remove water) before isolation and drying at elevated temperature to give dry powder. A comparison of the UV-vis

spectra of Sn(II) phthalocyanine before and after washing is made in Figure 2A (below). Due to the poor solubility of Sn(II) phthalocyanine in conventional solvents, these spectra are reported in concentrated sulfuric acid, in which Sn(II) phthalocyanine is both reasonably soluble and stable for at least 24 h [22]. The spectra are in good agreement with those reported for Sn(II) phthalocyanine in the literature [22,23]. Meanwhile, the infrared spectrum of the washed Sn(II) phthalocyanine (collected in the solid state on a Shimadzu IRAffinity-1S Fourier Transform Infrared Spectrophotometer) is shown in Figure 2B. The spectrum displays key bands as indicated, which Kroenke and Kenney have shown to be characteristic of Sn(II) phthalocyanine [24].

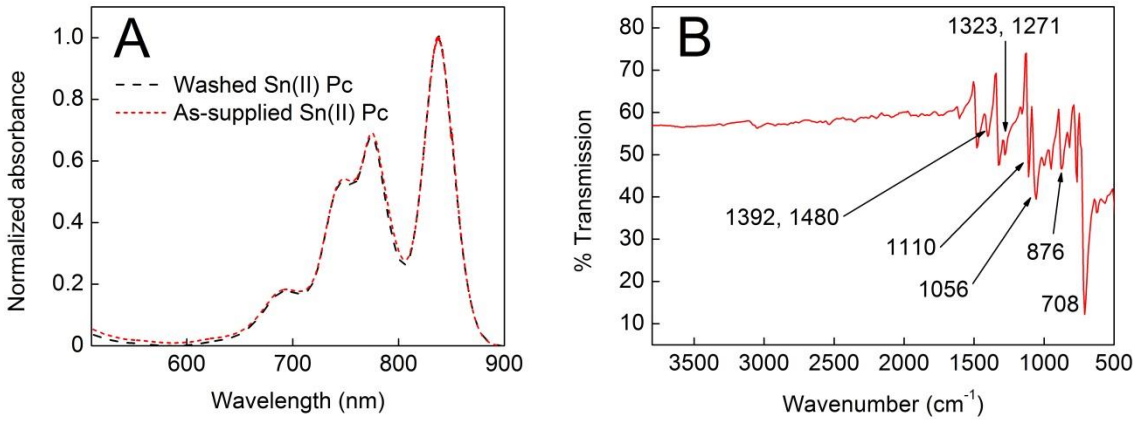

Figure 2A: Normalized UV-vis spectra of Sn(II) phthalocyanine in concentrated sulfuric acid before and after the washing procedure described above. The concentration of Sn(II) phthalocyanine was 35 µM in each case and plastic cuvettes were used. **2B:** Infrared spectrum of Sn(II) phthalocyanine in the solid state after the washing procedure described above.

2.5 Electrode preparation: After washing, 50 mg Sn(II) phthalocyanine was placed into 10 mL of ethanol and sonicated to make a suspension. A 25 µL aliquot of this suspension was

then placed on the 2 × 1 cm carbon foil electrode surface and allowed to dry. Successive 25 µL aliquots of the suspension were then placed on the electrode in the same way (with some perturbation of the previously-deposited layer(s) so as to make as even a layer as possible) until a loading of 1 mg cm^{-2} (total loading of 2 mg) of Sn(II) phthalocyanine was achieved (as gauged by measuring the mass difference of a dry electrode after each drop-casting cycle).

2.6 Inductively Coupled Plasma Mass Spectrometry: Samples of various electrolytes were analyzed by Inductively Coupled Plasma Mass Spectrometry on an Agilent 7700 ICP-MS instrument at the Department of Pure and Applied Chemistry at the University of Strathclyde (UK). All samples were treated with concentrated nitric acid to aid analysis (final pH of samples was pH 1 – 1.3).

3. Results and Discussion

We began our investigation of tin phthalocyanines as nitrogen reduction electrocatalysts by conducting cyclic voltammetry as shown in Figure 3. Comparison of a glassy carbon foil electrode (area = 2 cm^2) functionalised with Sn(II) phthalocyanine by drop-casting from suspension in ethanol (loading = 1 mg cm^{-2}, see Materials and Methods section) with an unmodified (bare) glassy carbon electrode is shown in Figure 3A. Hence the modified electrode showed a number of reductive waves under a nitrogen atmosphere, the biggest of which occurred at around −0.2 V (*vs.* RHE). Meanwhile, the bare electrode showed no such waves over this potential range under both nitrogen and argon atmospheres.

We were initially encouraged by this result, but considerable confusion subsequently arose when we conducted control reactions with the modified electrode under argon (Figure 3B).

These studies suggested that all the waves present for the Sn(II) phthalocyanine complex under nitrogen were also present under argon with at least an equivalent intensity. We repeated this control experiment multiple times, and in no cases were we ever able to identify processes occurring under nitrogen that did not occur to a similar extent under argon. Hence (by cyclic voltammetry at least), our data provide no evidence for any electrocatalytic processes connected explicitly with nitrogen reduction by Sn(II) phthalocyanine under these conditions. Instead, by analogy to previous literature on the reduction of main group phthalocyanine complexes, we tentatively assign the cathodic processes evident in Figure 3 to reduction of the phthalocyanine ring [25,26]. It is noteworthy that the original communications do not report any controls under argon, and only show data collected under a nitrogen atmosphere [17,18].

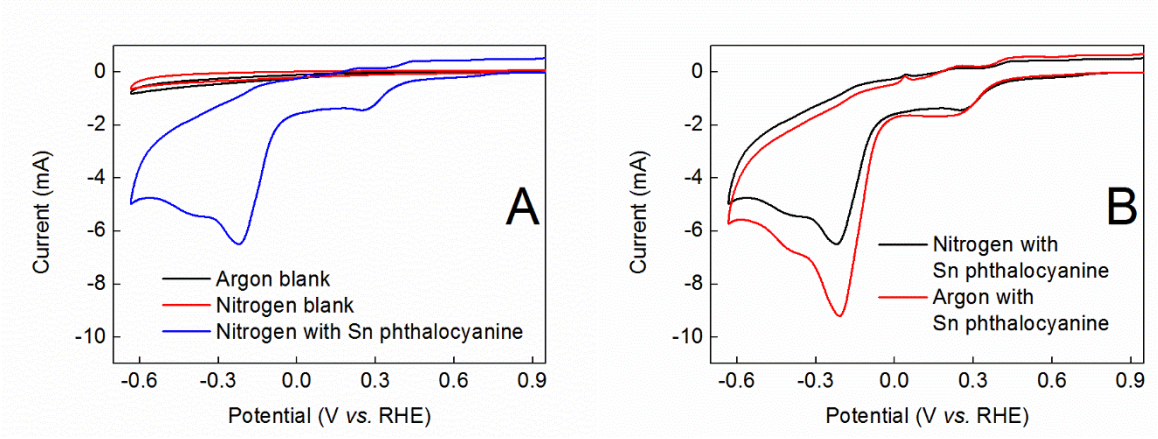

Figure 3A: Cyclic voltammograms of a bare 2 cm^2 carbon foil electrode under argon (black line) and nitrogen (red line), and the same electrode after decoration with Sn(II) phthalocyanine (blue line; loading = 1 mg cm^{-2}). **3B:** Cyclic voltammograms of a 2 cm^2 carbon foil electrode decorated with Sn(II) phthalocyanine (loading = 1 mg cm^{-2}) under nitrogen (black line) and argon (red line). In all the spectra, a Pt counter electrode and Hg/HgO reference electrode were used in 1 M KOH at a scan rate of 100 mV/s.

The original reports of activity with this material do not report any cyclic voltammetry data, and instead rely on the use of a colorimetric ammonia detection protocol in conjunction with bulk electrolysis. In order to determine if ammonia was produced by this system under bulk electrolysis conditions, we therefore conducted bulk electrolysis with our modified electrodes in 1 M KOH at an applied bias of −0.4 V (*vs.* RHE), as in the original reports. We note at this juncture that all our electrolyses were conducted over a period of 45 minutes compared to around 22 minutes in the original work. Our loading of Sn(II) phthalocyanine complex was also around five times higher than that previously investigated, in order to provide the best chance of observing catalytic activity if any were present.

The first problem we encountered with this method was that simply immersing modified electrodes in the electrolyte was observed to lead to a significant rise in the ammonia concentration in solution. We attribute this to the possible presence of urea in the as-purchased Sn(II) phthalocyanine (heating a mixture of urea and phthalanhydride in the presence of the relevant metal salt is a common route to the generation of metal phthalocyanine complexes [27]), with this urea then undergoing hydrolysis to yield ammonia [28]. Accordingly, we washed our Sn(II) phthalocyanine complex with water multiple times, in order to remove any extraneous urea and/or ammonium salts that were present (see Materials and Methods section). Analysis of the aqueous washing solutions indicated that at least two such washes were required in order to bring the level of ammonia in solution down to a steady baseline value. In this regard, it is important to note that the original communications do not report any washing procedures for the complex, our assumption therefore being that these were used as supplied.

Electrodes modified with Sn(II) phthalocyanine that had been washed in this manner were then subjected to bulk electrolysis at −0.4 V (*vs.* RHE) under various conditions as

summarised in Figure 4. In all cases, experiments were conducted for 45 minutes, after which time the electrolyte was tested for ammonia using the indophenol method. The level of ammonia in solution was then compared to the level found in the electrolyte prior to immersion of the electrode. Figure 4A shows yields of ammonia obtained in this manner under various conditions; each set of conditions was probed multiple times, and the data reported are averages. Hence it is apparent that when no Sn(II) phthalocyanine is present on the electrode surface, then the yield of ammonia under both argon and nitrogen is very low. Similarly, when Sn(II) phthalocyanine is dropcast onto the electrode surface and then that electrode is merely immersed in the electrolyte, then the amount of ammonia detected is also low. This demonstrates that our washing procedure is effective in removing any ammonia (or ammonia-producing species) that are present in the as-purchased materials. In contrast, if electrodes decorated with Sn(II) phthalocyanine are subjected to potentials of −0.4 V (*vs.* RHE), then there is appreciable ammonia formation. However, this activity manifests under *both* nitrogen and argon (and if anything, more ammonia is detected when argon is used than when nitrogen is used), which calls into question whether the supplied nitrogen is the feedstock for generation of this ammonia.

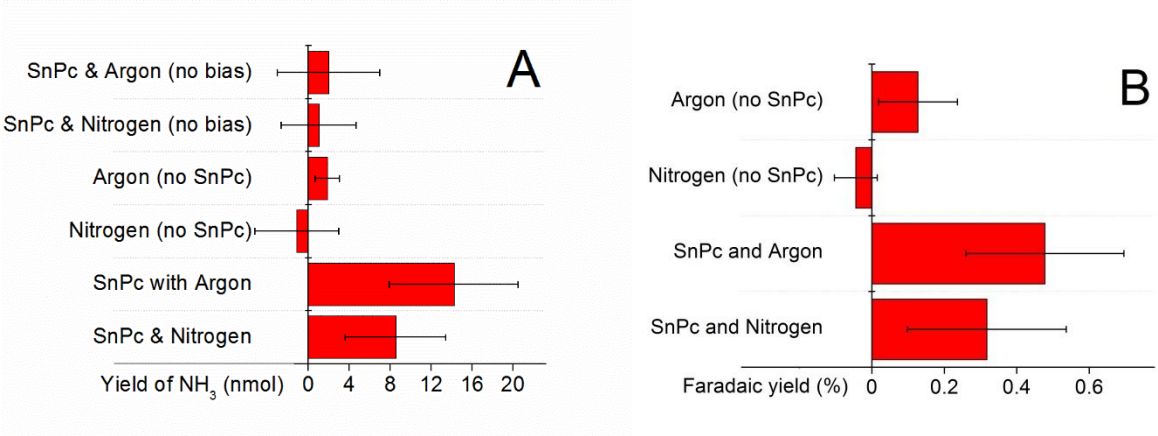

Figure 4A: Histograms showing the net yield (in nmol) of ammonia produced under various conditions (per 7.5 mL of electrolyte). **4B:** Histograms showing Faradaic yields for ammonia

production for those systems where electrical currents were flowing. In both panels, the data shown by the bars are averages of multiple runs (normally five, but four for Ar (no SnPc), six for SnPc with Nitrogen and seven in the case of Nitrogen (no SnPc)), and the error bars correspond to the standard deviation of these runs. The labels used are as follows: SnPc & Argon (no bias) = decorated electrode immersed in 1 M KOH under an argon atmosphere without any current flowing; SnPc & Nitrogen (no bias) = decorated electrode immersed in 1 M KOH under a nitrogen atmosphere without any current flowing; Ar (no SnPc) = bare carbon electrode held at −0.4 V for 45 minutes under argon; Nitrogen (no SnPc) = bare carbon electrode held at −0.4 V for 45 minutes under nitrogen; SnPc with Argon = decorated electrode immersed in 1 M KOH and held at −0.4 V for 45 minutes under argon; SnPc with Nitrogen = decorated electrode immersed in 1 M KOH and held at −0.4 V for 45 minutes under nitrogen.

Figure 4B then shows the production of ammonia from the four systems which were probed by electrochemistry in terms of their Faradaic yields for NH_3 generation. In the two cases where no Sn(II) phthalocyanine was employed, both of these yields are very low (−0.04 ± 0.06% under N_2 and 0.13 ± 0.11% under Ar), suggesting that what little charge is passed during these electrolyses is overwhelmingly not directed towards NH_3 generation. The apparent Faradaic yields when Sn(II) phthalocyanine is present on the electrode are much higher; however, this behaviour is again observed under both nitrogen and argon. Moreover, in both these latter cases, the Faradaic yield is much lower than that quoted by Furuya and Yoshiba (who quoted values of 1.85% at the start of electrolysis, falling to 1.2% after 20 minutes at −0.4 V). Clearly then, the ammonia that is detected in our studies is not emanating from the reduction of the supplied nitrogen stream, as better apparent metrics

(both in terms of Faradaic efficiency for NH_3 generation and overall production of NH_3) are evident under argon.

Given that essentially no ammonia is detected when there is no phthalocyanine complex present, our suspicions for the source of the ammonia we detected in these experiments thus fell on the Sn(II) phthalocyanine itself. Any ammonium salts (or species decomposing to such salts) that were present in the as-purchased materials had been removed by washing prior to electrolysis (see above). However, it was possible that the Sn(II) phthalocyanine itself might decompose under an applied bias to liberate ammonia, as is the case with thermal and photochemical degradation of metal-phthalocyanine complexes [29,30]. In support of this, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) performed on our electrolytes showed considerably higher levels of tin to be in solution after a bias potential of −0.4 V had been applied for 45 minutes than when no potential had been applied (see Table 1).

Table 1: The levels of tin detected by ICP-MS in various electrolytes (the labels correspond to those given in Figure 4).

Sample	**[Sn] in electrolyte (μg L^{-1})**
SnPc & Argon (no bias)	115.72 (±5.4)
SnPc & Nitrogen (no bias)	146.88 (±6.2)
Argon with no SnPc	155.07 (±8.0)
Nitrogen with no SnPc	175.91 (±10.9)
SnPc with Argon	321.68 (±7.1)
SnPc with Nitrogen	426.92 (±1.3)

As the Sn(II) phthalocyanine complex is essentially insoluble in 1 M KOH, it thus seems likely that the elevated levels of tin detected in our electrolytes after electrolysis have their origins in the decomposition of the Sn(II) phthalocyanine under an applied cathodic bias. Cyclic voltammetry seems to confirm that the complex decomposes when reduced; Figure 5 shows how the current observed at a given potential decreases markedly over three reduction cycles similar to those shown in Figure 3B.

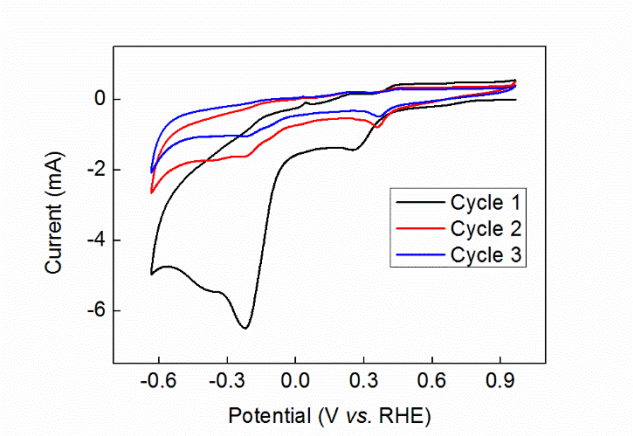

Figure 5: Cyclic voltammograms of 2 cm^2 carbon foil electrode decorated with Sn(II) phthalocyanine (loading = 1 mg cm^{-2}) under nitrogen over successive cycles as indicated. A Pt counter electrode and Hg/HgO reference electrode were used in 1 M KOH at a scan rate of 100 mV/s.

4. Conclusions

In summary, we have shown that Sn(II) phthalocyanine complexes are not electrocatalysts for the reduction of nitrogen to ammonia in 1 M KOH. When a cathodic bias is applied to such complexes, the concentration of ammonia in the electrolyte does increase, but this increase is of the same magnitude under both N_2 and Ar. Moreover, there is no evidence for

electrocatalysis by cyclic voltammetry. Ammonia (or species producing ammonia) are present in as-supplied Sn(II) phthalocyanine, and this complex also seems to decompose under cathodic bias (as indicated by cyclic voltammetry and ICP-MS). On the basis of these results, we suggest that any apparent ammonia formation is due to the decomposition of (or possible impurities in) the Sn(II) phthalocyanine, and not electro-reduction of N_2 as previously claimed.

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