



Letter

Electrolytic reduction of nitrate on copper and its binary composite electrodes



A B S T R A C T

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Copper electrode has a high catalytic activity for electrolytic reduction of nitrate with a drawback of high ammonia selectivity. This research aims to increase the nitrate reduction rate as well as selectivity to gaseous nitrogen by doping other metals. The experimental results showed that the first order kinetic constant for Cu₈₀Ni₂₀ and Cu₈₀Pb₂₀ was 0.50 and 0.54 h⁻¹, which was five times more than Cu electrode of 0.10 h⁻¹. Moreover, the selectivity to ammonia decreased from 76% to 63% & 61%, together with an elevated selectivity to gaseous nitrogen from 23% to 37% & 39%, respectively.

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1. Introduction

Electrolysis is an effective method for the removal of nitrate especially for wastewater with few or no organic compounds for de-nitrification, especially for high nitrate concentrated solutions in nuclear waste [1]. It owes the merits of effectiveness, easy management, no chemicals addition and sludge production etc [2]. The products of electrolytic de-nitrification include ammonia, nitrite, hydroxylamine, hydrazine, gaseous nitrogen etc, which have a close relationship with the electrode material [3]. Generally speaking, ammonia is one of the main hazardous by-products, which could be removed through anodic oxidation in the paired electrolysis process. Two main problems still impede the application of this technology. One is the slow nitrate reduction rate together with the low current efficiency, and the other is selectivity to the environmental friendly product of nitrogen gas. Moreover, the electrochemical analysis has been proposed by many researchers, and much effort has been put in the finding of new electrode materials with enhanced nitrate reduction activity [4,5].

Various metallic electrodes (Cu, Ni, Pb etc) have been investigated for the electrolytic reduction of nitrate, and copper was suggested by many researchers to be an active electrode material [5–8]. Previous research showed the doping of zinc or 10 wt% Sn can significantly strengthen the electrolytic catalytic activity of Cu electrode [9]. However, the selectivity towards hydrogenated products was typically high on copper electrode [10].

This research aims to increase the selectivity to nitrogen gas during electrolytic reduction of nitrate by binary Cu-X composite electrode. The hypothesis is that copper alloy can raise the selectivity to nitrogen as well as increase nitrate reduction rate. Another assumption is that high surface area was beneficial for electrolytic reduction of nitrate.

2. Materials and methods

2.1. Electrode preparation and characterization

Nano copper and the other metallic particles were mixed by ball milling method prior to further steps. Then metal particles were blended with PVDF (polyvinylidene fluoride) binder and acetylene black according to the ratio of 10:1:2 with NMP (N-Methyl pyrrolidone) as the solvent to form sticky slurry. Thin electrode film (150 μm) was got by plating the slurry onto the surface of copper foil pretreated with acid/base solution, alcohol and distilled water subsequently. Finally, it was put into a 60 °C vacuum oven until dry. The XRD, SEM and BET analyses were performed with X-ray diffractometer (XRD, Bruker D8 Advance, German), scanning electronic microscopy (SEM, Philips XL30, Netherlands) and Physisorption Analyzer (ASAP 2020, Micromeritics, USA), respectively.

2.2. Electrochemical analysis

The reduction of nitrate on various electrodes was investigated by linear sweep voltammetry with a three electrode cell connected to CHI 660E electrochemical workstation (Chenhua Co. Ltd., Shanghai, P.R. China). The geometrical surface area of the prepared working electrode was 0.5 cm². The electrolyte was prepared with 1 M NaOH and 0.01–0.2 M nitrate. The scans were performed with a rate of 20 mV/s within the potential of –0.6 V ~ –1.7 V determined by pre-tests. Constant potential electrolysis strategy was employed to study the kinetics and products with a two compartment electrolytic cell separated by a Nafion 117 membrane. The working electrode (8 cm²) was immersed into the mixture of NaNO₃ and NaOH solution, while the Pt electrode was set in the cathodic compartment with NaOH solution only.

2.3. Analytic methods

Ammonia was determined through Nessler's method spectrophotometrically. Aqueous nitrate concentration was measured by a UV spectrophotometric method (Shimadzu UV-2600). Total nitrogen was monitored through a TOC/TN analyzer (Multi N/C 3100; Analytik Jena Company).

3. Results and discussion

Fig. 1 shows the XRD patterns of Cu/Pb/Pd/Fe/Ni powders, Cu, Cu₈₀Pb₂₀, Cu₈₀Pd₂₀, Cu₈₀Fe₂₀, Cu₈₀Ni₂₀ electrodes, respectively. For copper powder, the intensive diffraction peaks at 2θ of 43°, 51° and 74° are indexed to the (111), (200) and (220) diffraction planes of face centered cubic structure (PDF #04-0836) [11]. For Pb powder, diffraction peaks were observed at 2θ of 31, 32°, 33°, 36°, 48°, 52°, 62° and 65°, similar to cubic structure (PDF #04-0686) [12]. For Pd powder, diffraction peaks were found to be at 2θ of 40°, 48° and 68°, which can be assigned to the (111), (200) and (220) diffraction planes of Pd (PDF #46-1043) [13]. For Fe powder, diffraction peaks of (110) and (200) were found to be at 2θ of 44° and 65°, which can be attributed to the body central cubic structure of α-Fe structure (PDF #87-0721) [14]. For Ni powder, diffraction peaks were found to be at 2θ of 45°, 52° and 77°, representing the (111), (200) and (220) diffraction planes of Ni nanoparticle with face central cubic structure (PDF #04-0850) [15].

For Cu, Cu₈₀Pb₂₀, Cu₈₀Pd₂₀, Cu₈₀Fe₂₀, Cu₈₀Ni₂₀ electrodes, main diffraction peaks were all found at 2θ of 43°, 51° and 74°, which were similar to copper powder since copper powder was the main metallic component. The other metallic atom might go into the void space of copper atoms, and thus no significant X-ray diffraction peak was observed. Similar phenomenon was observed by the XRD studies of Ag-rich alloys, which showed that X-ray diffraction patterns only showed the solid solution of silver if the alloy contained 10–40% Li [16]. It was also worthy to note that the intensity of the diffraction peaks changed significantly when the nano copper particles were coated on the electrode. This phenomenon might indicate the variation of crystal structure, which had a direct relationship with catalytic efficiency. Previous research had reported that Cu (100) had more reactive surface for the formation of hydroxylamine than Cu (111) [17]. Moreover, electrode prepared with nano copper powder can provide large amount of active

sites when compared with pure copper plate, which led to a faster electrolytic nitrate reduction rate as a result.

SEM micrographs of Cu, Cu₈₀Pb₂₀, Cu₈₀Fe₂₀, Cu₈₀Pd₂₀, Cu₈₀Ni₂₀ electrodes were shown in Fig. 2 A–E, respectively. It was obviously that binding metallic atoms were packed together and formed large amount of pores. The sizes of the metallic particles were around 100 nm, which aggregated into flocs during the preparation of electrodes. This size was much smaller than the Cu-Ni materials prepared by high energy ball milling [18]. The doped metallic atoms might distribute into the void space of copper atom, which may affect the electrolytic nitrate reduction rate as well as the selectivity to different products [4,18]. No significant change of the morphology was observed during the doping of heterogeneous metallic atoms from the aspects of floc size and pore distribution.

For all the five electrodes, the average pore sizes were within the range of 3.8–6.7 nm belonging to mesopores. The BET surface areas were determined to be 6.7, 2.1, 3.8, 2.3 and 3.4 m²/g, respectively, which proved that heterogeneous metallic atoms went into the void space of copper lattice and decreased the surface area. The average pore volumes decreased from 6.5 to 2.5, 5.9, 3.8 and 4.9 mm³/g, which also proved the distribution of other metallic atoms into the void space of copper lattice. This conclusion declined the hypothesis that high surface area was the main reason for the high catalytic capacity of binary copper alloy.

Fig. 3 (a)–(e) shows the linear sweep voltammograms for nitrate reduction on Cu₈₀Fe₂₀, Cu₈₀Pd₂₀, Cu₈₀Ni₂₀, Cu₈₀Pb₂₀ and Cu electrodes, respectively. All the peak currents were found to be larger than common copper plate reported in one previous research [19]. Two significantly reduction peaks could be observed for all the electrodes. According to previous research, the first reduction peak around –0.9 V might indicate the generation of hydroxylamine while ammonia was formed in the second peak near –1.3 V [17]. Hydroxylamine is not stable and can quickly decompose to gaseous nitrogen, which can lead to the reduction of total nitrogen in aqueous phase. Moreover, all of the peak currents were found to increase linearly with nitrate concentration within the range of 0.01–0.2 M. The peak potential shifts to the negative direction with an increase in nitrate concentration, which is in accordance with the behavior of the irreversible charge transfer reactions [20]. Compared with single copper, Cu₈₀Pb₂₀ electrode had the highest peak current around –0.9 V, which might indicate that Pb doping was beneficial for the reduction of nitrate to gaseous product.

As shown in the constant potential electrolysis experiment, the electrolytic reduction of nitrate was found to follow the first order kinetics by plotting ln[NO₃⁻] vs. time with the data in Fig. 3 (f). As shown in Table 1, Ni and Pb doping showed the highest catalytic activity with first order kinetic constants of 0.50 and 0.54 h⁻¹, respectively, which was five times higher than copper of 0.10 h⁻¹. The effect of high surface area was excluded by material characterization. Thus it was more possible that high catalytic activity resulted from the synergetic effect of binary metallic atoms.

Moreover, the selectivity to final products changes significantly. For example, the selectivity to ammonia could be calculated according to equation [1]. Among the entire nitrate removed, 76%, 61%, 63%, 83% and 63% was converted to ammonia on Cu, Cu₈₀Pb₂₀, Cu₈₀Ni₂₀, Cu₈₀Fe₂₀ and Cu₈₀Pd₂₀ electrode, respectively. Moreover, the final total nitrogen (TN) concentration was determined to be 78.9, 61.7, 64.1, 83.2 and 64.4 mg N/L for Cu, Cu₈₀Pb₂₀, Cu₈₀Ni₂₀, Cu₈₀Fe₂₀ and Cu₈₀Pd₂₀, respectively, leading to selectivity to gaseous nitrogen of 23%, 39%, 37%, 17% and 36%. It can be concluded that nitrate was converted to gaseous nitrogen through multiple steps as shown in reference [20]. The doping of Pb, Ni and Pd all increased the selectivity to gaseous nitrogen with Fe as the only exception. Considering both aspects of nitrate reduction rate and

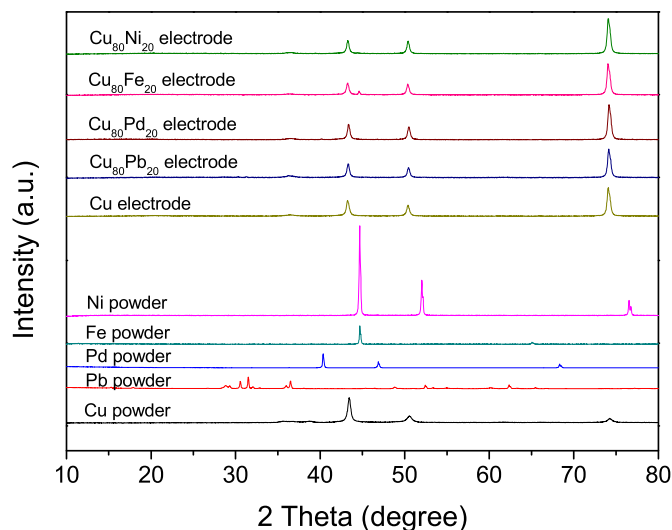


Fig. 1. XRD patterns of various electrodes and its raw materials.

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