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Fast Screening Method for Nitrogen Reduction Reaction (NRR) Electrocatalytic Activity with Rotating Ring-Disc Electrode (RRDE) Analysis in Alkaline Environment

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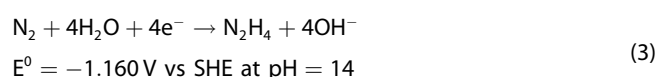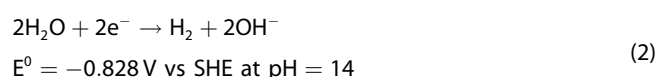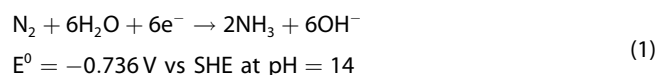
The Haber-Bosch process for NH_3 production leads to a considerable greenhouse gas release due to the remarkable use of fossil fuels. Therefore, there is an increasing interest in developing alternative and environmental friendly approaches. Among the possible solutions, the electrocatalytic conversion of N_2 has recently gained significant attention; on the other hand, not only scientific but also important technical aspects remain fundamental issues to be clarified. Particularly relevant is the need to improve the analytical protocols to ascertain that any detected NH_3 is actually produced from N_2 rather than from any external contaminations or partial decomposition of the catalyst itself. Here, a rotating ring-disc electrode (RRDE) setup is used for the first time to study the N_2 electroreduction process with the aim to recognize the product species formed at the disc and detected at the ring electrodes, respectively. We demonstrated that this experimental approach is effective to discern also a low-level ammonium concentration through monitoring the ammonia oxidation peak at the ring electrode for a fast and preliminary electrocatalytic performance evaluation and to prevent false positives. The versatility of the RRDE method employed as a fingerprint of new electrocatalyst candidates could allow to reserve time and cost.

Introduction

Ammonia (NH_3) is considered one of the most important raw chemicals for both industry and agriculture, and also a renewable energy storage intermediate. The traditional Haber-Bosch process for NH_3 production (operative at high temperature and pressure conditions) leads to a considerable greenhouse gas release due to the use of fossil fuels; therefore, there is a growing interest to research alternative and sustainable approaches for its preparation.[1] Electrochemical synthesis of ammonia (ESA) through the nitrogen reduction reaction (NRR) has attracted significant attention.[2–4] The electrocatalytic reduction process is considered as an environmentally-friendly approach for NH_3 production; in fact it can be performed at mild conditions, such as room temperature and atmospheric pressure, and it can also be powered by renewable energy.[5]

The development of a sustainable ESA process requires primarily the knowledge of the thermodynamic aspects in the specific working environment [Eq. (1)], i.e. aqueous alkaline environment, that can be summarized by the following standard reduction potential, and needs to include the side HER [Eq. (2)] and hydrazine production [Eq. (3)]:[6]

$$N_2 + 6H_2O + 6e^- \rightarrow 2NH_3 + 6OH^-$$
$$E^0 = -0.736\,V \text{ vs SHE at } pH = 14 \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
$$E^0 = -0.828\,V \text{ vs SHE at } pH = 14 \tag{2}$$

$$N_2 + 4H_2O + 4e^- \rightarrow N_2H_4 + 4OH^-$$
$$E^0 = -1.160\,V \text{ vs SHE at } pH = 14 \tag{3}$$

However, as recently pointed out by S. Z. Andersen et al.,[7] there are few fundamental issues, not only scientific but also technical aspects, to be clarified, both related to the fact that the major part of experimental studies accounted for low selectivity and conversion efficiency. The amount of produced ammonia is usually so low that it cannot be certainly related to electrochemical NRR rather than contamination from ammonia that is either present in the experimental setup. A considerable number of recent studies have investigated the importance to improve the measurement protocol to make sure that any detected NH_3 is actually produced from N_2 rather than any external contaminations or breakdown of the catalyst itself.[8]

Concerning ammonia detection, the spectrophotometric methods, also known as the colorimetric methods, are commonly used for ammonia detection in aqueous environment.[9,10] In particular, the indophenol blue method

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based on the Berthelot reaction is frequently adopted as a reference method for identifying also low product concentrations.[11] Briefly, the reaction is catalyzed by sodium nitroprusside necessary to promote an evident color development. However, in some cases the blue color of indophenol is replaced by different color shades, resulting in ambiguous evidences. Nowadays, the salicylate method based on a modified Berthelot reaction[12] is more frequently used than the phenate method, to avoid the formation of toxic and volatile reagents.[13] However, large amounts of reagents have to be used to obtain a comparable sensitivity. Finally, the Nessler's method,[14] based on the ammonia reaction with the Nessler's reagent (containing K_2HgI_4) to give a colored complex, is a faster approach than the standard salicylate method, but it requires pretreatment steps to eliminate different interfering agents such as of metal ions, residual chlorine, sulfides, etc. Another adverse factor is that the Nessler's reagent contains mercury, which is very toxic and dangerous to the environment. It is also important to evidence that commercial products based on the colorimetric methods such as ammonia colorimetric assay kits have been used for simpler and rapid procedures; anyway their use cannot be cost sustainable for every screening test of new NRR electrocatalyst candidates.
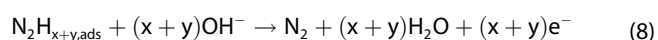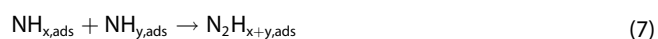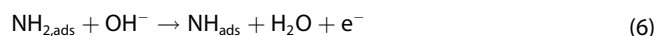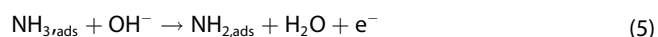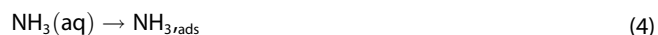
Recently, S. Z. Andersen et al.[7] proposed a strict procedure using $^{15}N_2$ to detect and quantify the electrochemical reduction of N_2 to NH_3. They demonstrated the importance of different contamination sources and showed how to remove labile nitrogen-containing compounds from the nitrogen gas as well as how to perform quantitative isotope measurements with the recycling of $^{15}N_2$ gas to contain the costs. However, it is necessary to determine ammonia generation in real time during the experimental investigation, also including a dynamically reduction potential modification.

A rotating ring-disc electrode (RRDE) tool could represent a sustainable, cost effective and primarily a rapid alternative method to study qualitatively the NRR process by the identification of products formed at the disc and detected at the ring electrode, respectively.[15]

The RRDE tool, already adopted in many electrochemical labs, has been extensively used to study the kinetics of different electrochemical systems mainly centered on Oxygen Reduction Reaction (ORR). More recently (2014), the RRDE technique has been used by Lates et al.[16] to study the electrochemical reduction of CO_2 on Au-based electrocatalysts to produce carbon monoxide. In 2018 Brett and coworkers[17] extended the RRDE to characterize the CO_2 reduction process by Cu-based nanocatalysts resulting in the production of different hydrocarbon species. Other interesting research papers explored the use of RRDE to study particular electrochemical aspects including OER,[18,19] the chlorine evolution side reaction[20,21] and hydrogen peroxide selectivity in ORR.[22]

Since different products can be generated simultaneously at the catalyst surface on the GC disc at highly negative potentials (i.e. NH_3, but also H_2, or N_2H_4), it is important to calibrate the ring electrode voltage to target ammonia electrogeneration. According to Miura and coworkers,[24] anodic ammonia oxidation process on Pt ring in alkaline environment could lead to

different N-oxygenated products, even if the mechanisms have not been yet completely understood, due in part to electrode poisoning. Most researchers consider reliable the Gerischer-Mauerer mechanisms [Eqs. (4)–(9)] based on the dehydrogenation steps of $NH_{3,ads}$ to N_{ads} and the recombination of two $NH_{x,ads}$. Using RDE/RRDE techniques, Miura and coworkers hypothesized that the most probable products of ammonia oxidation on platinum electrodes are NO_x species and NH_2OH from the degradation of NH_2 in alkaline solutions (6).

$$NH_3(aq) \rightarrow NH_{3,ads} \tag{4}$$

$$NH_{3,ads} + OH^- \rightarrow NH_{2,ads} + H_2O + e^- \tag{5}$$

$$NH_{2,ads} + OH^- \rightarrow NH_{ads} + H_2O + e^- \tag{6}$$

$$NH_{x,ads} + NH_{y,ads} \rightarrow N_2H_{x+y,ads} \tag{7}$$

$$N_2H_{x+y,ads} + (x+y)OH^- \rightarrow N_2 + (x+y)H_2O + (x+y)e^- \tag{8}$$

$$NH_2 + OH- \rightarrow NH_2OH + e^- \tag{9}$$

Here, we aim to investigate the NRR through a series of electrocatalytic rotating ring disc voltammetry experiments in alkaline aqueous environment, where the NH_3 product oxidation on the platinum electrode is most visible.[23] The consequent NH_3 product monitoring on the Pt ring electrode plays the role of an in situ detector as evidenced in the schematic concept reported in Figure 1.

Three different NRR electrocatalysts were prepared, according to literature procedures, and tested by the qualitative RRDE analysis tool and finally compared to data from quantitative colorimetric measurements. These three materials are representative of different situations we encountered during NRR testing and well elucidate the resilience of this qualitative technique to different scenarios.
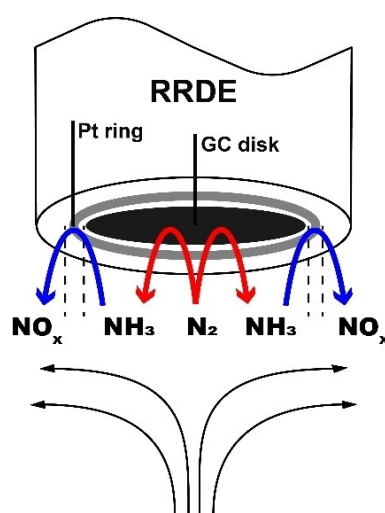

Figure 1. Schematics of the main NRR reactions occurring on GC/Pt electrodes of the RRDE setup.

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First, commercial carbon nanotubes (CNTs) supported Fe_2O_3 Nanoparticles (30% Fe_2O_3–CNTs)[25] were studied as an example of NRR electrocatalyst operating at low overpotentials, therefore giving to limited Faradaic Efficiencies (FEs), below 1%. Then, a ZIF-8 derived nitrogen-doped carbon (ZIF-1100-1h)[26] was evaluated as representative of a vast family of N-containing catalysts that showed high FE; however, these kind of materials are also potentially unstable and thusaffected by a secondary source of ammonia from their degradation, leading to possible false positives. Finally, a commercial Fe_2O_3 (Honeywell, pur. 99.98%)[27] was tested to document the class of electrocatalysts characterized by NRR activity at high overpotentials, where the simultaneous H_2 formation gives rise to technical measurement complications. In all the cases, the setup cleaning was of primary importance; therefore, ahead of each measurement, a rationalized protocol was adopted implying multiple washing steps of all the electrochemical components in the setup (i.e. cell, electrodes, bridges, frits, etc.). We demonstrated that this experimental approach is effective to discern also a low-level ammonium concentration through monitoring the ammonia oxidation peak at the ring electrode for a fast (in the order of minutes with a consolidated protocol) and preliminary electrocatalytic NRR performance evaluation and to prevent false positives.

Results and Discussion

Single-chamber electrochemical cells are characterized by the peculiarity of overcoming one possible ammonia contamination source, deriving from the polymeric membrane. The single-compartment cell used in this study consisted of a glass cell filled with 20 mL 0.1 M KOH electrolyte, equipped with a GC/Pt RRDE as the working electrodes (setup and used procedures are described in detail in Experimental Section).

In accordance with a literature overview, three different NRR electrocatalytic materials were reproduced to test the RRDE analysis tool at different working potentials and currents: a) CNTs supported Fe_2O_3 NPs (30% -CNTs),[25] b) a ZIF-8 derived nitrogen-doped carbon (ZIF-1100–1 h),[26] c) a commercial Fe_2O_3 (Honeywell, pur. 99.98%).[27]

GC/Pt RRDE preliminary blank tests

A preliminary electrochemical characterization was performed to evaluate the Pt ring sensitivity and its surface electrochemistry since different products can be generated simultaneously on the GC disc surface covered by the NRR electroactive materials at high negative potential values (i.e. NH_3 combined to H_2, and/or N_2H_4). To this purpose, CVs on Pt electrode were done in Ar-purified electrolyte solution (Figure 2a) and with the addition of 1 mM hydrazine (Fig-
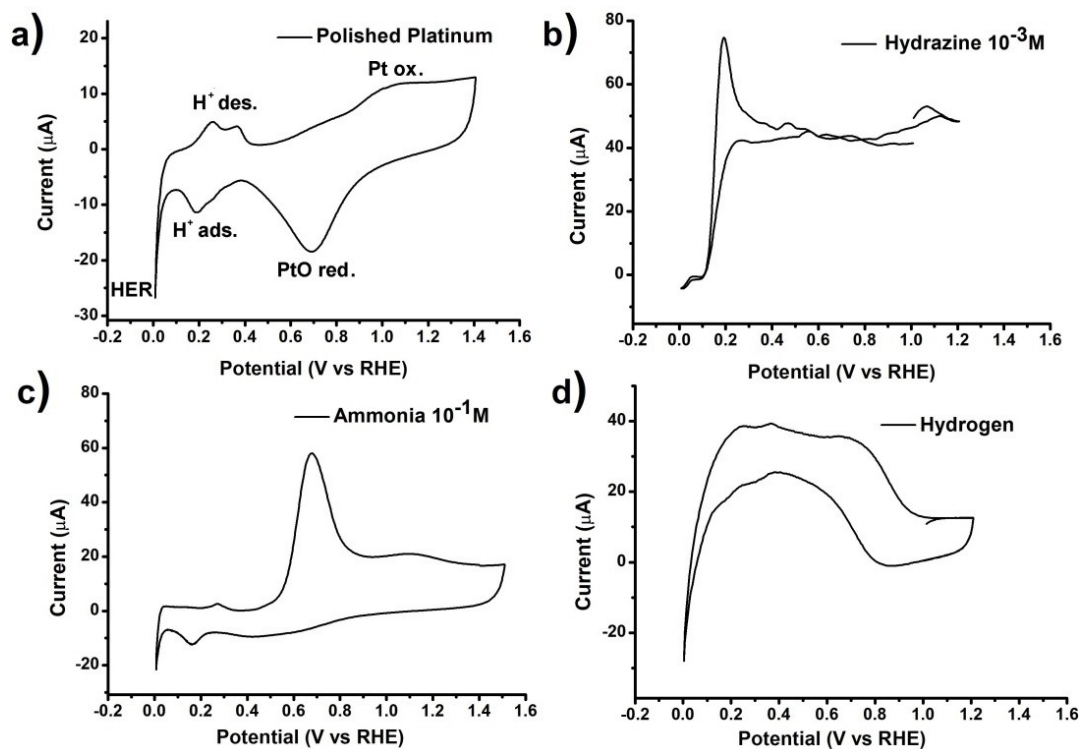

Figure 2. Cyclic Voltammetry scans of NRR involved products. CVs on polished Pt ring (a) with added hydrazine (b), ammonia (c) or in situ produced hydrogen (d).

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ure 2b) or 0.1 M NH_3 (Figure 2c), in the water stability window (0 ~ 1.4 V vs. RHE). Furthermore, in order to simulate the concomitant production of *in situ* H_2 (Figure 2d), the uncovered polished GC disc electrode was subjected to a CA at −1 V vs. RHE, generating a stable current of 0.2 mA. The obtained voltammograms for each specific product identification are in good accordance with literature, as detailed below. Platinum ring resulted highly active toward hydrazine oxidation, as represented by the oxidation peak at 0.2 V vs. RHE, followed by an oxidation plateau. Moreover, the N_2H_4 oxidation reaction is diffusion limited, therefore highly dependent on the rotation speed of the electrode.[28] Ammonia product, on the other hand, showed an irreversible oxidation peak at 0.7 V vs. RHE, for the most part independent from RRDE rotation speed.[24,29,30] Lastly, hydrogen showed a broad diffusion limited oxidation peak that spans from 0.0 V to roughly 1.0 V vs. RHE, where the platinum oxidation to platinum oxide deactivates the electrode surface for HOR.[31]

RRDE-based method employment

The NRR electrochemical activities of the three representative materials, prepared according to literature procedures, were firstly investigated by the use of the RDDE tool and the obtained data were confirmed by the quantitative analysis; finally, the resulting data were also compared to already published figures.

Electrocatalyst fingerprint for NH_3 production

A first scan of the catalytically relevant potentials was performed through a CV of the covered disc electrode, while the potential of the ring was kept fixed at 0.7 V vs. RHE, corresponding to the value at which the Pt is most sensible to the presence of dissolved NH_3 (Figure 2c). The resulting RRDE plot overview showed an increase for the ring current in N_2-saturated electrolyte for all the cases investigated

(Figure 3). The differences observed on the ring electrode (with only marginal currents deviation at the disk), while indicative, were not a conclusive proof of nitrogen activation due to the coexistence of hydrogen oxidation reaction (HOR) and ammonia oxidation at the Pt ring electrode at 0.7 V vs RHE; therefore, a full picture for the process is required by the use of combined disc/ring CVs.

The representative case of 30% Fe_2O_3–CNTs was referred to the most critical operative condition among the three studied electrocatalysts, due to the combination of low selectivity (FE to NH_3) and current performance at the investigated working potential. Its related ring current response at 0.7 V vs. RHE in Ar- (blank) and N_2-saturated 0.1 M KOH electrolyte during cycling of the catalytic material was reported in Figure 3a. While the CV on the disc showed little differences between Ar- and N_2- scans, the ring electrode recorded an earlier activation potential starting from −0.25 V vs. RHE for the NRR process. However, in literature it is reported that NRR on 30% Fe_2O_3–CNTs starts at lower overpotentials, despite with very low outputs in terms of current densities. Therefore, further combined RRDE-based experiments were needed to assess the NRR performance and to evaluate the method sensibility.

To get a more detailed understanding, CAs of the GC-supported materials were done at different potentials, while the ring electrode was scanned in the water stability window. The CVs on the supported catalysts in N_2-saturated electrolyte at OCP and in Ar-saturated electrolyte at operative potentials showed no evidence of the presence of NH_3, excluding impurities and material degradation as a secondary source of ammonia (Figure S2). Furthermore, the stability of Nafion® 117 as binder component was also confirmed in the operative conditions. For all the three catalyst, hydrazine-related peaks, near 0.2 V vs RHE, were never observed. The case of 30% Fe_2O_3–CNTs was summarized in Figure 4: local presence of ammonia was already detected in a single CV scan on the Pt electrode (20 s, Figure 4a). Exploiting a longer CA on the catalyst (1500 s, Figure 4b), a CV on the ring electrode can be then employed to probe the bulk accumulation of NH_3 during the CA test,
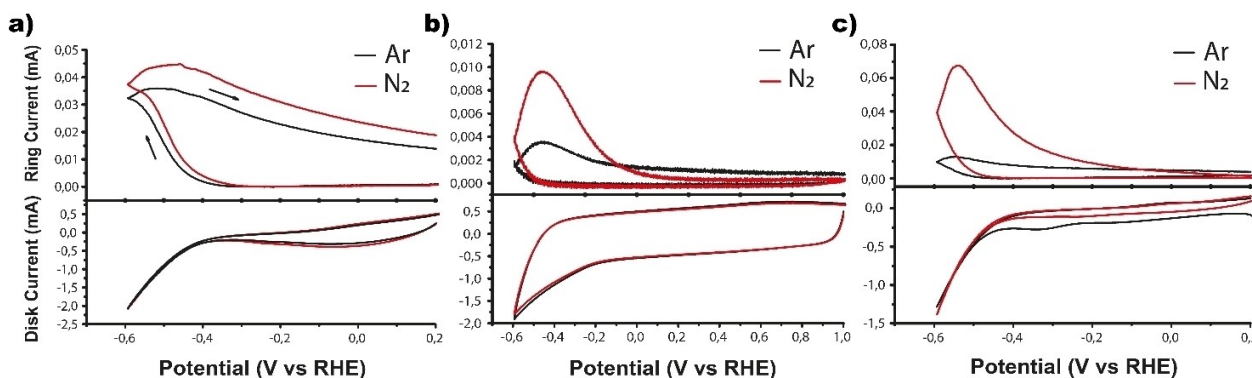

Figure 3. Disc and ring current responses recorded at 0.7 V vs RHE for Pt ring during cycling of the disc-supported catalytic material. Case of 30% Fe_2O_3–CNTs (a), ZIF-1100-1h (b) and Fe_2O_3 (c). RRDE rotation speed 200 rpm.
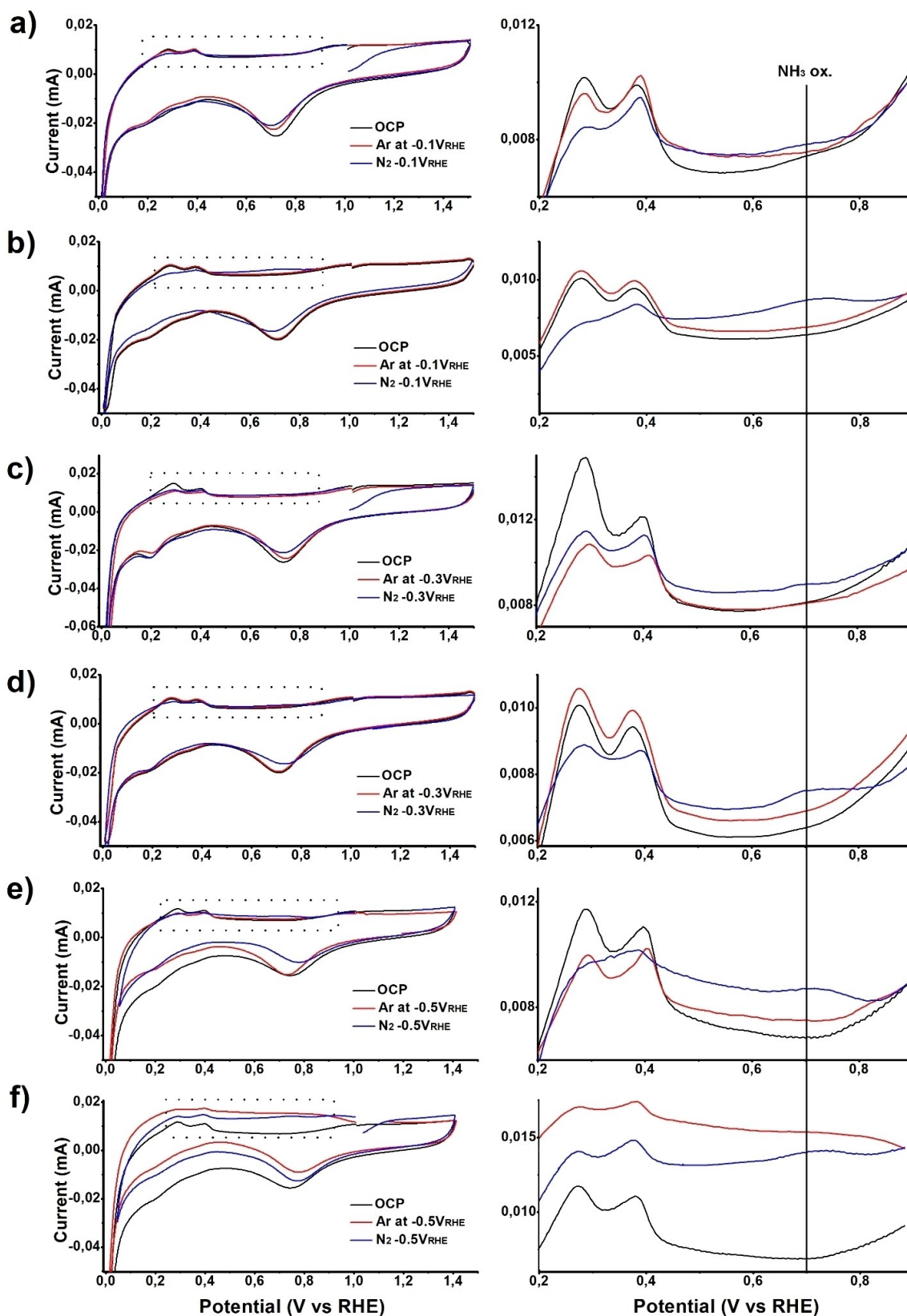
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Figure 4. CVs on Pt ring; GC covered by 30% Fe_2O_3–CNTs (a,b), ZIF-1100-1h (c,d) and Fe_2O_3 (e,f). The disc electrode was fixed at different operative potentials for 20 s (a,c,e, with zoomed onset on the right) and for 1500 s (b,d,f, with zoomed onset on the right). RRDE rotation speed 200 rpm.

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as also confirmed by conventional colorimetric analysis (Figure S5). Another noticeable difference was represented by the slight shift of the platinum oxide reduction peak. In a prolonged RRDE-based CA test this peak tends to decrease in magnitude, due to partial coverage of the platinum surface with strongly binding intermediates of the ammonia oxidation reaction.[24]

A recent investigation of Chen et al.[25] deepened the ammonia formation rates and FEs for the same 30% Fe_2O_3–CNT electrocatalyst in different electrolytes, accounting for the highest ammonia formation rate and FEs to NH_3 with alkaline 0.5 M KOH electrolyte in a gas flow cell. In particular, at −0.04 V vs. RHE, the authors accounted for an ammonia formation rate of 1.86×10^{-12} mol cm^{-2} s^{-1} with NH_3 Faradaic selectivity of 0.59%, in their optimized cell setup.

Otherwise, our prolonged CA tests were done in a single-chamber cell with a GC-RDE as the catalyst support. Nonetheless, the resulting currents compared well with reported values (Figure S4) and, similarly, we found a FE at −0.1 V vs. RHE of 0.5% (Table S1) and a formation rate of 3.66×10^{-12} mol s^{-1} cm^{-2} (Table S2) in 0.1 M KOH electrolyte.

Electrocatalytic material degradation: false positives identification

A further important application of the RRDE-based analysis technique was referred to the time stability evaluation of nitrogen – containing catalyst in the operative environment (i.e. alkaline environment). N-based materials have been suggested as one of the most promising class of electrocatalysts[32–34] for highly selective N_2 reduction at low overpotentials, but they are also looked in distrust because they could be themselves the nitrogen source, invalidating the NRR process analysis. Due to the high sensibility of RRDE setup, we employed the CV fingerprints in Ar-saturated electrolyte at OCP and at the investigated reductive potentials to identify possible false positives. To this purpose we investigated the electrocatalytic behavior of a ZIF based material. In this case, the setup cleaning was of primary importance in the following evaluations (as highlighted in the section "Cleaning process" of Supporting Information), as traces of environmental ammonia could false NRR results altering the expectation for these electrocatalytic materials. To this purpose a consecutive washings procedure (at least 4 times) was adopted to keep the NH_3 levels in solution below a detectable level on the Pt ring. The downward trend of ammonia levels was also visible in colorimetric analysis throughout the cleaning procedure (Figure S3).

ZIF-1100-1h showed high NRR performance in N_2-saturated 0.1 M KOH electrolyte, confirmed by the remarkable Pt ring currents increase (Figure 3b). The sole currents evaluation, however, does not preclude the possibility of catalyst breakdown interference; therefore, a further analysis at the Pt electrode was needed. Mukherjee et al, investigated the

electrocatalytic stability of ZIF-1100-1h at −0.3 V vs. RHE, where the best performances in terms of FE were observed.[26] Two colorimetric analysis confirmed NRR electroactivity at this potential value with a corresponding high FE of 6.5% and 4.0% by indophenol and Nessler method, respectively (Table S1) although the activity remained lower with respect to that of the other metal oxide-based catalysts considered in this paper (Figure S6). In the shorter CA test (20 s, Figure 4c), similarly to the 30% Fe_2O_3–CNTs case, a small peak shoulder was visible at 0.7 V vs. RHE in the CV scan under N_2 flow. The absence of peaks in the same operative conditions but under Ar flow was considered significant but not definitive of catalyst stability. A prolonged CA test (1500 s, Figure 4d) allowed us to confirm NRR performance stability of ZIF-1100-1h; in fact, in N_2-saturated electrolyte, the CV peak at 0.7 V vs. RHE showed the expected increase due to prolonged activity, while in Ar- saturated electrolyte no peak was observed. Moreover, a decrease in magnitude of the Pt-oxide reduction peak was also detected, in agreement with the observations on the previous catalyst.

Overcoming side H_2 generation

Hydrogen interference during NRR is one of the main problems in RRDE-based experiments due to the closeness of disk and ring electrodes. In fact, at high cathodic currents, the production of hydrogen exceeds the local solubility of the gas and results in the formation of bubbles. This is commonly registered by the ring electrode as a noisy CV that mostly resembles the hydrogen oxidation profile on Pt electrode reported in Figure 2d. This case of study is well represented by the Fe_2O_3 (commercial) investigated electrocatalyst. The corresponding ring currents on bulk RRDE tests (Figure 3c) suggested high activity toward NRR at high overpotentials; however, side H_2 production heavily occurred. The attempt to identify the NRR products by Pt ring CV during a disc CA, in accordance with the method discussed so far, resulted in unclear data, due to H_2 bubble interference (Figure S10).

In an attempt to overcome H_2-related noise, we gained a cleaner NRR profile with a rather noticeable ammonia peak, only when the CV on the Pt ring electrode was started after the end of the catalysis stage on the disk, by adopting a delay of 20 s. This approach resulted suitable for both short (20 s) and longer (1500 s) CAs, having care to remove all H_2 bubbles by flowing the sparging gas directly on the electrode surface (Figure 4e and 4f). The CVs profile still result in a high hydrogen plateau, but the ammonia peak is in this way perfectly appreciable. In the case of Fe_2O_3, the ammonia peak doesn't seem to grow significantly with time. Current deriving information could indicate a lower sensibility of the modified RRDE-based method due to the predominant diffusion of species during delay time assisted by the abundant production of H_2 bubbles; also, a loss in selectivity toward NRR during time could not be excluded.

In fact, at the low operative potentials, the surface iron oxide is slowly reduced to a mix of Fe and $Fe(OH)_2$ that is more active (Figure S8) in terms of generated current, but whose selectivity toward NRR remains unclear.[35]

A two-hours CA test at -0.5 V vs RHE was used to determine the $FE(NH_3)$ of the material, corresponding to 0.04% (Indophenol method) also confirmed by Nessler reaction (Table S1). This value is in the same order of magnitude of that reported by Furuya et al.,[27] despite different cell structure and operative conditions were used. Notably, our prolonged CA with respect to the short catalysis previously used[27] and the chemical modifications on the surface[35] could justify our hypothesis of a selectivity decrease with time.

Conclusions

The NRR electrochemical performance for ammonia production was investigated by the use of the RDDE-based analysis tool to provide a preliminary qualitative information and the obtained data were confirmed by the traditional quantitative colorimetric tests. Three well established NRR electrocatalysts were prepared in accordance with literature procedures to represent different working potentials and currents: a CNTs supported Fe_2O_3 NPs (30% Fe_2O_3–CNTs), a commercial Fe_2O_3 and a ZIF-8 derived nitrogen-doped carbon (ZIF-1100-1h). In the present work, the Pt ring electrode of the RRDE setup has been used to identify the products from N_2 reduction. Ammonia was identified as the unique product from electrochemical reduction of N_2 using all the three investigated electrocatalysts in 0.1 M KOH solution and room temperature. When the disc electrode was scanned, the ring electrode detected the oxidation peak when it was held at 0.7 V vs. RHE, indicating that the product from N_2 reduction was oxidized around this potential on the Pt ring electrode. This information was subsequently confirmed by scanning the ring electrode with the three different catalysts held at specific and proved reducing potentials (each corresponding to a consistent oxidation peak at 0.7 V vs. RHE on the ring electrode).

Different results were targeted by the use of this fast screening method for NRR electrocatalytic activity, in alkaline environment. Firstly, we demonstrated that the RRDE experimental approach is effective to discern also a low-level ammonia concentration that occurs in particular operative conditions such as low overpotentials and currents; this specific case was represented by the 30% Fe_2O_3–CNTs electrocatalyst, that was characterized by limited FEs, below 1%. Secondly, the high sensibility of RRDE setup, allowed us to employ the CV fingerprints obtained in Ar-saturated electrolyte, at both OCP and at reductive potentials, to identify false positives. To this purpose the case of ZIF-1100-1h was deepened to account for the class of N-doped carbon-based electrocatalysts as the most promising NRR materials but affected by possible fast degradation in the operative conditions, contributing with a secondary source of ammonia, capable of distorting NRR data. Finally, hydrogen interference during NRR is one of the main problems in RRDE-based experiments at high cathodic currents; this phenomenon is registered by the ring electrode as a noisy cyclic voltammograms. In an attempt to overcome H_2-related noise, we gained a cleaner NRR profile with a visible ammonia peak, only when the CV on the Pt ring electrode was started after the end of the catalysis stage on the disc, by adopting a delay of 20 s. This approach resulted suitable for both short and longer CAs, having care to remove all hydrogen bubbles. The CV profile still result in a high hydrogen plateau, but the ammonia peak was perfectly visible.

Based on the obtained results in different operative conditions, it is possible to assert that the excellent versatility of the investigated RRDE method, employed for a preliminary fingerprint of new NRR electrocatalyst candidates, could allow to quickly discern false positives and to reserve time and cost consuming analysis only for promising materials.

Experimental section

Materials synthesis

Iron nitrate nonahydrate $Fe(NO_3)_3 \cdot 9H_2O$, Hydrazine hydrate (N_2H_4, 60%), Salicilic acid, sodium citrate tribasic, sodium dichloroisocyanurate dihydrate, Nafion 117® 5% solution, nitric acid (HNO_3, 70%), Hydrochloric acid (HCl, 35%), Ethylene glycol (98%), Methanol (99,8%) were purchased from Sigma-Aldrich. Iron(III) oxide (99.98%) powder was bought from Honeywell. Sodium nitroprusside and 2-propanol were purchased from Carlo Erba. Ammonium hydroxide solution (NH_3, 25%), Zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$, 2-methyl Imidazole, potassium hydroxide (KOH, puriss. p.a. >85%) were purchased from Fluka. All experiments were conducted with milliQ water obtained by using a Direct-Q (Millipore) water purification system.

CNTs supported Fe_2O_3 NPs (30% Fe_2O_3–CNTs) were synthetized according to literature.[25] CNTs were first oxidized in concentrated HNO_3 at reflux for 2 h, then washed in DI water and dried under reduced pressure at 60°C. $Fe(NO_3)_3$ was dissolved in a 25 mL DI water and 1 mL ethylene glycol dispersion of the obtained o-CNTs. A 5% ammonia solution was added dropwise till pH 8 and then the product was filtered and dried at 120°C. Finally, the material was calcinated in a tubular furnace under Ar gas at 400°C. The obtained catalyst was characterized by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to check for effective iron loading.

ZIF-8 derived nitrogen-doped carbon (ZIF-1100-1h) was synthetized according to literature.[26] First, ZIF-8 were prepared mixing equal volumes of methanol solutions of reactants (2-methylimidazole and $Zn(NO_3)_2 \cdot 6H_2O$ to obtain a final molar ratio of 4:1. The solution was aged for 24 h at 60°C and then the solid was collected through centrifugation and consecutive methanol washing to remove excess reactants. The obtained material was pyrolyzed under Ar flow for 1 h at 1100°C in a tubular furnace and then washed in 0.1 M HCl solution.

Iron(III) oxide (99.98%) was bought from Honeywell and used without further purification steps.[27]

Electrochemical testing

The catalyst performances were evaluated at room temperature on an Autolab 302 N electrochemical workstation (Metrohm) equipped with a GC/Pt rotating ring disk electrode (RRDE Autolab, Metrohm, geometric Surface Area 0.196 cm^2, calculated Collection Efficiency 0.25) as the working electrode. This is composed of a glassy carbon disc and a platinum ring electrode with a 375 μm PTFE gap in between. A platinum plate and a saturated calomel electrode (SCE, KCl sat.), counter and reference electrodes respectively, were separated from the main cell chamber via bridges equipped with Vycor® frits. All measured potentials were converted to reversible hydrogen electrode (RHE).

Prior to each measurement a standardized cleaning protocol of the entire electrochemical setup (cell, bridges, electrodes and gas inlet, frits, etc.), was adopted to avoid external interferences; therefore, the glass cell was filled with milliQ water, and everything was kept soaking. Every 20 minutes, the water was removed, and the process repeated for at least 6 times. Finally, the cell was filled with the desired amount of electrolyte. The detailed cleaning sequence and checks is reported in the "Cleaning process" section of Supporting Information.

All the inks were prepared in a 3:1 H$_2$O iPrOH mixture with the addition of 5% (v/v) Nafion® 117 solution and then sonicated for 30 minutes. The dispersion concentrations were kept at 2.5 mg mL^{-1}. The catalyst ink composed of each catalyst powder was drop-casted on the surface of the glassy carbon RRDE disc; a variable ink volume was coated on the GC disc to achieve a designed loading of 300, 300 and 100 μg cm^{-2} for 30% Fe$_2$O$_3$—CNTs, ZIF-8 derived nitrogen-doped carbon and commercial Fe$_2$O$_3$, respectively, allowing a better comparison with published data. Prior to each NRR test, the complete assembled system was degassed with pure Ar for 30 min.

Electrocatalytic activities were evaluated in a N$_2$-saturated KOH 0.1 M solution. Three different types of measurements were used to characterize the set of the three different NRR electrocatalysts. First, the electrocatalyst material deposited on the disk electrode was cycled in cyclic voltammetries (CVs) from Open Circuit Potential (OCP) to −0.6 V vs. RHE, while the Pt ring potential was set to 0.7 V vs. RHE, corresponding to the potential value where NH$_3$ oxidation takes place. (Figure 2c)

As a second set of experiments, the same GC-supported electrocatalysts were subjected to relatively fast (time order of seconds) chronoamperometric tests (CAs) at fixed potential values corresponding to those where the materials would be active toward NRR, while the Pt ring would cycle in CVs inside the water stability window (0 ~ 1.4 V vs. RHE). During the complete sequence of measurements, the CV scan speed was set to 100 mV s^{-1} to both limit the formation of bubbles on the catalyst layer and have clear electrochemical peaks on the platinum ring. For similar reasons the rotation speed of the RRDE setup was limited to 200 rpm.[24]

A further set of prolonged CAs (time order of hours for product accumulation) was finally done to ascertain the faradaic efficiency (FE), by two different colorimetric analysis, and its closeness to published data. In accordance with the previous experimental setup the electrocatalysts were supported on the GC disc of RRDE electrode and subjected to three CAs measurements in different operative conditions: i) the first one was performed with the disk electrode at OCP in N$_2$-saturated electrolyte to check for impurities coming from the experimental setup; ii) the second one was recorded at the NRR operative potentials in Ar- saturated solution to check for stability of the

material; iii) and finally the third CA test was collected at operative potentials in N$_2$-saturated electrolyte; these steps were completed including the systematic quantitative spectrophotometric NH$_3$ detection (Figure S1). More details are reported in the Supporting Information.

Conflict of Interest

The authors declare no conflict of interest.

[1] J. W. Erisman, M. A. Sutton, J. Galloway, Z. Klimont, W. Winiwarter, *Nat. Geosci.* **2008**, *1*, 636–639.
[2] X. Cui, C. Tang, Q. Zhang, *Adv. Energy Mater.* **2018**, *8*, 1800369.
[3] J. H. Montoya, C. Tsai, A. Vojvodic, J. K. Nørskov, *ChemSusChem* **2015**, *8*, 2180–2186.
[4] C. J. M. Van Der Ham, M. T. M. Koper, D. G. H. Hetterscheid, *Chem. Soc. Rev.* **2014**, *43*, 5183–5191.
[5] T. H. Rod, A. Logadottir, J. K. Nørskov, *J. Chem. Phys.* **2000**, *112*, 5343–5347.
[6] S. G. Bratsch, *J. Phys. Chem. Ref. Data* **1989**, *18*, 1–21.
[7] S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh, B. A. Rohr, M. J. Statt, S. J. Blair, S. Mezzavilla, J. Kibsgaard, P. C. K. Vesborg, M. Cargnello, S. F. Bent, T. F. Jaramillo, I. E. L. Stephens, J. K. Nørskov, I. Chorkendorff, *Nature* **2019**, *570*, 504–508.
[8] L. F. Greenlee, J. N. Renner, S. L. Foster, *ACS Catal.* **2018**, *8*, 7820–7827.
[9] L. Zhou, C. E. Boyd, *Aquaculture* **2016**, *450*, 187–193.
[10] P. T. T. Le, C. E. Boyd, *J. World Aquacult. Soc.* **2012**, *43*, 885–889.
[11] P. L. Searle, *Analyst* **1984**, *109*, 549–568.
[12] H. Verdouw, C. J. A. Van Echteld, E. M. J. Dekkers, *Water Res.* **1978**, *12*, 399–402.
[13] M. S. Roberts, R. A. Anderson, J. Swarbrick, *J. Pharm. Pharmacol.* **1977**, *29*, 677–683.
[14] R. H. Leonard, *Clin. Chem.* **1963**, *9*, 417–422.
[15] M. C. Hatzell, Y.-H. Liu, *ECS Meet. Abstr.*, **2019**, p. 1682.
[16] V. Lates, A. Falch, A. Jordaan, R. Peach, R. J. Kriek, *Electrochim. Acta* **2014**, *128*, 75–84.
[17] X. Zhu, K. Gupta, M. Bersani, J. A. Darr, P. R. Shearing, D. J. L. Brett, *Electrochim. Acta* **2018**, *283*, 1037–1044.
[18] J. Scholz, M. Risch, K. A. Stoerzinger, G. Wartner, Y. Shao-Horn, C. Jooss, *J. Phys. Chem. C* **2016**, *120*, 27746–27756.
[19] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.* **2013**, *135*, 16977–16987.
[20] J. G. Vos, T. A. Wezendonk, A. W. Jeremiasse, M. T. M. Koper, *J. Am. Chem. Soc.* **2018**, *140*, 10270–10281.
[21] J. G. Vos, M. T. M. Koper, *J. Electroanal. Chem.* **2018**, *819*, 260–268.
[22] A. J. J. Jebaraj, N. S. Georgescu, D. A. Scherson, *J. Phys. Chem. C* **2016**, *120*, 16090–16099.
[23] L. Marinčić, F. B. Leitz, *J. Appl. Electrochem.* **1978**, *8*, 333–345.
[24] K. Endo, Y. Katayama, T. Miura, *Electrochim. Acta* **2005**, *50*, 2181–2185.
[25] S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, *ACS Sustainable Chem. Eng.* **2017**, *5*, 7393–7400.

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[26] S. Mukherjee, D. A. Cullen, S. Karakalos, K. Liu, H. Zhang, S. Zhao, H. Xu, K. L. More, G. Wang, G. Wu, *Nano Energy* **2018**, *48*, 217–226.

[27] N. Furuya, H. Yoshiba, *J. Electroanal. Chem.* **1990**, *291*, 269–272.

[28] V. Rosca, M. T. M. Koper, *Electrochim. Acta* **2008**, *53*, 5199–5205.

[29] H. Gerischer, A. Mauerer, *J. Electroanal. Chem.* **1970**, *25*, 421–433.

[30] S. Le Vot, L. Roué, D. Bélanger, *J. Electroanal. Chem.* **2013**, *691*, 18–27.

[31] W. Sheng, H. A. Gasteiger, Y. Shao-Horn, *J. Electrochem. Soc.* **2010**, *157*, B1529.

[32] Y. Abghoui, E. Skúlasson, in *Procedia Comput. Sci.*, Elsevier B. V. **2015**, pp. 1897–1906.

[33] X. Mao, S. Zhou, C. Yan, Z. Zhu, A. Du, *Phys. Chem. Chem. Phys.* **2019**, *21*, 1110–1116.

[34] Y. Liu, Y. Su, X. Quan, X. Fan, S. Chen, H. Yu, H. Zhao, Y. Zhang, J. Zhao, *ACS Catal.* **2018**, *8*, 1186–1191.

[35] B. T. Hang, D. H. Thang, *J. Alloys Compd.* **2016**, *655*, 44–49.

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Detect, faster, better: Rotating ring disk electrode-based analysis for the nitrogen reduction reaction represent a fast preliminary approach to identify promising candidate electro-catalysts for a sustainable ammonia electro-synthesis and it appears effective to discern also low-levels ammonium concentration. Moreover, CVs on platinum ring can detect N_2H_4 side product and reveal catalyst modification and/or degradation. Finally, hydrogen interference from HER in aqueous environments can be minimized by optimizing the system setup.
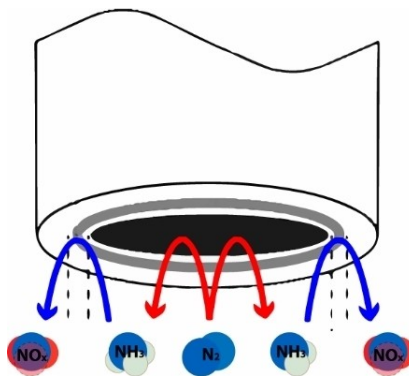
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Fast Screening Method for Nitrogen Reduction Reaction (NRR) Electrocatalytic Activity with Rotating Ring-Disc Electrode (RRDE) Analysis in Alkaline Environment