

Supporting Information

Manganese Carbonate as an Efficient Electrocatalyst for the Conversion of Ammonia ($\text{NH}_4^+/\text{NH}_3$) to Dinitrogen

Iranna Udachyan,^a Jayesh T. Bhanushali,^a Amir Mizrahi,^b Tomer Zidki,^a Dan Meyerstein.^{a, c*}

- a. Department of Chemical Sciences and The Radical Research Center Ariel University, Ariel, Israel, E-mail: danm@ariel.ac.il
- b. Chemistry Department Nuclear Research Centre Negev, Beer-Sheva, Israel.
- c. Department of Chemistry, Ben-Gurion University, Beer-Sheva, Israel.

Experimental Section:

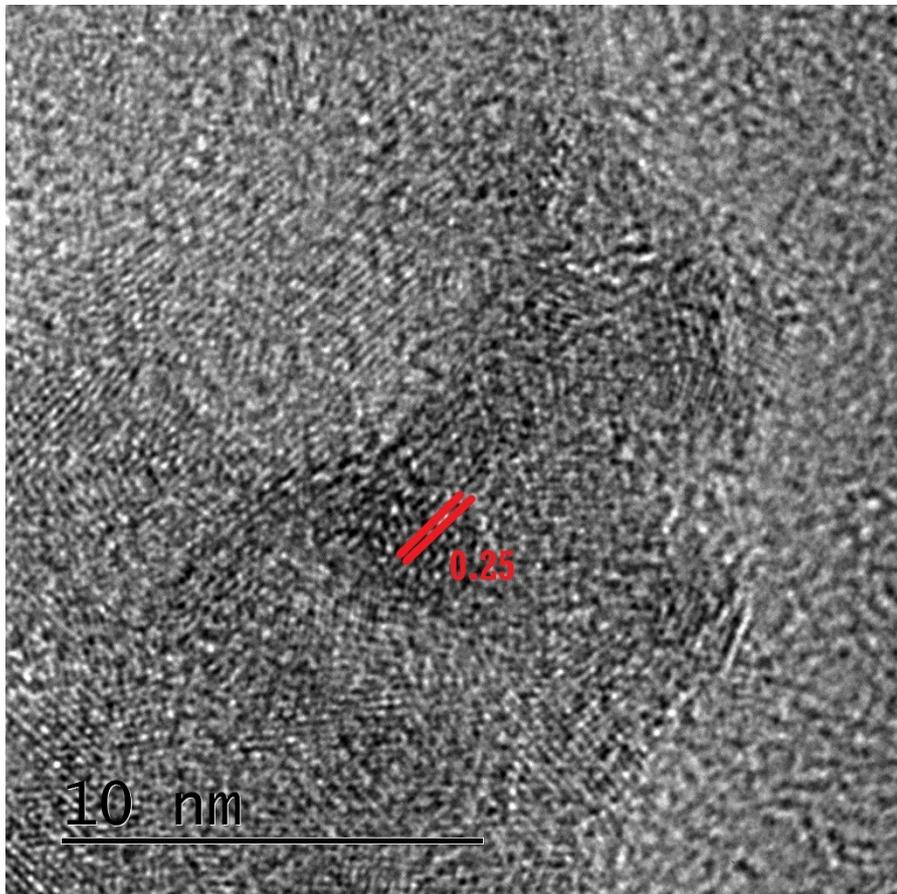
The chemicals were obtained (Alfa Aesar) and used without any further purification process for all experimental studies. All the solutions were prepared using Millipore water (final resistivity of $> 10 \text{ M}\Omega\cdot\text{cm}$). Prior to the electrochemical experiments, the Pd electrode was washed and polished using $1 \text{ }\mu\text{M}$ and $0.5 \text{ }\mu\text{M}$ Al_2O_3 , in order to remove oxides and other impurities from its surface and sonicated with the help of 1:1 water ethanol mixture for 30 s, respectively. The electrochemical synthesis and characterizations were performed in three-electrode cell setup consisting of Ag/AgCl (3 M KCl solution) electrode as a reference and platinum as a counter electrode under N_2 inert atmosphere using a PalmSens4 Instrument. The electrodeposition of $\text{Mn}_2(\text{CO}_3)_3$ with the help of chronoamperometry was done on the Pd surface at 1.3 V vs. Ag/AgCl in a solution containing 0.30 mM MnCl_2 and 0.10 M NaHCO_3 for 1.0 hour. The current density values are presented in accordance with geometrical area. Upon successful deposition, the electrodes were rinsed thoroughly with deionized water and later subjected for drying under air atmosphere before being utilized for their further analysis and electrochemical measurements.

Electrode Characterizations

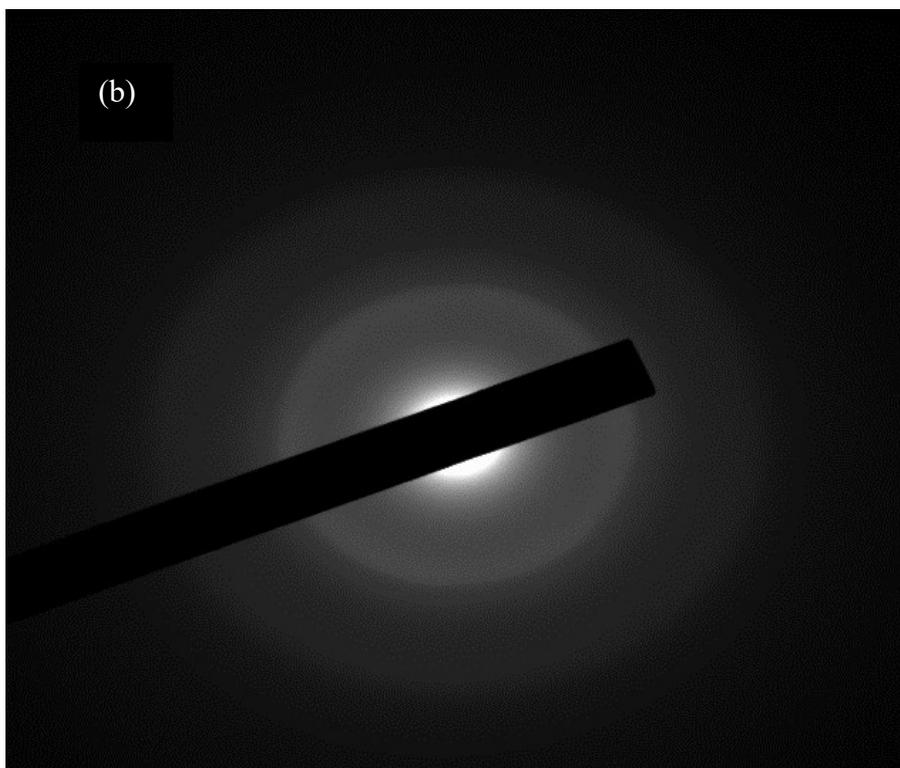
The morphological determination of the precipitate formed on the Pd electrode was determined using scanning electron microscopy by subjecting it to ultrasonication and deposited on a Cu grid using a TESCAN MAIA3 scanning electron microscope (SEM). Further, the composition was determined by elemental analysis using an Aztec materials Characterization System. The evaluation of functional groups on the electrode were recorded over Bruker Alpha 2 FT-IR instrument. The oxidation states of the elements present in the precipitate were investigated by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 250 ultrahigh vacuum (1×10^{-9}) apparatus with an Al $\text{K}\alpha$ X-ray source and a monochromator. All spectra were calibrated with respect to the C1s peak positioned at 284.8 eV. Fitting of the XPS spectra were done by the Gauss function. The crystallinity of electrodeposited $\text{Mn}_2(\text{CO}_3)_3$ on the stainless-steel surface was determined by Powder XRD measurements performed using a Rigaku

Smart Lab SE X-ray diffractometer having Cu K α (1.54 Å) radiation operated at 40 kV and 30 mA.

The electrochemical experiment was performed as reported in literature.¹



(a)



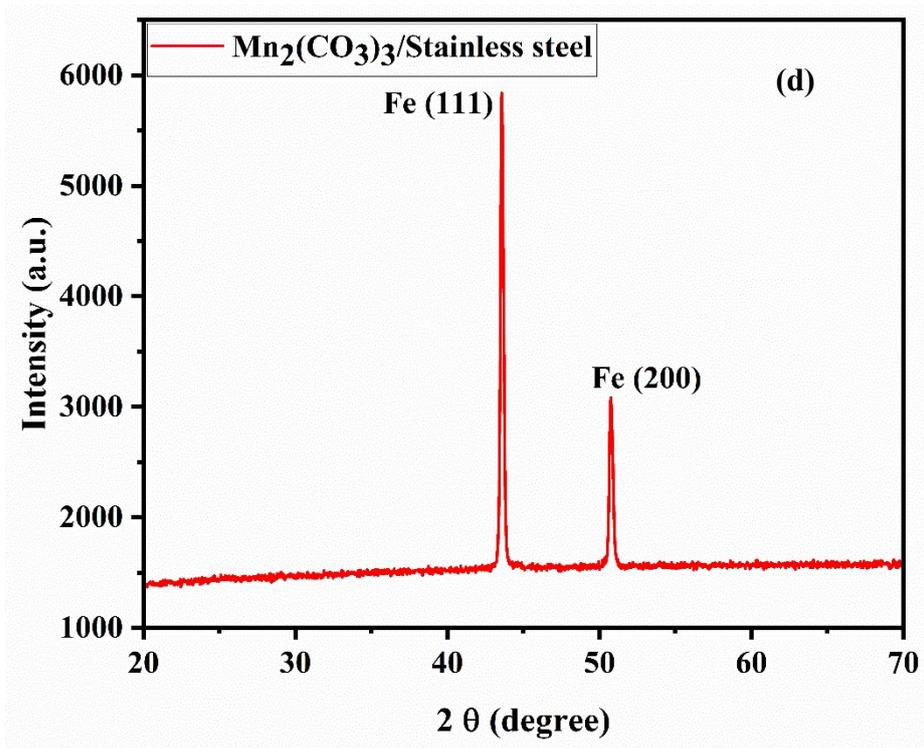
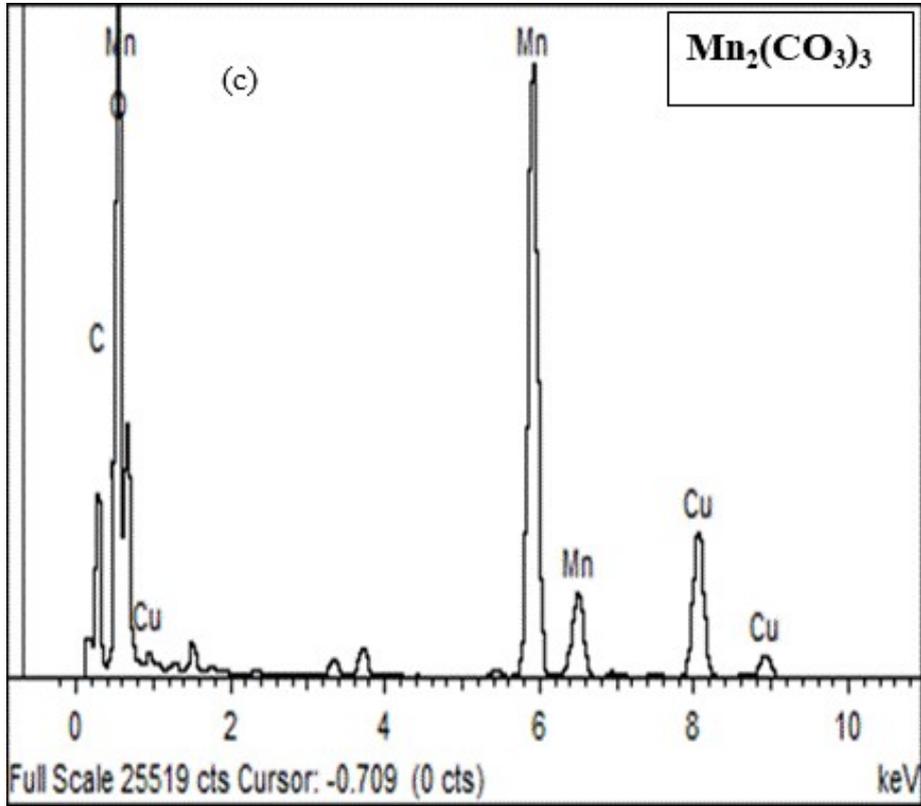


Figure S1: HRTEM image (a), SAED pattern (b), EDS analysis (TEM) (c), XRD spectrum (d) of $\text{Mn}_2(\text{CO}_3)_3$.

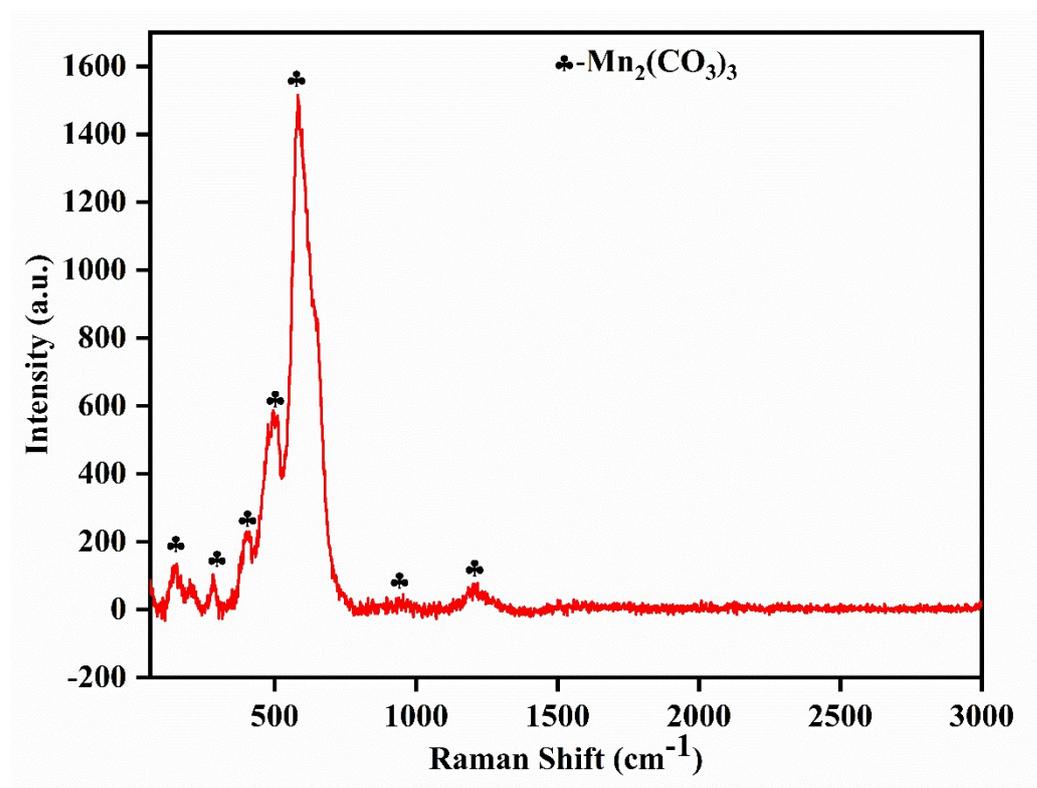


Figure S2: Raman analysis spectra of $\text{Mn}_2(\text{CO}_3)_3$.

Table S1. Comparison of activity towards oxidation of ammonia.

Electrodes and Catalyst	Electrolytes	Ammonia [M]	J ($\text{mA}\cdot\text{cm}^{-2}$)	$E_{p,a}^{\text{anodic}}$ potential (NHE)	Ref.
Pd	1 M Na_2CO_3	0.5	0.5	1.16 V	Present work
NiO	0.1 M NaNO_3	0.2	2.2* 4.0**	1.1 V* 1.2 V**	2
NiO-TiO ₂	0.1 M NaNO_3	0.2	3.5* 5.0**	1.3 V* 1.4 V**	2
Boron-doped diamond	0.1 M KCl	0.1***	0.2	1.1 V	3
CuCr/C	0.1 M KOH	0.1	22	1.1 V****	4
$\text{Mn}_2(\text{CO}_3)_3/\text{Pd}$	1 M Na_2CO_3	0.5	6.4	1.16 V	Present work

*: Corresponding values at pH 10, **: Corresponding values at pH 12, ***: percentage, ****; $E_{p,a}$ Vs. RHE.

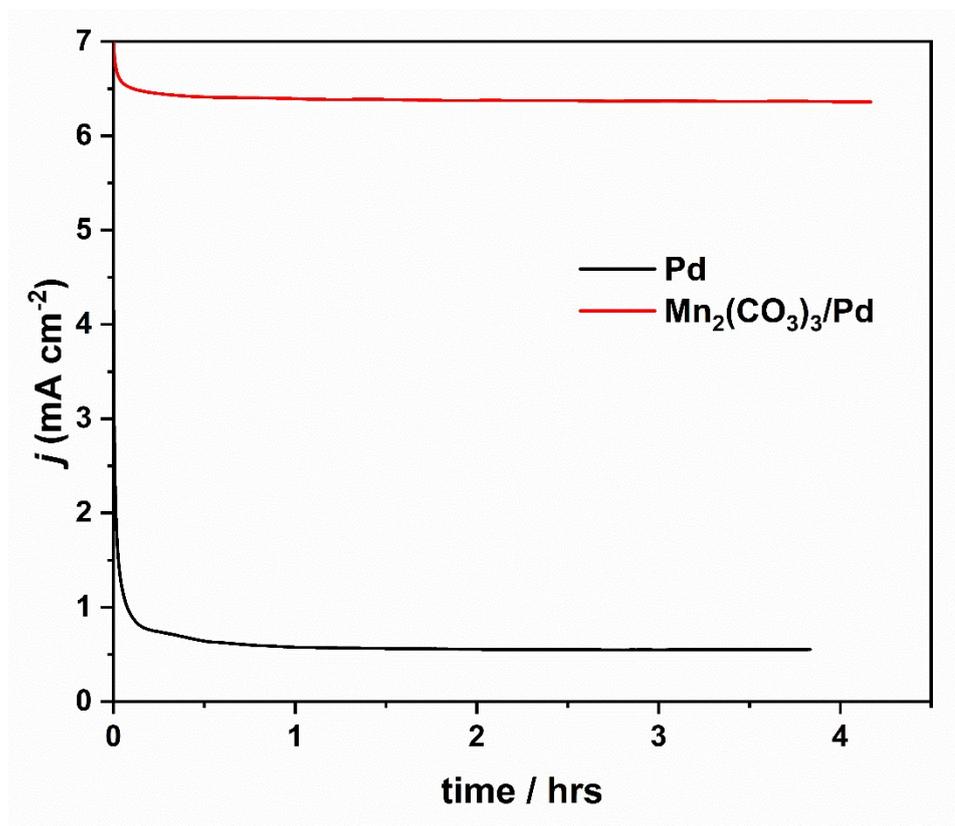
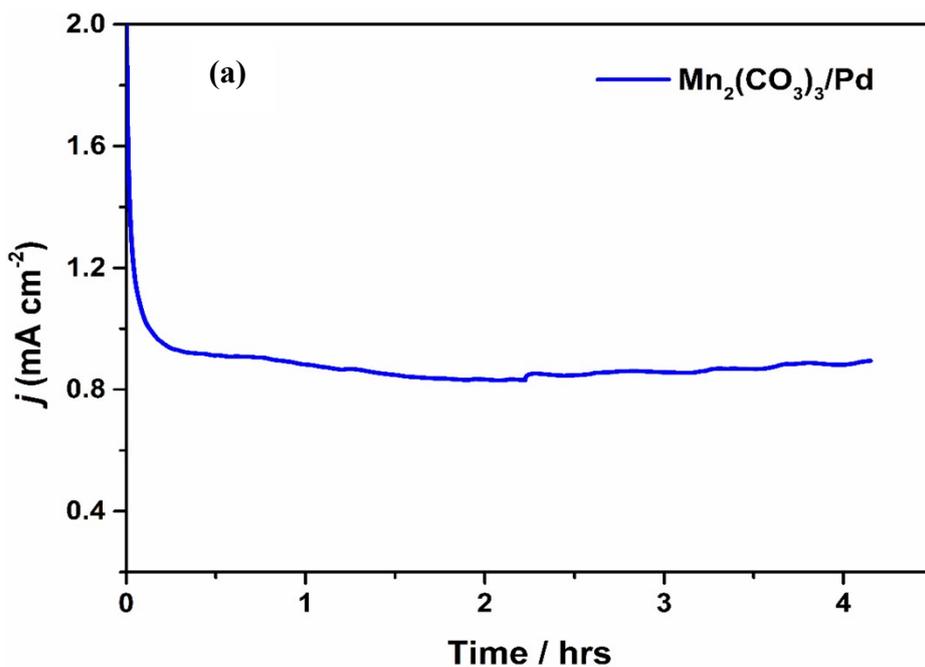


Figure S3. Long term stability of $\text{Mn}_2(\text{CO}_3)_3/\text{Pd}$ in 1.0 M Na_2CO_3 at 1.16 V vs NHE constant potential (a), Long term stability of $\text{Mn}_2(\text{CO}_3)_3/\text{Pd}$ and Pd electrode at 1.16 V vs. NHE in 1.0 M Na_2CO_3 with 0.5 M NH_4OH solution (b).

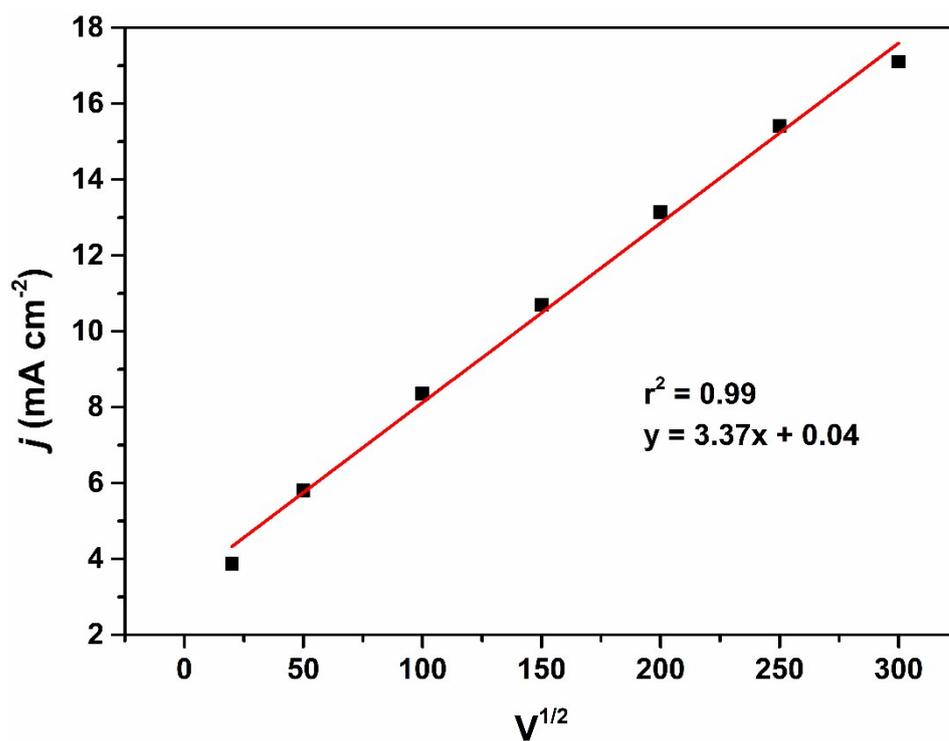
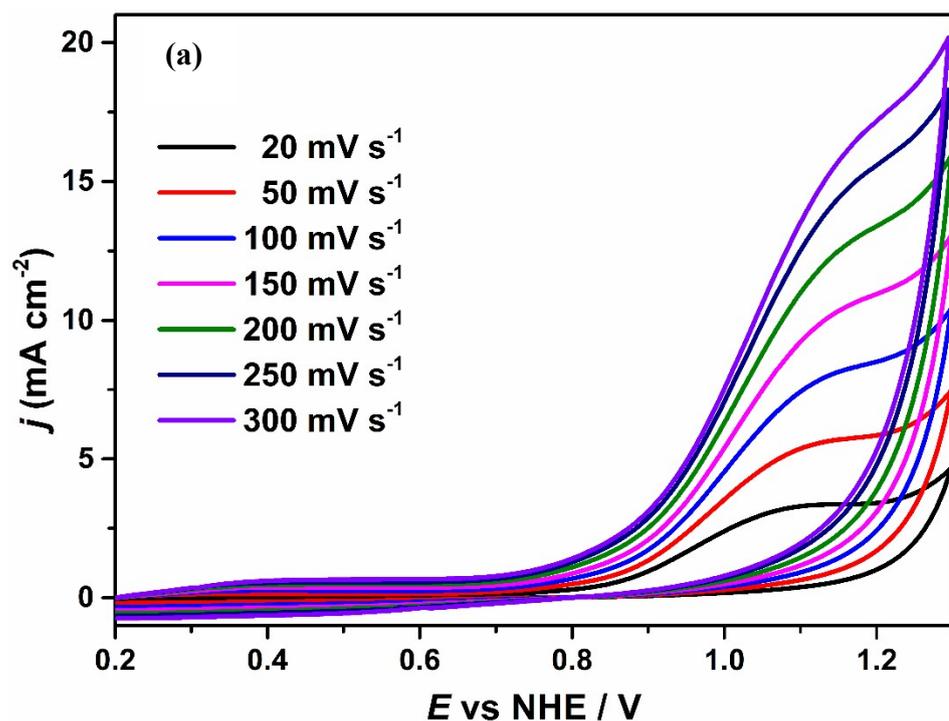


Figure S4. Cyclic voltammograms of $\text{Mn}_2(\text{CO}_3)_3/\text{Pd}$ electrode with different scan rates in 1 M Na_2CO_3 and 0.5 M NH_4OH solution (a), plot of anodic current density vs. the square root of the scan rate (b).

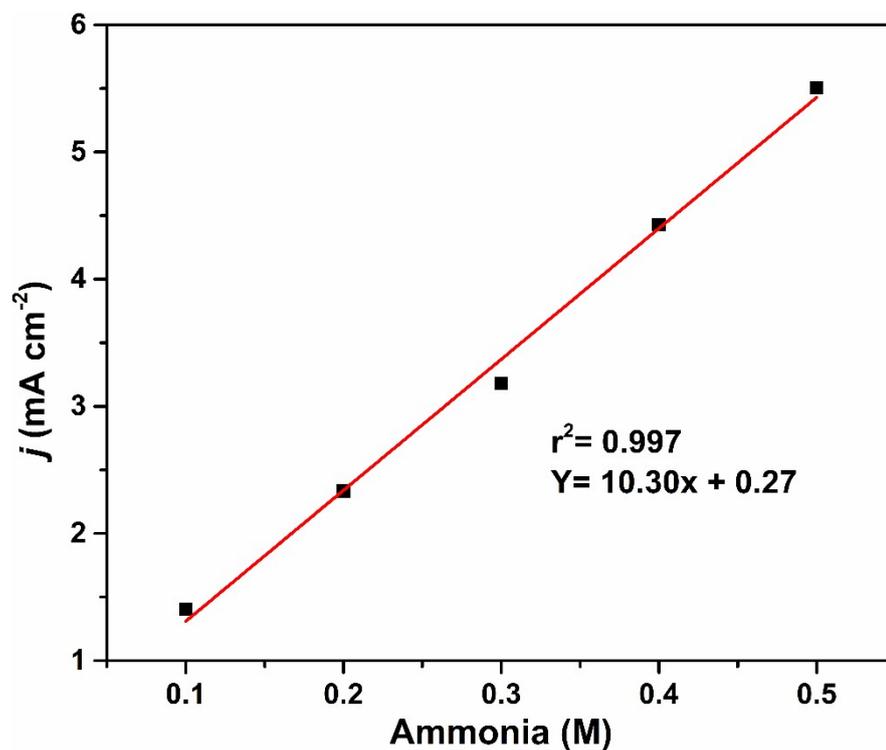
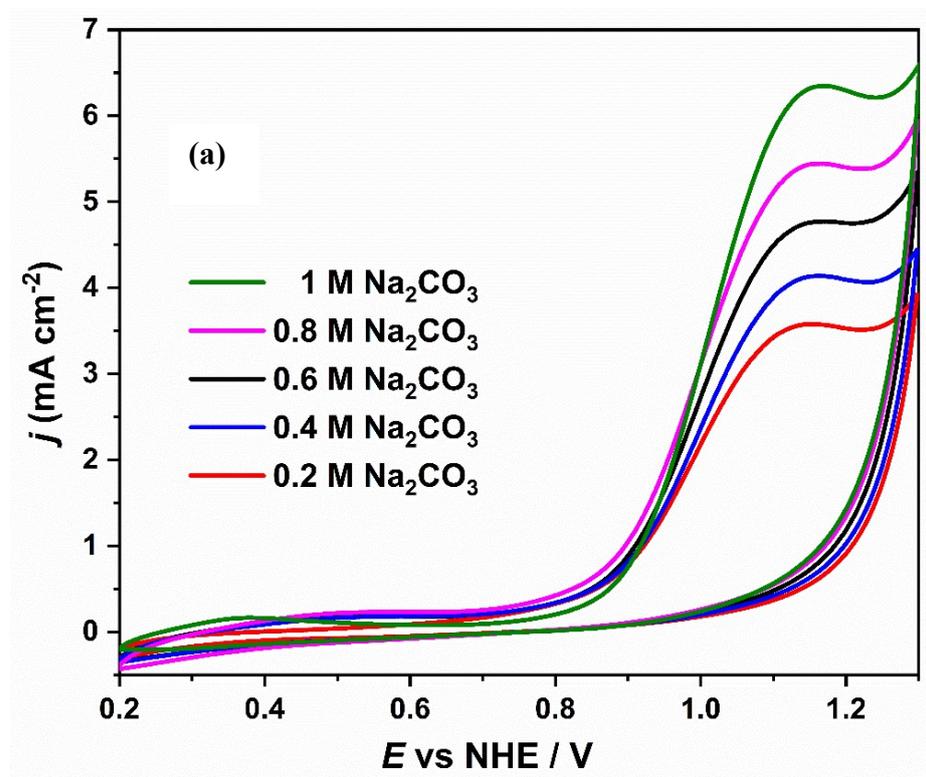


Figure S5. Linear fit of the different concentration of ammonia in 1.0 M Na₂CO₃.



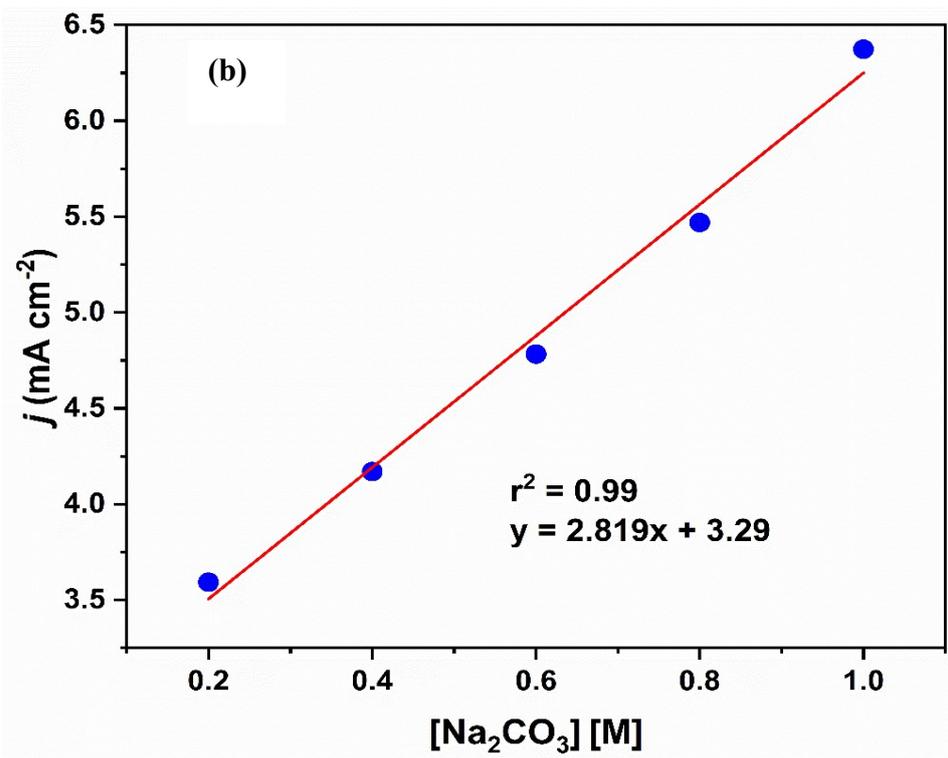


Figure S6. Cyclic voltammograms of $\text{Mn}_2(\text{CO}_3)_3/\text{Pd}$ electrode with different concentrations of Na_2CO_3 and 0.5 M NH_4OH solution (a). Linear fit of the current vs. variation of Na_2CO_3 concentration with 0.5 M NH_4OH (b).

Product analysis: The products obtained from the electrooxidation of ammonia were determined by using gas chromatography. After the completion of reaction, the product samples through a gas tight syringe were inserted into the GC instrument. The specifications for GC instrument are as follows, split/ split less with the split ratio of 15:1 was used as inlet with 140 °C temperature. The oven temperature was initially maintained at 50 °C with a hold time of 7 min. Further, the oven temperature was increased with constant rate of 30 °C.min⁻¹ to 180 °C and held at the same temperature for 2 min. The compounds in the reaction mixture were identified by the TCD maintained at 250 °C. The confirmation of the products was done using the injection of authentic samples. N_2 gas was only detected in the gaseous sample injected into GC and no other products were observed at the retention time of 12 minutes. This can be confirmed by comparing GC results of NH_3 oxidation with the GC results of authentic N_2 sample. The respective GC. results are presented in Fig S7. Furthermore, the UV analysis of the reaction mixture before and after oxidation of ammonia was also performed. The data from Fig. S8 states that there is no variation in the reaction medium

before and after the oxidation of ammonia. Therefore, it can be inferred that upon ammonia oxidation only N_2 is formed and no other intermediates are present in the solution. Also, ion chromatography was performed to determine whether NO_3^- and NO_2^- were formed along with N_2 after the oxidation of ammonia. The results obtained (Fig S9) do not show any peaks corresponding to NO_3^- and NO_2^- from 2-15 min of retention time. This confirms the formation of N_2 as the only product.

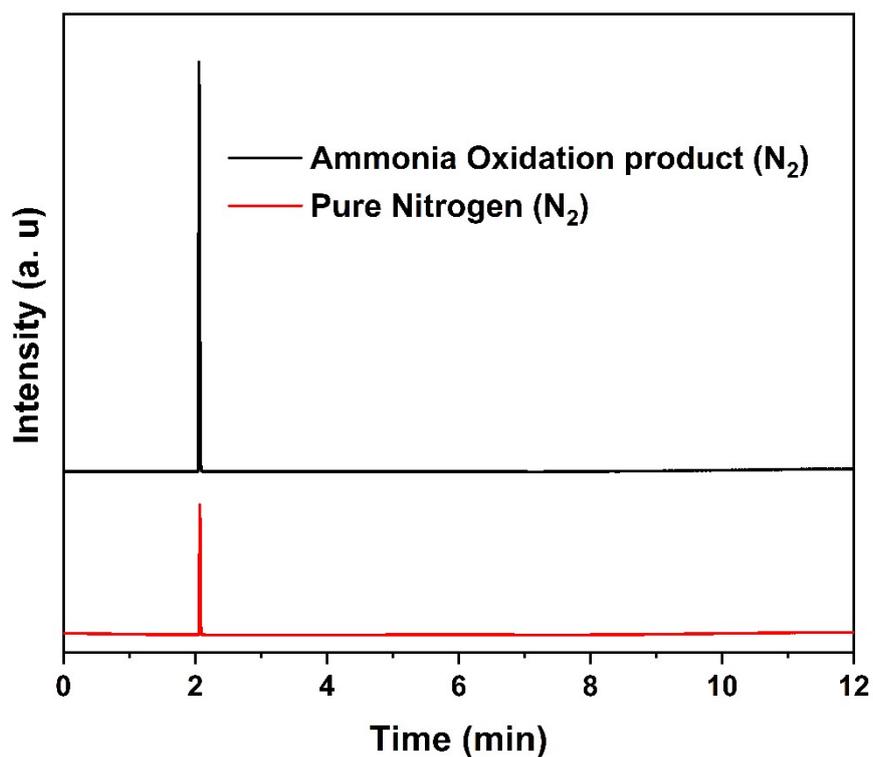


Figure S7. GC results of pure nitrogen and ammonia electrooxidation.

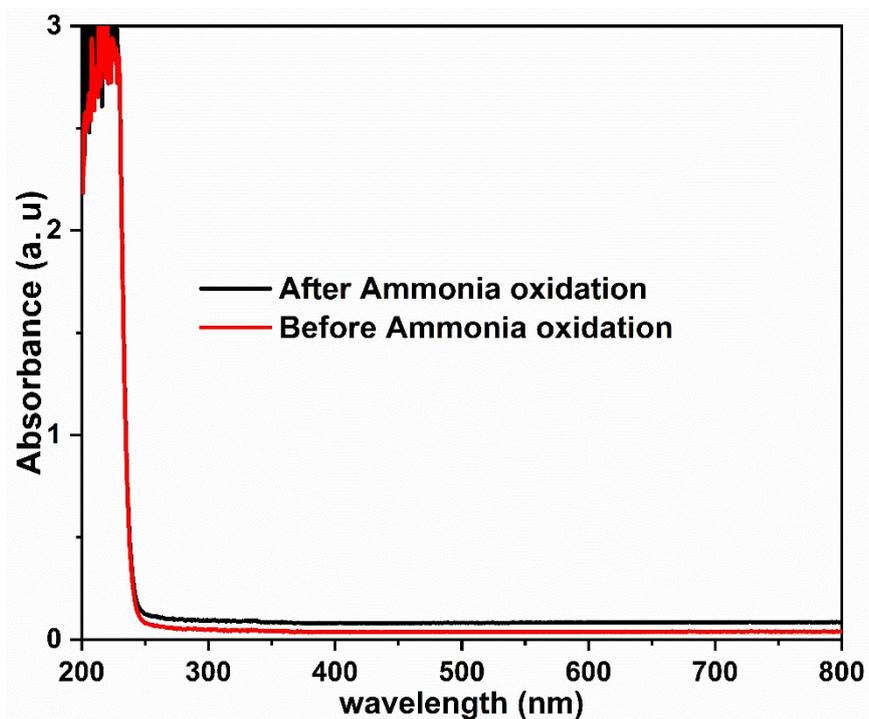


Figure S8. UV-vis spectroscopy results of the reaction medium before and after ammonia oxidation.

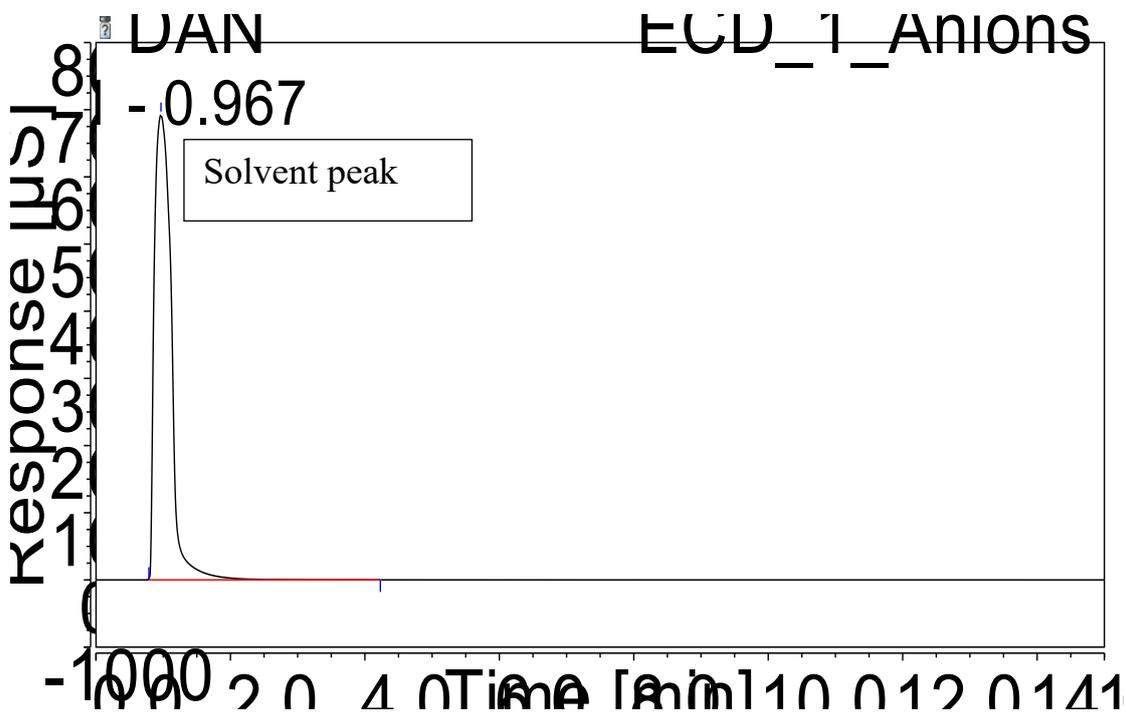


Figure S9. Ion chromatography results of products obtained after ammonia oxidation reaction.

References

- 1 I. Udachyan, J. T. Bhanushali, A. Mizrahi, T. Zidki and D. Meyerstein, *ACS Appl. Energy Mater.*, 2022, **5**, 13903–13912.
- 2 F. Almomani, R. Bhosale, M. Khraisheh, A. Kumar and M. Tawalbeh, *Int. J. Hydrogen Energy*, 2020, **45**, 10398–10408.
- 3 X. Ji, C. E. Banks and R. G. Compton, *Analyst*, 2005, **130**, 1345–1347.
- 4 A. Cleetus, H. Teller and A. Schechter, *ChemCatChem*, 2023, e202300035.