# A High-Energy Aqueous Zn||NO<sub>2</sub> Electrochemical Cell: A New

### **Strategy for NO<sub>2</sub> Fixation and Electric Power Generation**

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#### **Experimental section**

**Preparation of nano-NiO:** Ni(OH)<sub>2</sub> (1.0 g, 10.79 mmol) is added into a vial, then 2.0 ml of H<sub>2</sub>O:isopropanol (2:1) is added to the above vial. The suspension is sonicated at room temperature for 4 h to make it a homogeneous mixture. Water and isopropanol are then removed using a rotary evaporator under vacuum condition. The resulting wet slurry is dried in an oven at 50 °C overnight. The solid powder is then heated to 300 °C in a furnace for 3 h to obtain the nano NiO particles.

**Preparation of NO<sub>2</sub> gas**: The pure NO<sub>2</sub> gas is prepared by reducing concentrated nitric acid with copper metal at room temperature. The rate of gas production is controlled by controlling the drop acceleration rate of concentrated nitric acid. The different concentration of NO<sub>2</sub> gas is prepared by mixing different volumes of pure NO<sub>2</sub> with air using a gas pump.

Materials characterization: Crystallographic data is collected by a Bruker D2 Phaser X-ray diffractometer with Cu K $\alpha$  irradiation ( $\lambda = 0.154$  nm) operating at 30 kV and 10 mA, respectively. Surface morphology is investigated by scanning electronic microscopy (SEM, JEOL JSM-6335F), transmission electronic microscopy (TEM, Philips CM20), and high-resolution transmission electron microscope (HRTEM, JEOL

2100F). The chemical state and composition are analyzed using an ESCALAB 250 photoelectron spectroscopy (Thermo Fisher Scienctific) at  $1.2 \times 10^{-9}$  mbar using Al Ka X-ray beam (1486.6 eV). All XPS spectra are calibrated by shifting the detected adventitious carbon C 1s peak to 284.4 eV. For ex-situ studies, the cycled electrodes were washed with a copious amount of water and thoroughly dried in a vacuum at room temperature. The chemical coordinated information is obtained by X-ray absorption fine spectroscopy (XAFS) spectra conducted at the beamline 1W1B of Beijing Synchrotron Radiation Facility (BSRF) at Institute of High Energy Physics, Chinese Academy of Sciences. The storage rings of BSRF are conducted at 2.5 GeV with an average current of 250 mA. The data collection is conducted in transmission mode using ionization chamber when using Si (111) double-crystal monochromator. The data is processed and analyzed similar to previous procedures using ATHENA and ARTEMIS for X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra, respectively.

**Electrochemical tests:** Firstly, an electrocatalyst/Ketjen black mixture slurry is prepared by dispersing 8 mg of electrocatalyst and 2 mg Ketjen black into 1 mL of mixture solution of 2-propanol, distilled water, and Nafion solution (5 wt %) (10:40:1). Then, the gas electrode is fabricated using a spraying above mixture slurry on carbon

cloth and dried at room temperature for 24 h. The loading mass is  $0.5 \text{ mg} \cdot \text{cm}^{-2}$  for all catalysts. A polished Zn plate serves as the anode and the electrolyte is 2 M ZnCl<sub>2</sub> aqueous solution for rechargeable Zn||NO<sub>2</sub> batteries. The gas diffusion layer has an effective area of 1 cm<sup>2</sup> and allows NO<sub>2</sub> gas to reach the catalyst sites. The charge/discharge polarization are determined utilizing an electrochemical workstation (CHI 760e, Chenhua). The galvanostatic test are performed using a Keithley 2450 source measurement unit at room temperature.

For ammonia synthesis, the fabrication of the dual-compartment cell and relevant electrocatalytic reduction is shown in detail as follows. A piece of TiO<sub>2</sub>/carbon cloth (3 cm  $\times$  2 cm) is combined with a piece of pre-activated Nafion membrane (NRE-211, 3.5 cm  $\times$  2.5 cm) by a hot press process at 140 °C for 0.5 h. The combination is assembled with two pieces of silicone and custom-made graphite bipolar plates (4 cm  $\times$  3 cm) with grooves to fabricate the dual-compartment cell. Next, 20 mL of pure water and NO<sub>2</sub><sup>-</sup> solution (from Zn||NO<sub>2</sub> cell) are recycled in the anode and cathode compartment with the help of two peristaltic pumps, then both reactions are driven by two Zn||NO<sub>2</sub> cells connected in series.

**Characterization of liquid products:**  $NO_2^-$ ,  $NO_3^-$ , and  $NH_4^+$  productions are detected colorimetric detection methods coupled with UV-vis spectroscopy (PerkinElmer

Lambda 2S spectrometer). Detailed detection methods for each kind of ions are shown as following:

### (1) Colorimetric detection of NO<sub>2</sub>-

First, diluted electrolyte (5 mL) is mixed with solution containing HCl (0.10 mL, 2.0 M) and sulfanilamide (10 g·L<sup>-1</sup>). After 10 min, a  $C_{12}H_{14}N_2$ ·2HCl solution (100 µL, 10 mg·mL<sup>-1</sup>) is added into the above solution with gentle shaking. The absorption of NO<sub>2</sub><sup>-</sup> is measured at a wavelength range from 650 to 450 nm after 30 min. The absorbance value of NO<sub>2</sub><sup>-</sup> is obtained at the wavelength of 540 nm. Similar to the aforementioned procedure, the standard calibration curve can be obtained by fitting the absorbance of the different known concentrations of NaNO<sub>2</sub> (0, 4, 8, 12, and 16 µM).

### (2) Colorimetric detection of NH<sub>4</sub><sup>+</sup>

The indophenol blue method is used to detect  $NH_4^+$ . Electrolyte diluted with a  $H_2SO_4$  solution (0.05 M) is used as the test sample. A solution (1.25 mL) consisting of NaOH (0.625 M), salicylic acid (0.36 M), and sodium citrate (0.17 M) is added into test sample (2 mL). A sodium nitroferricyanide solution (150 µL, 10 mg mL<sup>-1</sup>) and NaClO solution (75 µL, available chlorine 4.0 wt %) are further added. After placing the solution in ambient temperature for 2 h, absorption spectra were collected, and the absorbance value at the wavelength of 658 nm is obtained to characterize the  $NH_4^+$  concentration. For standard calibration curve, different  $NH_4^+$  solutions of known concentrations (0, 5,

10, 15, 20  $\mu$ M) are obtained by dissolving (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> into H<sub>2</sub>SO<sub>4</sub> (0.05 M). The obtained absorbance values are then linear fitted for calibration.

#### (3) Colorimetric detection of NO<sub>3</sub>-

The electrolyte is diluted with  $H_2SO_4$  (0.05 M) before testing. Then, a HCl solution (0.10 mL, 1.0 M) is added into a test solution (5 mL). After 15 min, the absorption of  $NO_3^-$  is measured at a wavelength range from 300 to 200 nm. The characteristic absorbance of  $NO_3^-$  is calculated based on the absorbance value difference at 220 and 275 nm. The standard calibration curve is obtained by fitting different known concentrations of NaNO<sub>3</sub> (0, 5, 10, 15, and 20  $\mu$ M).

**Computational Details:** All spin-polarized density functional theory (DFT) calculations are performed by employing the projector-augmented wave method implemented in VASP code.<sup>1, 2</sup> Perdew-Burke-Ernzerhof flavor of generalized gradient approximation is applied for the exchange-correlation functional.<sup>3</sup> The kinetic energy cutoff, energy and force convergence criteria are set as 400 eV,  $10^{-5}$  eV, and 0.05 eV/Å, respectively. The K-points mesh is set as  $3\times3\times1$  for Brillouin zone sampling. DFT-D3 method with Becke-Jonson damping is used to the van der Waals interaction correction.<sup>4, 5</sup> DFT+U scheme is applied to correct the self-interaction error for 3*d* electrons, and U-J values are set as 5.3, 3.32, 6.2, and 7.29 eV for Fe, Co, Ni, and Cu, respectively.<sup>6, 7</sup> A vacuum layer with the thickness of 15 Å is added to avoid the spurious interactions between adjacent cells. The charge density difference distribution (CDDD)  $\Delta\rho$  of adsorbed \*NO<sub>2</sub> is calculated as  $\Delta\rho = \rho(*NO_2) - \rho(*) - \rho(NO_2)$ , where

 $\rho(*NO_2)$ ,  $\rho(*)$ , and  $\rho(NO_2)$  denote charge density distribution of adsorbed \*NO<sub>2</sub>, clean surface, and NO<sub>2</sub> only. The number of charge transfer is estimated by Bader charge analysis.<sup>8</sup> The Gibbs free energy change  $\Delta G$  is calculated by  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ , where  $\Delta E$ ,  $\Delta ZPE$ , and  $\Delta S$  denotes the changes in DFT-calculated total energy, zeropoint energy, and entropic contributions, respectively. The temperature is set as 298K, and the entropy value for HNO<sub>2</sub> (g) is extracted from the NIST database (https://doi.org/10.18434/T4D303). Nørskov's computational hydrogen electrode (CHE) model<sup>9</sup> is used in the calculations. For ORR, a pH correction term  $\Delta G_{pH} =$ kTln10×pH was applied.<sup>9</sup>

**Cost analysis:** Using electricity, each ton of NO<sub>2</sub> gas captured costs ~3600 CNY. Capturing the same amount of NO<sub>2</sub> gas, the Zn||NO<sub>2</sub> electrochemical cells cost ~17000 CNY. It is important to note as well that the electricity generated by the electrochemical cell will be worth ~10000 CNY. So, the cost of the Zn||NO<sub>2</sub> electrochemical cells is ~7000 CNY. Although the use-cost of the Zn||NO<sub>2</sub> electrochemical cells is higher than electricity, we offer an important strategy for the net reduction of NO<sub>2</sub> emissions.



Figure S1. Total and partial density of states (DOS) for NO<sub>2</sub> adsorbed on (a) NiO, (b)

CoO, (c) CuO, and (d) FeO.



Figure S2. Structures of NO<sub>2</sub> adsorption configuration 1 on (a) NiO, (b) CuO, (c) FeO and (d) CuO surfaces. Structures of NO<sub>2</sub> adsorption configuration 2 on (e) NiO, (f) CuO, (g) FeO and (h) CuO surfaces. The charge transfers from NiO, CoO, FeO and CuO surface to  $*NO_2$ .



**Figure S3.** Charge density difference distribution (CDDD) of adsorbed \*NO<sub>2</sub> on (a) NiO, (b) CoO, (c) FeO, and (d) CuO with the isosurface value of 0.005 e Bohr<sup>-3</sup>. The charge transfers from NiO, CoO, FeO, and CuO surface to \*NO<sub>2</sub>.



FeO, CoO, NiO and nano-NiO electrodes at a scan rate of 5 mV·s<sup>-1</sup> in 2M ZnCl<sub>2</sub> aqueous solution and (b) corresponding Tafel plots of these catalysts. (c) NO<sub>2</sub> reduction reaction polarization curves of the nano-NiO electrodes at 5 mV·s<sup>-1</sup> in 2M Zn(OTf)<sub>2</sub>, 2M ZnSO<sub>4</sub>, 6M KOH and 2M ZnCl<sub>2</sub> aqueous solutions and (d) corresponding Tafel plots.



Figure S5. SEM images of nano-NiO.



Figure S6. A. C. impedance to examine ionic conductivity of 2M ZnCl<sub>2</sub> aqueous electrolyte.

The testing system is assembled with sandwich structure. In detail, the ionic conductor is placed between middle of two Ti foils. Resistance of the ionic conductor is investigated by measuring the high-frequency intercept of the semi-circle in the Nyquist plot. Resistivity of the ionic conductor is calculated by the equation:

$$\rho = (R^*A)/d$$

where  $\rho$  is the resistivity of ionic conductor, R is the resistance, A is the area of ionic conductor, and d is the thickness of the ionic conductor respectively.



Figure S7. Full discharged profiles recorded at current densities of 1 mA  $\cdot$  cm<sup>-2</sup> with 3 vol.% NO<sub>2</sub>/Ar and 3 vol.% NO<sub>2</sub>/Air diffused.



Figure S8. XRD patterns of nano-NiO before and after cyclic test.



**Figure S9.** (a) The home-made operando pH detection configuration. (b) Dischargecharge curves of first cycle recorded at 2 mA·cm<sup>-2</sup> over 2 h for one cycle, and corresponding discharged/charged times dependence of pH changes during cycling.



Figure S10. Pie chart depicting the optimal weight distribution in cell component at

553.2 Wh·kg<sup>-1</sup><sub>(cell)</sub> specific energy.



Figure S11. The optical photo of the  $Zn||NO_2$  pouch cell to assess its total weight.



Figure S12. (a) The UV-Vis absorption spectra and (b) standard calibration curve for

different concentrations of NO<sub>2</sub><sup>-</sup> ions.



Figure S13. The UV-vis absorption spectra to determine the yield of  $NO_2^-$  by aqueous  $Zn||NO_2$  electrochemical cell (a) at different current density of 0.2, 0.5, 1, 2, 5, 10 mA·cm<sup>-2</sup>, and over different discharging time of 1, 2, 4, 6 h at 2 mA·cm<sup>-2</sup>.



**Figure S14.** Comparison of Gibbs free energy diagrams for NO<sub>2</sub><sup>-</sup>-\*NO<sub>2</sub> conversion and ORR (pH=5, 7) on NiO.



**Figure S15**. High-resolution Ni 2*p* and O 1*s* spectra of nano-NiO at (a, b) initial, (c, d) discharged and (e, f) charged states. Ni 2*p* spectra at (a) initial, (c) discharged and (e) charged states. O 1*s* spectra at (b) initial, (d) discharged and (f) charged states.



Figure S16. (a) The UV-Vis absorption spectra and (b) concentration-absorbance standard calibration curve using the indophenol blue method for different concentrations of  $\rm NH_4^+$  ions.



**Figure S17**. The UV-vis absorption spectra to determine the yield of  $NH_4^+$  by selfpower conversion system over different discharging time of 1, 2, 4, 8 h.

# References

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