

Oxidation of Carbon Monoxide in Basic Solution Catalyzed by Nickel Cyano Carbonyls at Ambient Condition and the Prototype of a CO-Powered Alkaline Flow Battery Type Fuel Cell

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Supplementary Information

Experimental:

All experiments were performed under carbon monoxide gas using standard Schlenk techniques unless stated otherwise. The starting materials NaCN, PPh₄Cl, BzPPh₃Cl, Et₄NCN, NiCl₂·6H₂O, NaOH, and Ba(OH)₂ were purchased from Acros or Fisher and used as received. Carbon Monoxide (99.5%) were purchased through Techair. Dichloromethane and hexanes were purchased from Acros and used without further treatment. PPh₄CN were prepared according to literature methods.^{S1} Elemental Analyses were performed by Robertson Microлит Laboratories.

Preparation of PPh₄[Ni⁰(CN)(CO)₃].0.25CH₂Cl₂: To a green solution of NiCl₂·6H₂O (238 mg, 1.00 mmol) in 30 mL H₂O under 1 atm CO, a solution of NaCN (49 mg, 1.0 mmol) and NaOH (800mg, 20mmol, excess) in 10 mL H₂O was added. The mixture was stirred under CO for 24 hours to give a clear colorless solution. A solution of PPh₄Cl (263 mg, 0.70 mmol) in 30 mL CH₂Cl₂ was added to the colorless aqueous solution and stirred under 1 atm CO for another hour. The CH₂Cl₂ layer was collected under 1 atm CO, dried under vacuum to afford 313 mg (59% yield) PPh₄[Ni⁰(CN)(CO)₃] as off-white solid. Elemental analysis calculated for NiC_{28.25}H_{20.5}NO₃PCl_{0.5}: C 64.10%, N 2.65%, H 3.90%; found: C 64.11%, N 2.58%, H 4.15%. IR (CH₂Cl₂): 1966cm⁻¹ (CO, vs), 2049cm⁻¹ (CO, m), 2098cm⁻¹ (CN, w). IR (H₂O): 1989cm⁻¹ (CO, vs), 2056cm⁻¹ (CO, m), 2123cm⁻¹ (CN, w).

Preparation of BzPPh₃[Ni⁰(CN)(CO)₃].CH₂Cl₂: The BzPPh₃⁺ salt of Ni⁰(CN)(CO)₃⁻ was prepared similarly except BzPPh₃Cl (272mg, 0.70mmol) was used. The amount of BzPPh₃[Ni⁰(CN)(CO)₃].CH₂Cl₂ isolated was 340mg (56% yield).

Preparation of (PPh₄)₂[Ni⁰(CN)₂(CO)₂]: To a colorless solution of PPh₄[Ni⁰(CN)(CO)₃].0.25CH₂Cl₂ (120 mg, 0.23 mmol) in 5 mL CH₂Cl₂, a solution of PPh₄CN (83 mg, 0.23 mmol) in 2 mL CH₂Cl₂ was added and the resulting solution was stirred for 2 hours. 20 mL hexane was added to the reaction mixture and pale green crystalline material was precipitated. The light green crystalline material was filtered and rinsed three times by 3 mL hexane and dried in vacuo to afford 105 mg (55% yield) (PPh₄)₂[Ni⁰(CN)₂(CO)₂] as light green powder. IR (CH₂Cl₂): 1866cm⁻¹ (CO, s), 1942cm⁻¹ (CO, s), 2063cm⁻¹ (CN, w). IR (H₂O): 1922cm⁻¹ (CO, s), 1980cm⁻¹ (CO, s), 2077cm⁻¹ (CN, w).

Crystallization:

Single crystals of BzPPh₃[Ni⁰(CN)(CO)₃].CH₂Cl₂ were grown by carefully covering hexanes on a CH₂Cl₂ solution containing BzPPh₃[Ni⁰(CN)(CO)₃] and kept at -20°C for 3 days. The single crystals of (Et₄N)₂[Ni⁰(CN)₂(CO)₂] were grown by carefully covering hexanes on a CH₂Cl₂ solution containing 1:1 ratio of PPh₄[Ni⁰(CN)(CO)₃] and Et₄NCN and kept at -20°C for 2 weeks.

Single crystal X-ray diffraction:

Single crystal data were collected in a Bruker SMART instrument with APEXII CCD area detector using graphite-monochromated and 0.5 mm-MonoCap-collimated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected and analyzed by the APEX2 software. (APEX2 (version 2012.10), Program for Bruker CCD X-ray Diffractometer Control, Bruker AXS Inc., Madison, WI, 2012.)

Kinetics measurement:

Gas volume change was measured in a setup shown in **Figure S3**. 5.9mM Ni⁰(CN)(CO)₃⁻, 1.0M NaOH, 17mL H₂O, 4.4mL O₂ and 58.3mL CO were delivered to the reaction vessels at 25°C. Gas volumes were recorded periodically over 12 hours. The amount of O₂ consumed was calculated as one third of the gas

volume decrease and the amount of CO consumed was calculated as two thirds of the gas volume decrease.

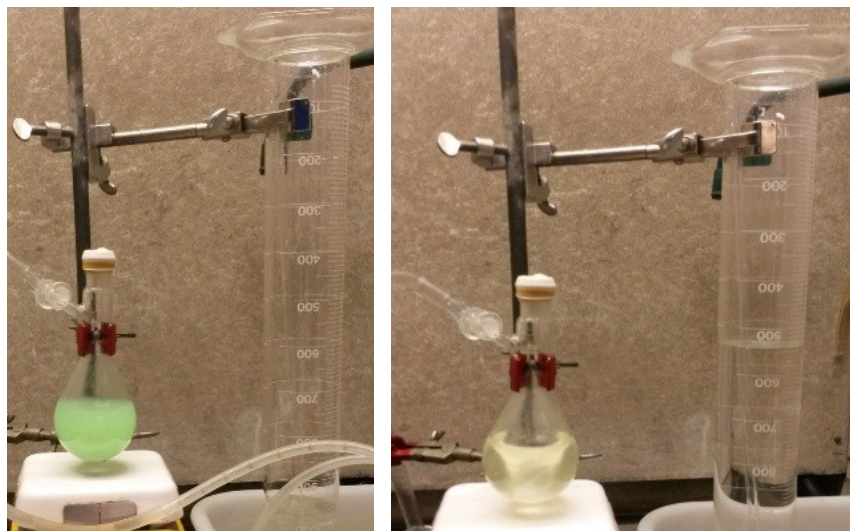


Figure S1: The reaction setup of 5mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 5mmol NaCN and 50mmol NaOH in 50mL H_2O under 1 atm CO at the beginning (left) and end (right) of the reaction. A 1000mL graduated cylinder was used to measure gas volume change.

Cyclic Voltagram of $\text{Ni}^0(\text{CN})(\text{CO})_3^-$

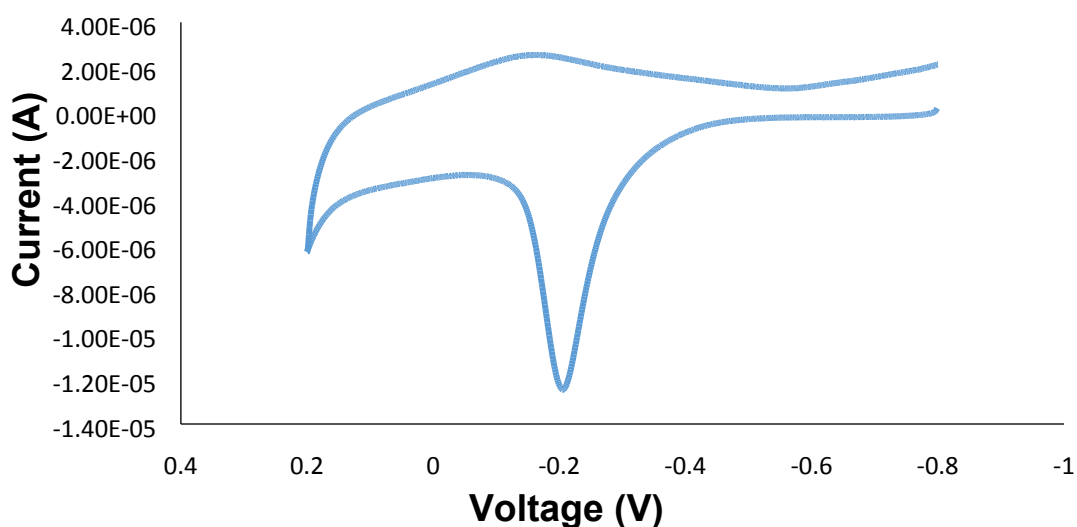


Figure S2: Cyclic Voltagram of $\text{Ni}^0(\text{CN})(\text{CN})_3^-$ (2mM) in 0.13M NaOH solution. Scan started from -800mV to 200mV and back to -800mV. Scan rate was 100mV per second. An Ag/AgCl electrode was used as reference electrode, a platinum disk electrode was used as working electrode and a platinum wire was used as auxillary electrode. Cyclic Voltagram was recorded using a BASi 100 electrochemical workstation.



Figure S3: Gas volume change measurement setup. (graduated pipet immersed in mineral oil)

Table S1: Gas volume reading over 12 hours and the corresponding O₂ partial pressure.

Time (min)	Reading (mL)	Volume of CO (mL)	Volume of O ₂ (mL)	Total Volume (mL)	O ₂ Partial Pressure (atm)	Ln(PO ₂)
0	0.3	58.3	4.4	62.7	0.0702	-2.66
14	1.2	57.7	4.1	61.8	0.0663	-2.71
81	4.5	55.5	3.0	58.5	0.0513	-2.97
101	5.3	55.0	2.7	57.7	0.0474	-3.05
129	6.3	54.3	2.4	56.7	0.0423	-3.16
174	7.6	53.4	2.0	55.4	0.0355	-3.34
218	8.6	52.8	1.6	54.4	0.0300	-3.51
287	9.7	52.0	1.3	53.3	0.0238	-3.74
327	10.2	51.7	1.1	52.8	0.0208	-3.87
404	11.1	51.1	0.8	51.9	0.0154	-4.17
508	12.0	50.5	0.5	51.0	0.0098	-4.62
699	12.8	50.0	0.2	50.2	0.0046	-5.37

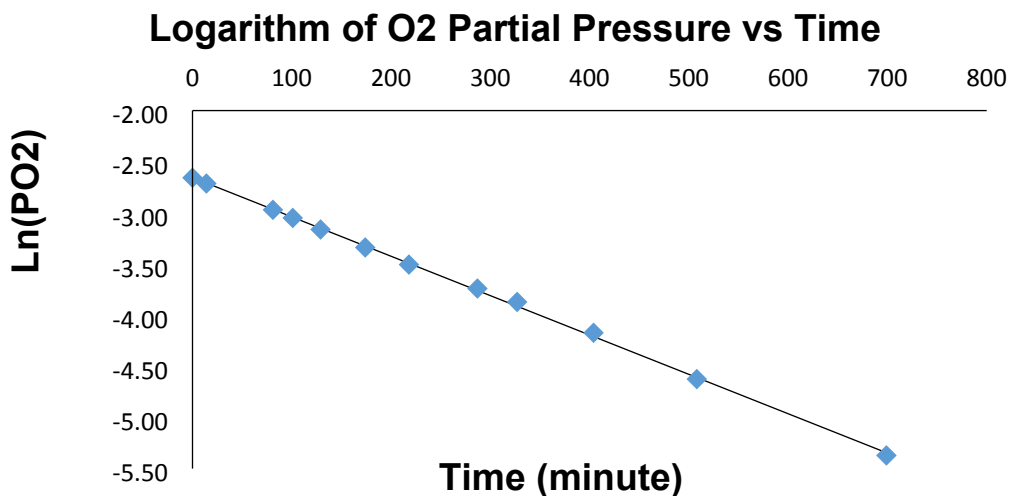


Figure S4: The oxidation of CO by O₂ in alkaline solution is first order on O₂ partial pressure.

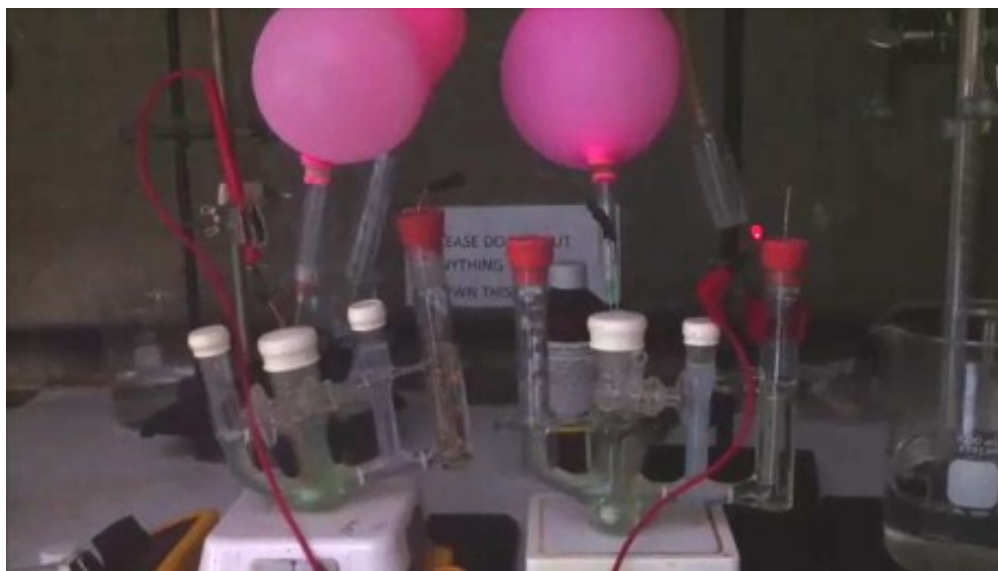


Figure S5: The setup of two primitive CO-powered fuel cells. CO was kept inside the balloon over the solution of 5mM Ni⁰(CN)(CO)₃⁻ and 1.0M NaOH. NaOCl (6%) was used as the oxidant. Agar gel containing 1.0M NaCl was used as salt bridge. Platinum net (right cell) and copper wire (left cell) were used as electrode. The voltages of the two cells were 1.1V. Connecting these two primitive CO-powered fuel cells has successfully lighted a LED light (requires 2.0V voltage and 1.0mA current) for more than 7 days.

Reference:

S1. S. Andreades, E. W. Zahnow, *J. Am. Chem. Soc.* **1969**, *91*, 4181–4190.