

Electronic Supplementary Information

A direct urea fuel cell – power from fertiliser and waste

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Methods

In our experiments, three alkaline membrane fuel cells were constructed based on alkaline membrane electrolytes.

Preparation of alkaline membrane:

The composite membrane was made of a commercial strong anion exchange resin (AER) (Amberlite IRA78, hydroxide form, Aldrich) and polyvinyl alcohol (PVA), (MW 50,000, Aldrich) at a weight ratio of 60/40. PVA was dissolved in de-ionised water and stirred at 85°C for two hours to form a gel. After the gel was cooled down to room temperature, the commercial resin was crushed into powder in an agate mortar first then mixed with PVA gel, cast on a glass plate and dried in a vacuum oven at room temperature to form an AER-PVA blend membrane.

Cell A:

Membrane electrode assemblies (MEAs) for fuel cells measurements were fabricated with a Pt/C anodes and AER-PVA blend membrane. Pt/C (30wt%, E-TEK) was used as anode at a loading of 0.6mg/cm². Carbon papers (Toray 090, water-proofed for anode, plain for cathode, E-TEK) were used as current collectors.

Cell B:

Nano-sized nickel was prepared from NiCl₂·6H₂O (Alfa, 99.3%), CrCl₃·6H₂O (Alfa, 99.5%) and KBH₄ (Alfa, 98%)(*l*). Some trisodium citrate was added into the NiCl₂ aqueous solution in order to obtain nano-sized nickel particles (primary particle size ~ 2 nm). The nickel was dried at room temperature only. The as-prepared nano-sized nickel was mixed with carbon (Carbot Vulcan XC-72R) at a 50/50 weight ratio to be used as anode. Nano-sized silver was prepared by a similar method to that for preparation of nickel using AgNO₃ (Alfa, 99.9+%) as the precursor. The silver was mixed with carbon (Cabot Vulcan XC-72R) by a weight ratio of 50/50. The loading of Ag at cathode and Ni at anode were ~20mg/cm². The other parameters are the same as in Cell A.

Cell C:

The same Ni/C anode as in Cell B was used. 20wt% MnO₂/C was prepared from KMnO₄ (Avacado, 99%), Mn(CH₃COO)₂·4H₂O (Aldrich, 99.99%) and carbon (Cabot

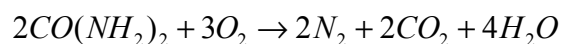
Vulcan XC-72R) by a co-precipitation method (2). The loading of MnO₂ at cathode and Ni at anode were ~ 20mg/cm². The other parameters are the same as in Cell A.

Fuel cell performance:

Urea solution at different concentrations was prepared from urea (Alfa Aesar, ACS grade) and de-ionised water. Commercial AdBlue (32.5% urea solution) supplied by a local garage. Human urine were also used as fuel for fuel cell tests. Urea solutions were pumped into the anode side by a peristaltic pump (Watson Marlow 323D). Wet air was supplied to the cathode by passing air through room temperature water. The cell area was 1cm². A Solartron 1287A electrochemical interface coupled with a CorrWare/CorrView software was used to measure the fuel cell performance.

Thermodynamic parameters for calculation of theoretical open circuit voltage (OCV) and efficiency.

Reaction:



Compounds	CO(NH ₂) ₂ (c)	O ₂ (g)	N ₂ (g)	CO ₂ (g)	H ₂ O(l)
ΔG_f^0 (kcal/mol)	-47.19	0	0	-94.254	-56.687
ΔH_f^0 (kcal/mol)	-79.71	0	0	-94.051	-68.315
S^0 (cal/K·mol)	25.00	49.003	45.77	51.06	16.71
C_p^0 (cal/K·mol)	22.26	7.016	6.961	8.87	17.995

* Data from CRC Handbook of Chemistry and Physics, Editor: R. C. Weast. 63th Edition. CRC Press, Inc. Boca Raton, Florida. 1983.

Thermodynamic value of urea dissolution in water:

Compounds	CO(NH ₂) ₂ dissolution
ΔG_f^0 (kJ/mol)	-6.86
ΔH_f^0 (kJ/mol)	-14
S^0 (J/K·mol)	69.5
C_p^0 (J/K·mol)	4.31 [§]

* Data from:

Charles A. Liberko and Stephanie Terry, A Simplified Method for Measuring the Entropy Change of Urea Dissolution, *J. Chem. Edu.*, **78**, 1087-1088 (2001).

[§] Assuming heat capacity of dilute urea solution equals to that of water.

During the estimation, it has been assumed that thermal capacitances of compounds do not change in the temperature range. In a real situation, they do change but will have little contribution to free energy change.

Table S1 Comparison of energy density of different materials.

Compounds	Density (g cm ⁻³)	Gravimetric H ₂ density (% H ₂)	Volumetric H ₂ density (kg H ₂ l ⁻¹)	Energy density (MJ l ⁻¹)
Gaseous H ₂	0.00008988	100	0.00008988	0.01079
Compressed H ₂ (700bar)	0.039	100	0.039	5.6
Liquid H ₂	0.071	100	0.071	10.1
NH ₄ OH (28%)	0.89	2.4	0.021	1.17
Liquid NH ₃	0.747	17.6	0.13	12.6
CO(NH ₂) ₂	1.335	10.07*	0.134	16.9

* Effective density including hydrogen from water molecules for hydrolysis.

Sources: R. K. Graupner “Guanidine – Safe, Clean, and Flexible”

<http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2006/OregonSustainableEnergy.pdf>

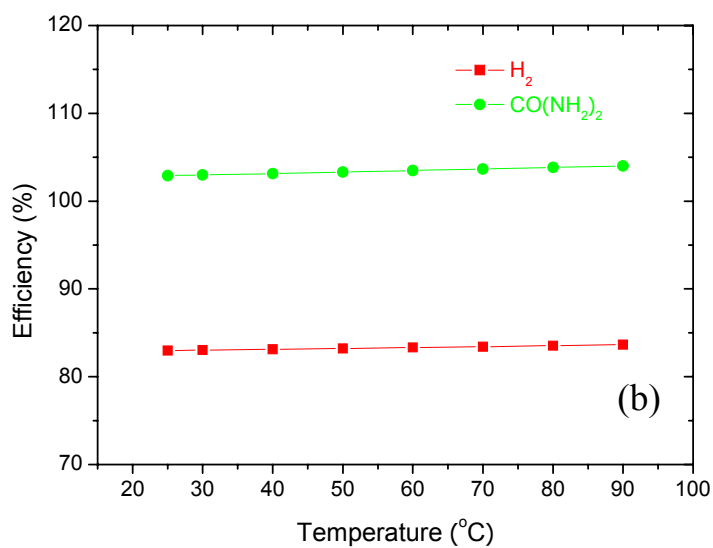
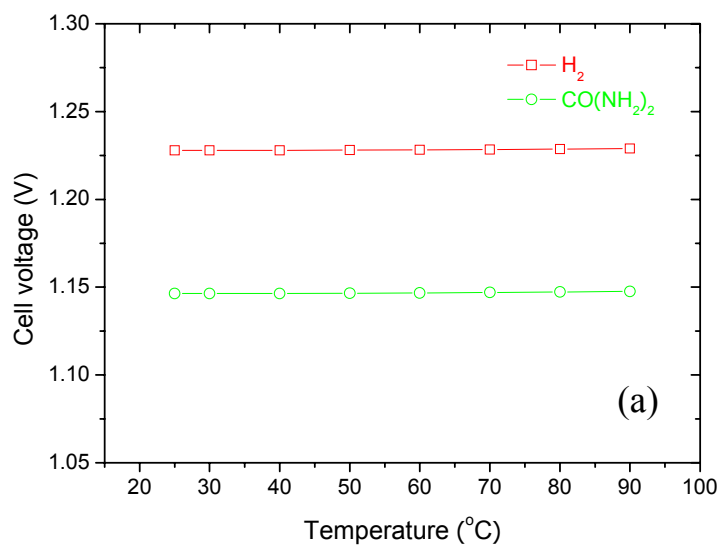


Fig. S1 (a), Theoretical cell voltage of fuel cells, H₂ (□) and CO(NH₂)₂ (○). **(b)**, efficiency of fuel cells H₂ (■), CO(NH₂)₂ (●).

References

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- 2 Xu, C. J., Li, B. H., Du, H. D., Kang, F. Y. & Zeng Y. Q. Electrochemical properties of nanosized hydrous manganese dioxide synthesized by a self-reacting micromulsion method. *J. Power Sources*, 2008, **180**, 664 – 670.