A direct urea fuel cell – power from fertiliser and waste†

Rong Lan,[a] Shanwen Tao[*a] and John T. S. Irvine[b]

For the first time, a working direct urea and direct urine fuel cell has been developed to generate electricity directly from urea or urine.

Urea is a non-toxic low-cost industrial product which is widely used as fertiliser. Urea can be synthesised from ammonia produced from natural gas or coal in large quantities.[1] The conversion of natural gas to ammonia has energy efficiency about 60–65%[2] which is just slightly lower than the production of hydrogen from reforming of natural gas (65–75%).[3] The energy conversion from natural gas to urea is about 55%.[4,5] AdBlue, a 32.5% urea solution developed by Europe's AdBlue urea-selective catalytic reduction (SCR) project is available world-wide to remove NO$_x$ generated by diesel powered vehicles. Despite the high availability of urea, there is currently no technology able to generate electricity from urea or AdBlue.

During the industrial synthesis of urea, a large amount of waste water with varying urea concentrations is formed.[6] A large amount of human or animal urine, containing about 2–2.5 wt% urea, is produced everyday. There is a significant level of urea in municipal waste water but the available denitrification technologies are expensive and inefficient.[7] Recently it has been reported that hydrogen can be generated from urine or urea-rich waste water through electrolysis.[8] However, to generate electricity directly from urine or urea-rich waste water would be more efficient.

The energy density of urea is higher than compressed or liquid hydrogen which makes it a potential energy carrier (Table S1†).[5] Unlike hydrogen, urea is a solid powder and is easily stored and transported. Urea effectively contains 10 wt% hydrogen and is a potential indirect hydrogen storage material. Pure hydrogen remains a good energy vector; however, on-board hydrogen storage

[a]Department of Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK. E-mail: s.tao@hw.ac.uk; Tel: +44 131 451 4299
[b]School of Chemistry, University of St Andrews, St Andrews, Fife, KY16 9ST, UK
† Electronic supplementary information (ESI) available: Preparation of alkaline membrane and fuel cell performance. See DOI: 10.1039/b924786f

for transport applications is not yet available.[9] Implementation of hydrogen economy would be beneficial. For the hydrogen economy to be viable, new hydrogen delivery infrastructures are required while for urea a delivery system is already in place.

Fuel cells are devices which can directly convert chemical energy into electricity with high efficiency.[10–16] Urea fuel cells would be an efficient method of generating power from fertiliser urea, urine and waste water. Potentially, urea fuel cells can use urine as the fuel. In this case, urine, a product of human/animal excretion, is not a waste, but an energy source (Fig. 1). If an adult human produces 1.5 L of urine containing 2 wt% urea, it would produce 11 kg of urea each year which is equivalent to the energy in 18 kg of liquid hydrogen that can be used to drive a car for 2700 km if powered by a urea fuel cell.[17]

The hydrolysis of urea will produce ammonia (reaction 1), a weak base, which is not compatible with the acidic Nafion® membrane and therefore conventional proton exchange membrane fuel cells (PEMFCs) can not be operated on urea fuels.[2] A considerable amount of papers concentrate on the small-scale reformation of ammonia in order to produce hydrogen[18–20] but a direct use of ammonia or ammonia produced from urea would be more cost effective.

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (1)$$

For conventional alkaline fuel cells using 6M KOH solution as the electrolyte, the reaction between CO$_2$ from the air and KOH remains a typical problem.[21] CO$_2$ is produced in a urea fuel cell therefore urea is not a suitable fuel for conventional alkaline fuel cells. Alkaline
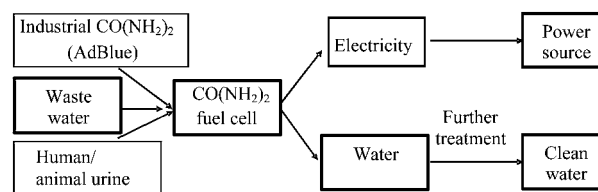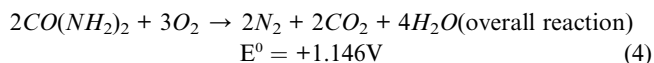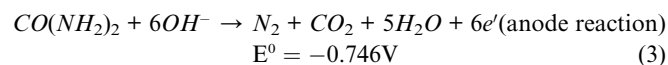

Fig. 1 Schematic diagram of applications of urea fuel cells.

Broader context

Urea is a non-toxic chemical and is widely used as an inexpensive fertiliser. Urea is also a major component in waste water and human/animal urine. Urea has a high energy density (two times higher than compressed hydrogen at 700 bar and ~70% higher than liquid hydrogen), and is therefore useful as an alternative energy vector and an indirect hydrogen storage material. AdBlue, a urea solution used for removal of NO$_x$ in diesel powered vehicles is widely available throughout the world using existing infrastructure. Here, for the first time, we demonstrate the operation of direct urea and direct urine fuel cells. These fuel cells are based on an alkaline membrane electrolyte and non-noble catalysts. Operation of a urea/urine fuel cell will make it possible to convert the chemical energy in urea/urine into electricity. This type of fuel cell has the potential to be used for portable, transport and other applications to generate power from urine, waste water, fertiliser urea and commercial urea such as AdBlue.

---

membrane fuel cells have attracted the attention of researchers in the fuel cell community.[22–26] Currently developed alkaline membranes are mainly based on organic quaternary ammonium hydroxide linked to polymers.[17,19] It has been reported that this type of alkaline membrane is compatible with CO_2 and introduction of CO_2 at the cathode can improve the cell performance,[27] therefore air can be directly used in a fuel cell without removal of CO_2. Low-cost non-precious catalysts (such as nickel, silver, MnO_2) can be used in alkaline membrane fuel cells because they are stable in an alkaline environment.[28,29] Currently there is a scarcity of alkaline membranes on the market. The preparation of a simple blend alkaline membrane based on available mass-produced commercial precursors (anion exchange resin (AER) and polyvinyl alcohol (PVA)) is presented in this report (see ESI† for details).

The operating mechanism of a direct urea fuel cell using an alkaline membrane electrolyte is described below.

$$O_2 + 2H_2O + 4e' \rightarrow 4OH^- \text{(cathode reaction) } E^0 = +0.40V \quad (2)$$

$$CO(NH_2)_2 + 6OH^- \rightarrow N_2 + CO_2 + 5H_2O + 6e' \text{(anode reaction)}$$
$$E^0 = -0.746V \quad (3)$$

$$2CO(NH_2)_2 + 3O_2 \rightarrow 2N_2 + 2CO_2 + 4H_2O \text{(overall reaction)}$$
$$E^0 = +1.146V \quad (4)$$

The theoretical open circuit voltage (OCV) and the efficiency of hydrogen and urea fuel cells at a temperature range of 25–90 °C have been estimated through available thermodynamic data (Fig. S1†). The theoretical OCV of a urea/O_2 fuel cell is 1.146 V at room temperature, slightly lower than the 1.23 V for a H_2/O_2 fuel cell. However, the theoretical efficiency of a urea fuel cell is 102.9% at room temperature which is about 20% higher than that of a H_2/O_2

fuel cell (83.0% at room temperature). The high theoretical efficiency of a urea fuel cell is due to the positive entropy change of reaction (4). When the efficiency is over 100%, physically, the fuel cell absorbs heat from ambiance and converts it completely into electricity together with the chemical energy of the reactants alleviating the heat exchange issue as in the case of conventional hydrogen PEMFCs.[30]

Urea fuel cells, using an alkaline membrane, were investigated using either Pt/C as both electrodes (Cell A); a non-noble Ni/C anode and an Ag/C cathode (Cell B) or a Ni/C anode and a MnO_2/C cathode (Cell C).

The urea/air fuel cell performance for Cell A is shown in Fig. 2a. An OCV of 0.5 V was observed for urea/air when a 1M urea aqueous solution was used as the fuel. The lower OCV at room temperature indicated that the catalytic activity of Pt was not high enough at room temperature causing a polarisation loss on both electrodes. The OCV of the cell decreased when 3M and 5M urea solutions were used. The performance of a dilute urea solution has also shown to be higher, indicating a high concentration is not beneficial under the operating conditions. In order to confirm this phenomenon, a different urea source was used in the fuel cell.

AdBlue, a commercial 32.5% (~5M) urea aqueous solution was also tested. Higher OCVs were observed for comparable urea concentrations when various concentrations of AdBlue were used as the fuel (Fig. 2b). The maximum power density was 0.3 mW/cm² for AdBlue, higher than the 0.2 mW/cm² achieved when 5M urea was used (Fig. 2a). High power density benefits from the relative higher voltage although the maximum current density is slightly lower. These experiments indicate that the trace amounts of impurities in different sources of urea do affect fuel cell performances calling for further investigations to be carried out. When AdBlue solutions at
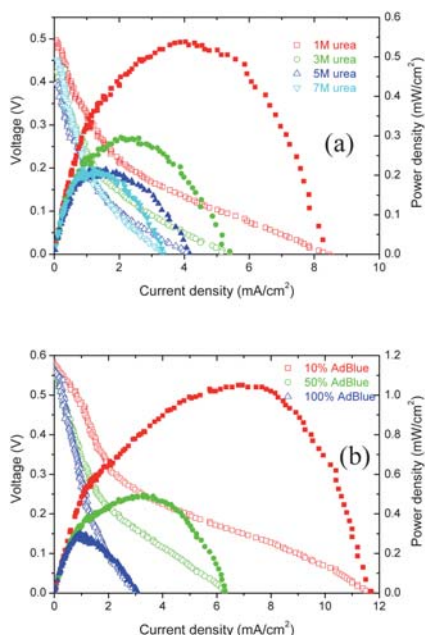

Fig. 2 (a) Fuel cell performance plots of Cell A using different concentrations of urea aqueous solution as the fuel. (b) Fuel cell performance plots of Cell A using different concentrations of AdBlue as the fuel. At room temperature, Pt/C as both the anode and cathode; an anion-exchange resin–PVA membrane was used as electrolyte.
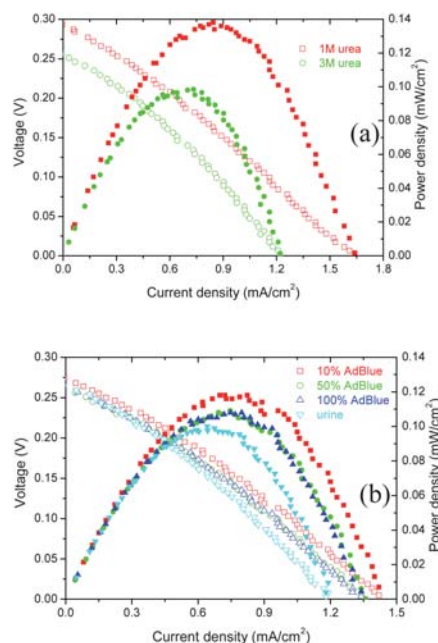

Fig. 3 (a) Fuel cell performance plots of Cell B using different concentrations of urea aqueous solution as the fuel at room temperature. (b) Fuel cell performance plots of Cell B using different concentrations of AdBlue and urine as the fuel at room temperature. Ni/C as anode and Ag/C as cathode and an anion-exchange resin–PVA membrane used as electrolyte.
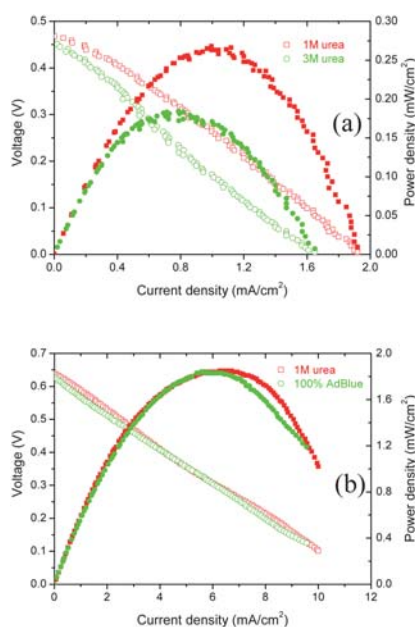
Fig. 4 (a), Fuel cell performance plots of Cell C using different concentrations of urea aqueous solution as the fuel at room temperature. (b) Fuel cell performance plots of Cell C using AdBlue and a 1M urea solution as the fuel at 50 °C. Ni/C as anode, MnO$_2$/C as cathode; an anion-exchange resin–PVA membrane was used as electrolyte.

different concentrations (by adding de-ionised water) were used as the fuel, the same trends were observed as for the urea solutions; the dilute AdBlue solutions exhibited better performance than pure AbBlue. The 10% AdBlue solution exhibits the highest current and power densities. As a molecule of urea is relatively large, the high concentration of urea may cause slow diffusion at the anode thus increasing the polarisation loss. Cross-flow of urea or the slow hydrolysis of urea to produce intermediate ammonia (reaction (1)) are other possibilities. Possible poisoning of the Pt electrode by CO can not be ruled out although similar trends were observed when a nickel anode was used (Figs. 3a and 4a). The urea concentration of the 10% AdBlue solution has the same level of urea as urine, indicating that urine could be a good fuel for our fuel cell.

One of the advantages of alkaline membrane fuel cells is that low-cost catalysts can be used as electrodes. Another two cells were constructed using Ni/C as anode, Ag/C or MnO$_2$/C as cathode as described in the ESI†. For Cell B, at room temperature, an OCV of 0.29 V was observed when a 1M urea solution was used as fuel, which is lower than the 0.5 V achieved when Pt/C was used at both electrodes. The power density is about 75% lower than in Cell A indicating Pt is still a better catalyst for urea fuel cells. Performance was again lowered when a 3M urea solution was used (Fig. 3a). AdBlue at different concentrations was also used as the fuel. As observed in Cell A, dilute AdBlue solutions exhibit better performance (Fig. 3b). The performance of human urine was also tested as fuel for Cell B. It was found that the performance is just slightly lower than that of AdBlue but comparable with a 3M urea solution. This experiment indicates that urine can be used for fuel cells.

When MnO$_2$/C was used as the cathode, the OCV of the cell was higher than that of the cell when Ag/C was used (Fig. 4a). The power density is also slightly higher which benefits from the relatively higher OCV.

In general, the catalytic activity on electrodes increases at elevated temperatures. This is confirmed by the higher OCV and power density when the operating temperature of Cell C was increased to 50 °C. A maximum power density of 1.7 mW/cm^2 has been achieved using a 1M urea solution as the fuel (Fig. 4b). This is six times higher than that of the cell operating at room temperature (Fig. 4a). Performance of alkaline membrane fuel cells based on low-cost catalysts at 50 °C is better than those using Pt electrodes at room temperature. Higher operating temperature is desired when low-cost catalysts are used in urea fuel cells. The performance of AdBlue is almost identical to the 1M urea solution indicating that AdBlue can also be used as fuel for Cell C based on low-cost catalysts.

This work has demonstrated the direct urea/urine fuel cells based on low-cost alkaline membrane electrolytes and non-noble catalysts such as nickel, silver and MnO$_2$. Wet air was used as an oxidant at the cathode. For stationary power generation from urine or waste water, high power density is not a stringent requirement as long as the cost of the cell itself is low. High power can be achieved by using an enlarged fuel cell area or increased numbers of single cells. However, for transport applications, higher power density is required. It should be noted that the development of low temperature direct urea fuel cells based on inexpensive materials is still at an early stage. With further optimization, hopefully the power density will be significantly improved. Urea fuel cells have the potential to be used for stationary, portable, transport, space shuttles, submarines and other applications. They can also be used to clean up municipal waste water and generate electricity. Based on this work, it is possible to develop renewable and sustainable urine fuel cells.

Acknowledgements

Notes and references

1 P. Heffer and M. Prud'homme, *Turkish J. Agric. Forestry*, 2008, **32**, 159.
2 G. Thomas, G. Parks, Potential Roles of Ammonia in a Hydrogen Economy, (US DOE report), 2006, http://www.hydrogen.energy.gov/pdfs/nh3_paper.pdf.
3 T. N. Veziroglu, S. Y. Zaginaichenko, D. V. Schur, B. Baranowski, A. P. Shpak and V. V. Skorokhod, in Hydrogen Materials Science and Chemistry of Carbon Nanomaterials, *NATO Science Series II: Mathematics Physics and Chemistry*, Springer Netherlands, ISBN 978-1-4020-2668-3. DOI: 10.1007/1-4020-2669-2. 2006, pp. 467–472.
4 J. Parikh, C. R. D. Biswas, C. Singh and V. Singh, *Energy*, 2009, **34**, 954.
5 R. K. Graupner, *Guanidine – Safe, Clean, and Flexible*, http://www.energy.iastate.edu/Renewable/ammonia/ammonia/2006/OregonSustainableEnergy.pdf.
6 W. Simka, J. Piotrowski, A. Robak and G. Nawrat, *J. Appl. Electrochem.*, 2009, **39**, 1137.
7 D. C. Bouchard, M. K. Willams and R. Y. Surampalli, *J. Am. Water Works Assoc.*, 1992, **84**, 85.
8 B. K. Boggs, R. L. King and G. G. Botte, *Chem. Commun.*, 2009, **32**, 4859.
9 L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353.
10 B. C. H. Steele and A. Heinzel, *Nature*, 2001, **414**, 345.
11 S. D. Park, J. M. Vohs and R. J. Gorte, *Nature*, 2000, **404**, 265.
12 S. M. Haile, D. A. Boysen, C. R. I. Chisholm and R. B. Merle, *Nature*, 2001, **410**, 910.
13 S. W. Tao and J. T. S. Irvine, *Nat. Mater.*, 2003, **2**, 320.
14 S. W. Tao, J. T. S. Irvine and J. A. Kilner, *Adv. Mater.*, 2005, **17**, 1734.
15 J. C. Ruiz-Morales, J. Canales-Vazquez, C. Savaniu, D. Marrero-Lopez, W. Z. Zhou and J. T. S. Irvine, *Nature*, 2006, **439**, 568.
16 R. Bashyam and P. Zelenay, *Nature*, 2006, **443**, 63.

17 B. Sørensen, *Hydrogen and Fuel Cells*, Elsevier Academic Press, 2005. p 217.
18 V. Prasad, A. M. Karim, A. Arya and D. G. Vlachos, *Ind. Eng. Chem. Res.*, 2009, **48**, 5255.
19 A. M. Karim, M. Ayman, V. Prasad, G. Mpourmpakis, W. W. Lonergan, A. I. Frenkel, J. G. G. Chen and D. G. Vlachos, *J. Am. Chem. Soc.*, 2009, **131**, 12230.
20 B. K. Boggs and G. G. Botte, *J. Power Sources*, 2009, **192**, 573.
21 A. Tewari, V. Sambhy, M. Urquidi Macdonald and A. Sen, *J. Power Sources*, 2006, **153**, 1.
22 J. R. Varcoe, R. C. T. Slade, E. L. Yee, S. D. Poynton, D. J. Driscoll and D. C. Apperley, *Chem. Mater.*, 2007, **19**, 2686.
23 L. Wu, T. W. Xu and D. X. Wu, *J. Membr. Sci.*, 2008, **310**, 577.
24 K. Scott, E. Yu, G. Vlachogiannopoulos and M. N. Shivare, *J. Power Sources*, 2008, **175**, 452.
25 J.-S. Park, S.-H. Park, S.-D. Yim, Y.-G. Yoon, W.-Y. Lee and C.-S. Kim, *J. Power Sources*, 2008, **178**, 620.
26 S. Ewing, R. Lan, X. X. Xu and S. W. Tao, *Fuel Cells*, 2009, DOI: 10.1002/fuce.200900102, in press.
27 M. Unlu, J. F. Zhou and P. A. Kohl, *Electrochem. Solid-State Lett.*, 2009, **12**, B27.
28 A. Verma and S. Basu, *J. Power Sources*, 2007, **168**, 200.
29 S. F. Lu, J. Pan, A. B. Huang, L. Zhuang and J. T. Lu, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 20611.
30 S. G. Kandlikar and Z. J. Lu, *Appl. Therm. Eng.*, 2009, **29**, 1276.

This journal is © The Royal Society of Chemistry 2010

Energy Environ. Sci., 2010, **3**, 438–441 | 441