

**Original citation:**

Xu, Weijun, Wu, Zucheng and Tao, Shanwen. (2016) Urea based fuel cells and electrocatalysts for urea oxidation. Energy Technology . doi: 10.1002/ente.201600185

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# Urea based fuel cells and electrocatalysts for urea oxidation

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**Abstract:** Urea is a new member of hydrogen-storage materials for low-temperature fuel cells. It avoids issues of toxicity and safety compared to ammonia and hydrazine. The main limitation of urea fuel cells is the relative low power density due to the sluggish anode reaction. Rapid advances in nano-catalysts for urea electrooxidation have been achieved in order to lower overpotential and improve activity. Urine, as a natural resource of urea, is also an environmental pollutant. Most technologies of treating urine with self-generation electricity are based on microbial fuel cells. However, microbes are only able to utilize the organic substrates rather than urea in urine. Chemical fuel cells in contrast directly oxidize urea to nitrogen gas and removed from urine. Thus urea fuel cells have been used as an alternative method to treat urine. In the paper, the progress in urea based fuel cells and electrocatalysts for urea oxidation is reviewed.

## 1. Introduction

The fast increase in electrical power consumption and environmental issues have driven researchers to seek for efficient, durable and green energy systems in the recent decades. Among various electrochemical energy storage and conversion methods, low-temperature fuel cells have attracted great attentions. As shown in Fig.1, conventional metallic batteries and redox flow batteries are limited in both mass and volumetric energy density of several  $10^1$  and up to  $10^2$  Wh  $\text{kg}^{-1}$  or Wh  $\text{L}^{-1}$ . On the contrary, fuel cells usually have high energy density, is normally in the order of  $10^3$  Wh  $\text{kg}^{-1}$  or Wh  $\text{L}^{-1}$ . According to this value, by using fuel cells with 40% electric efficiency, 200 g of ethanol will be sufficient to support a laptop (25 W) for 24 hours. The representative achievement is proton exchange membrane fuel cells (PEMFC) using  $\text{H}_2$  as the fuel. PEMFC can obtain power density of 500 to 600 mW  $\text{cm}^{-2}$  with 40 to 60 % efficiency, making it a promising and clean power source for many commercial applications such as transportation, stationary and portable power generation<sup>[2]</sup>.

Besides hydrogen, some liquid fuels such as methanol, ethanol, and formic acid *et al.* are also applied in PEMFCs to produce electricity<sup>[3]</sup>. These liquid fuels have largely expanded the energy sources of fuel cells, as they can be easily derived from biomass. Apart from organic fuels, more and more attentions have been paid to nitrogen-based fuels such as ammonia and hydrazine solutions<sup>[4]</sup>. Some studies intend to convert ammonia and hydrazine to hydrogen gas via thermal,

catalytic and electrolytic methods firstly, and then produce electricity from the generated hydrogen<sup>[5]</sup>. Others focus on direct ammonia fuel cells and direct hydrazine fuel cells without any pre-conversion<sup>[6]</sup>. No matter which method is used, the final oxidation products are nitrogen gas and water. Thus nitrogen-based fuels are regarded as promising carbon-free energy sources with high energy density. All the liquid fuels are convenient to stockpile when compared to gaseous fuels, leading to a great reduce in storage cost.

Despite many virtues of liquid fuels, it still faces problems in the aspect of safety such as toxicity<sup>[7]</sup> and volatilization, especially for ammonia. Ammonia and aqueous ammonia are more dangerous than hydrogen. One possible solution is to use other fuels with high energy density to low risks. Normally, solid materials have low volatility. Thus, much safer solid fuels such as sugar and urea are proposed for low-temperature fuel cells<sup>[16-8]</sup>. Urea has liquid fuels' advantages such as ideal energy density ( $16.9 \text{ MJ L}^{-1}$ ) and high solubility ( $1079 \text{ g L}^{-1}$ ,  $20 \text{ }^\circ\text{C}$ ), and also overcomes the disadvantages of toxicity and volatility<sup>[9]</sup>. The sources of urea production can be  $\text{NH}_3$  and  $\text{CO}_2$ , thus it is a  $\text{CO}_2$ -neural energy<sup>[10]</sup>. Usage of solid fuels like urea has again enlarged the fuels family of fuel cells. Recent advances in anode nano-catalysts for urea electrooxidation based on transition metal of nickel have shown great increase of current density to well replace noble metal catalysts. With its features such as enhanced energy-storage densities, high levels of safety and fast fuel reloading, urea has the possibility to promote application of fuel cells in portable electronic devices. On the other hand, urea is also a common environmental pollutant mainly from agriculture fertilizer and urine, causing eutrophication<sup>[11]</sup>. Urine is a major source of nitrogen in domestic wastewater and the nitrogen removal has always been a tough task in wastewater treatment which is considered as an energy-intensive process. Great efforts have been paid on dealing with nitrogen-rich water with energy recovery such as microbial fuel cells, but it is still a long way to go to improve power density for commercial use<sup>[12]</sup>. Recent urea fuel cells testify that urine can be directly oxidized on electrocatalysts, and it provides a novel routine to clean water with self-generating electricity. This review is about electrocatalysts based fuel cells to produce electricity from urea and its application in environmental technology.

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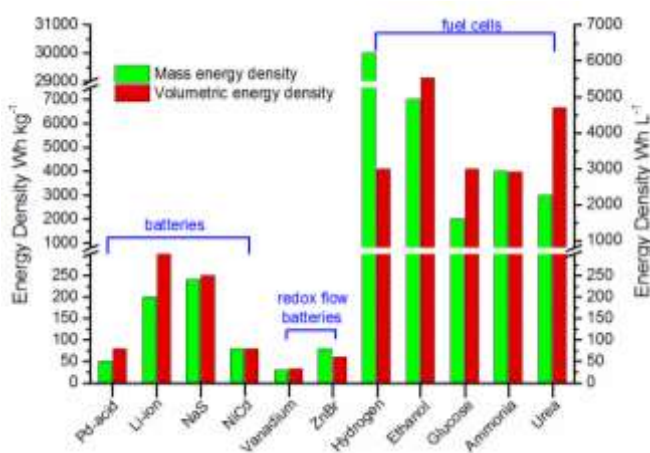
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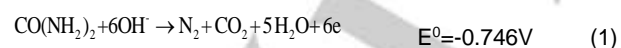


**Figure 1.** Comparison of energy density between electrochemical energy storages.

## 2. Electrochemical energy conversion of urea

The first attempt of electrochemical approach to oxidize urea and gain electricity is made by S. J. YAO *et al.* in the early 1970s<sup>[13]</sup>. They used a sandwich-typed cell consisted of Pt-black electrodes and an anion exchange membrane with 5 mM glucose in bicarbonate buffer at anode and flowing air at cathode. The cell voltage increased from 0.41 V to 0.57 V after adding 5 mM urea in anode solution under 5 Ω loading. Typical direct urea fuel cells (DUFCs) use anion exchange membrane (AEM) as solid electrolyte to avoid the possible poisoning of cation exchange membrane<sup>[1d, 4a]</sup>, as shown in Fig.2. Whilst two N atoms in urea is directly electrooxidized to nitrogen gas at anode<sup>[14]</sup>, six electrons are released and transferred to cathode through the external circuit with the electroreduction of oxygen gas to OH<sup>-</sup> at cathode. The generated OH<sup>-</sup> will act as charge carriers and run toward anode through AEM to complete the current circulation. Reaction mechanism of DUFC is shown as followings<sup>[1d]</sup>:

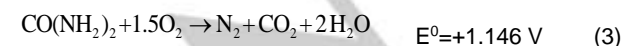
Anode reaction:



Cathode reaction:



Overall reaction:



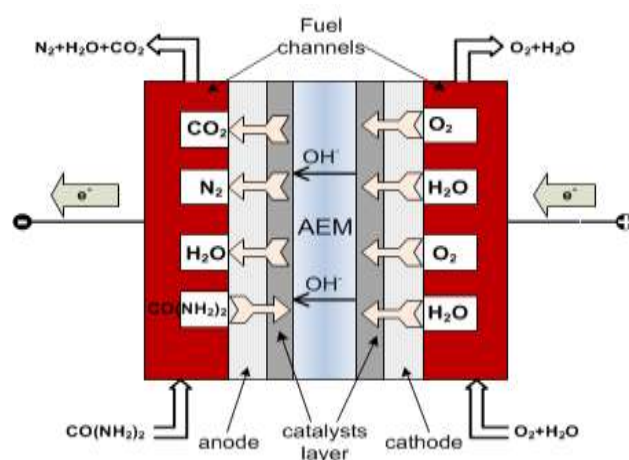
The first use of DUFCs in the literature came from the work by Rong Lan *et al.* using anion-exchange resin-PVA membrane as separator<sup>[1d]</sup>. An open-circuit voltage (OCV) of 0.6 V and a maximum power density of 1.8 mW cm<sup>-2</sup> are achieved when fuelled by 1 M urea solution. Higher concentration of urea solution up to 7 M was tested but results were inferior to 1 M.

This might be attributed to the crossover of urea. They further prepared nano-sized nickel for anode catalysts and improved the DUFC to about 13 mW cm<sup>-2</sup> at 0.35 V of cell voltage at 60°C<sup>[8a]</sup>. However, the power density at 20° was only about 1 mW cm<sup>-2</sup>. They also found that the humidity of cathode O<sub>2</sub> is quite important for power density.

The direct oxidation of urea on nickel electrocatalyst is a relatively sluggish reaction with large overpotential, and some effort has been directed into nickel alloys. Xu *et al.* reported a bimetallic nickel-cobalt catalyst with lower overpotential and higher electric conductivity than monometallic nickel catalyst<sup>[10a]</sup>. The best atom ratio of nickel:cobalt for DUFC anode catalyst is 4:1, with OCV of 0.64 V and maximum power density of 1.57 mW cm<sup>-2</sup> when using 0.33 M urea. Increasing of temperature up to 60°C can enhance the cell performance. Furthermore, nickel-cobalt nanowire arrays (Ni-Co NWAs) catalysts toward DUFC anode have been prepared by Fen Guo *et al.* via electrodeposition<sup>[15]</sup>. Similarly, the onset potential of urea oxidation is observed to be lower as the addition of Co into nickel. Urea and hydrogen peroxide are used as anode fuel and cathode oxidising reagent in DUFC, respectively. It is claimed that the maximum power density of DUFC will increase with urea concentration up to 0.33 M, and then it will decrease if urea concentration rises further. The addition of KOH into anode fuel can greatly enhance the cell performance. A maximum power density of 7.4 mW cm<sup>-2</sup> and an OCV of 0.92 V were achieved with 9.0 mol L<sup>-1</sup> KOH and 0.33 mol L<sup>-1</sup> urea as anode fuel, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> as cathode fuel.

Another strategy to improve the polarization of urea oxidation is to operate DUFC at intermediate temperatures. Masahiro Nagao *et al.* developed a DUFC with Sn<sub>0.920</sub>Sb<sub>0.08</sub>P<sub>2</sub>O<sub>7</sub>-PTFE composite electrolyte as hydroxide ion conductors, Pt/nitrogen-doped graphene as cathode, Ru/C as anode<sup>[16]</sup>. Argon gas passed through a urea solution or urine bubbler was heated up to 300°C and supplied to anode. The maximum power density increased from less than 1 mW cm<sup>-2</sup> at 100°C to 16.7 mW cm<sup>-2</sup> at 300 °C with human urine. The peak power density for 20 wt.% urea solution at 300 °C reached 26.5 mW cm<sup>-2</sup>.

The by-products of anode reaction have been confirmed by Serban *et al.* using mass spectrometry analyses<sup>[14]</sup>. Results

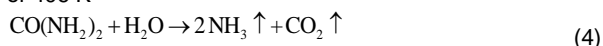


**Figure 2.** Schematic diagram of a direct urea fuel cell.

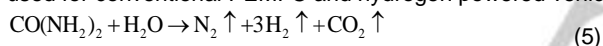
showed that the urea was electrooxidized to  $N_2$  with a high selectivity close to 100%, and other by-products like  $NO_x$  are negligible. The urea solution was mixed with NaOH as anode fuel, so the  $CO_2$  by-product was detected in solution as a form of  $NaHCO_3$ . The addition of NaOH for alkaline urea solution will improve the OCV and current density of fuel cell, because the anode reaction of urea electrooxidation would consume  $OH^-$  anions<sup>[17]</sup>.

Gan *et al.* developed a urea photo-electrochemical fuel cell by using NiO doped  $TiO_2$  nanotube as anode catalyst and Pt as cathode catalyst<sup>[18]</sup>. The OCV reaches 0.46 V and 0.37 V when using UV light and visible light, respectively. The photo-electrochemical fuel cell can generate electricity via the photodecomposition of urea solution, together with hydrogen evolution at cathode when the cell was air-tight or oxygen-free.

Besides directly oxidizing urea to  $N_2$ ,  $CO_2$  and  $H_2O$ , there are researches aiming to convert urea to hydrogen gas first before electricity production. The usual conversion ways are heat and electrolysis. Urea starts to decompose to ammonia and carbon dioxide at 333 K, and can be rapidly cracked at low temperature of 406 K<sup>[19]</sup>

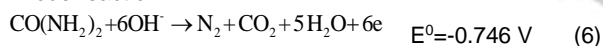


The produced ammonia can be used as fuel in direct ammonia fuel cells<sup>[6a-c]</sup>, or further heating of the products over catalysts will continually decompose ammonia to  $N_2$  and  $H_2$ , which can be used for conventional PEMFC and hydrogen powered vehicles.



Thermal urea reform requires relative large energy to maintain temperature and the efficiency is up to 55%. One facile routine of producing hydrogen gas from urea would be electrolysis<sup>[20]</sup>. Urea is electrooxidized at anode with hydrogen evolution reaction (HER) at cathode:

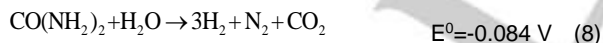
Anode reaction:



Cathode reaction:



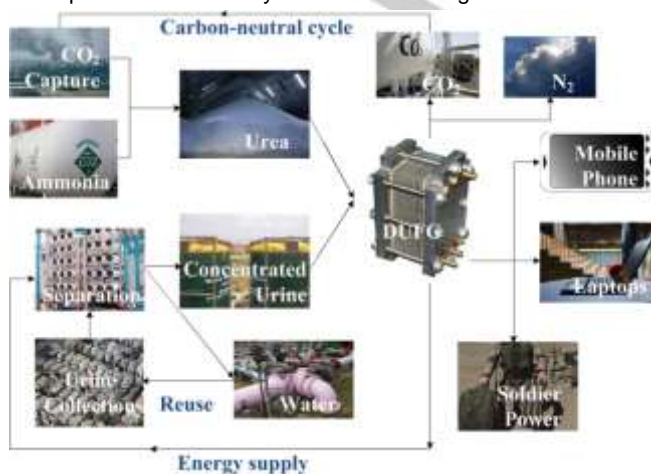
Overall reaction:



Theoretically, only 0.084 V is required to produce  $H_2$  from urea electrolysis, which is 93% less than overall voltage of water electrolysis (1.23 V). Boggs *et al.* have investigated the use of nickel as anode catalyst and Pt as cathode catalyst for electrolysis of 0.33 M urea in 5 M KOH. Pure  $H_2$  was collected at cathode and 96.1% of  $N_2$  was detected at anode by gas chromatography<sup>[20b]</sup>.

Urea at present is produced from ammonia and carbon dioxide, and its cost is largely depended on ammonia production (accounting for ca. 80%)<sup>[34]</sup>. Although the manufacture cost of urea is slightly higher than ammonia, urea is much safer and suitable as a distributed energy storage material. The carbon dioxide will be recycled during urea production and consumption, so urea is also a nearly carbon-neutral fuel, as shown in Fig.3. Another possible source of urea is renewable urine, which contains about 22 g  $L^{-1}$  of urea, together with some organic substrates and salts. Harvesting energy from urine wastes will be very promising, as large amounts of urines are produced

sustainably and steadily every day. DUFCS have a high energy density up to 3000 Wh  $kg^{-1}$ , which exceeds the energy density of other portable batteries by a factor of ~10. Fig.3 demonstrates



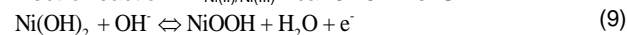
**Figure 3.** Diagram of DUFCS using urea/urine as fuels and its applications.

the promising applications of DUFCS in small size power such as replacement of portable batteries (5–30 W) and equipping soldier as wearable power (20 W) on the battlefield. The existing problem of DUFCS is low power density at room temperature. This is possibly improved by developing advanced anode catalysts for urea electrooxidation.

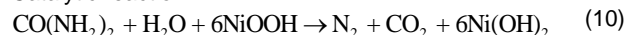
### 3. Nano-catalysts for urea electro-oxidation (UEO)

The anode reaction of UEO is relatively sluggish, accounting for the limiting current density of both DUFCS and urea electrolysis. Thus there have been numerous investigations into the anode catalysts for UEO including Pt and Pt alloys, Ni and Ni alloys, Ag-ZnO, Ti-Ru oxide, boron-doped diamond (BDD), Sb-SnO<sub>2</sub>, IrO<sub>2</sub><sup>[20c, 21]</sup>. Among these catalysts, nickel is widely studied as it is a relatively low-cost material and is reported to be more active toward UEO than noble metal like platinum<sup>[20b, 22]</sup>. The UEO reaction on nickel catalyst is based on EC' mechanism, i.e. the electrochemical reaction of Ni(II)→Ni(III) happens first, and then urea is oxidized by the intermediate Ni(III) species via chemical reaction<sup>[10a, 21b, 23]</sup>.

Electro-reaction:  $E_{Ni(II)/Ni(III)} = ca. -0.45 \text{ V vs. SHE}$



Catalytic reaction:



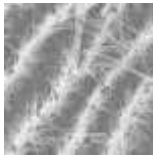


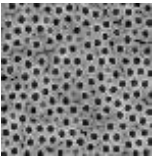
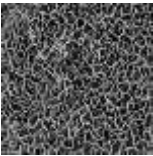


It means that the onset potential of UEO is depended on the redox potential of Ni(II)/Ni(III). However, the conversion of Ni(II)↔Ni(III) is observed to proceed at high potential of ca. 0.45 V vs. SHE in cyclic voltammetry, leading to a large overpotential of more than 1 V for UEO on nickel catalyst. This large overpotential will significantly influence the current density and energy efficiency of DUFCS and urea electrolysis.

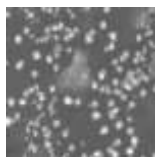
Recent improvements of nickel-based catalysts toward UEO have been achieved from morphology designing, surface composition, element doping and advanced supporting material.

One way to reduce overpotential of nickel is to incorporate other metals with less redox potential into nickel. Nickel alloys may gain unique electron properties and have more active sites exposed on catalysts surface, giving rise to improved activity<sup>[24]</sup>. Results show that the using of Ni-Co bimetallic catalysts can successfully reduce the onset potential by 50 to 100 mV<sup>[10a, 21b, 25]</sup>. The onset potential is further reduced as the content of Co increased. However the oxidation current density is also observed to decrease if Co content exceeds about 50%, because Co is supposed to be inactive toward urea

electrooxidation. Wei Yan *et al.* synthesized Ni-Zn catalyst via electrodeposition (ED) method, and it decreased the onset potential of UEO by 40 mV meanwhile increased peak current density by 2 times when compared to Ni catalysts<sup>[21a]</sup>. Yanhui Liang *et al.* reported the growth of NiMoO<sub>4</sub>·xH<sub>2</sub>O nanosheet arrays on Ni foam through a hydrothermal process with high catalytic activity and stability. It achieved specific current density of 830 mA cm<sup>-2</sup> mg<sup>-1</sup> at 0.5 V at a scan rate of 10 mV s<sup>-1</sup>, about 4.2 times enhancement compared to Ni(OH)<sub>2</sub> catalyst<sup>[26]</sup>.

**Table 1** Selected electrocatalysts for UEO reported in literatures.

catalyst material	catalyst morphology	catalyst size	electrode material	preparation method	onset potential	peak current density	Ref.
Ni nanowire arrays		6 μm in length and 50 nm in diameter	nickel sheet	ED on template	0.25 V vs. Ag/AgCl	160 mA cm <sup>-2</sup>	Fen Guo <i>et al.</i> <sup>[23a]</sup>
Ni-WC Nanocluster		lattice spacing of ca. 0.20 nm	glassy carbon disk	temperature programming reduction	0.42 V vs. Hg/HgO	700 mA cm <sup>-2</sup> mg <sup>-1</sup>	Lu Wang <i>et al.</i> <sup>[27]</sup>
Rh/Ni		0.5 to 1 μm nodules	nickel foil	ED	0.38 V vs. Hg/HgO	180 mA cm <sup>-2</sup>	G. G. Botte <i>et al.</i> <sup>[28]</sup>
Ni(OH) <sub>2</sub> nanocup arrays		150 nm	stainless steel foil	ED with polystyrene spheres template	0.31 V vs. SCE	32 mA cm <sup>-2</sup> mg <sup>-1</sup> at 0.41 V vs. SCE	Mao-Sung Wu <i>et al.</i> <sup>[29]</sup>
Nickel oxide nanosheets		2-50 nm	Ni foam and stainless steel	hydrothermal synthesis	0.25 V vs. SCE	330 mA cm <sup>-2</sup> mg <sup>-1</sup> at 0.52 V vs. SCE	Mao-Sung Wu <i>et al.</i> <sup>[30]</sup>
Ni(OH) <sub>2</sub> nano-ribbons		15-20 nm thickness, length up to several μm	Glassy carbon electrode	template-free hydro-thermal method	0.42 V vs. Hg/HgO	10 times higher than bulk Ni(OH) <sub>2</sub>	Dan Wang <i>et al.</i> <sup>[31]</sup>
Ni@carbon sponge		~500 nm in diameter	carbon sponge	ED	0.24 V vs. Ag/AgCl	290 mA cm <sup>-2</sup>	Ke Ye <i>et al.</i> <sup>[32]</sup>

graphene/ nickel  
nano-compositesgraphene  
thickness of ~1 nm  
Glassy  
carbonElectro-chemical  
reduction0.45 V vs.  
Hg/HgO2 times higher  
than pure NiDan Wang  
*et al.*<sup>[33]</sup>

Chen *et al.* used a new method to prepare nano-Ni by room temperature ionic liquid (RTIL) <sup>[34]</sup>. The prepared RTIL/Ni/graphite composite electrode presented a sensitivity of  $517 \mu\text{A mM}^{-1} \text{cm}^{-2}$  and good stability of UEO. Addition of noble metals into nickel via ED method turns out to be well-performed catalysts, such as Ni-Pt, Ni-Ru, Ni-Rh and Ni-Pt-Ir<sup>[20c, 28]</sup>. The prepared Ni-Rh electrodes reduced the overpotential for UEO and improved the current density by a factor of 200 compared to a Ni catalyst <sup>[20b, 20c]</sup>.

Table 1 demonstrates surface morphologies of some Ni-based catalysts including nanowire arrays, nanocluster, nanocup arrays, nanosheets and nanoribbons. Vertically-aligned NiO nanosheets supported on Ni foam are prepared via hydrothermal method by Mao-Sung Wu<sup>[30]</sup>. Tests show the NiO nanosheet configuration can boost the electrolysis of urea, improving current density from  $25 \text{ mA cm}^{-2} \text{mg}^{-1}$  (NiO powder) to  $330 \text{ mA cm}^{-2} \text{mg}^{-1}$  at 0.52 V vs. SCE. Ren-Yu Ji *et al.* developed nickel hydroxide nanotubes catalysts on 3-dimension nickel foam. They grow ZnO nanotubes template on nickel foam by electrodeposition at -0.8 V vs. SCE, then dipping into to nickel chloride solution and drying in air to form Ni(OH)<sub>2</sub> nanotubes. It exhibits a much higher current density than that with attached Ni(OH)<sub>2</sub> film during urea electrolysis due to increased surface area from surface porosity <sup>[35]</sup>. Chronoamperograms show the maximum efficiency of nickel hydroxide nanotubes catalysts could reach about 99%.

The application of supporting materials with high electrical conductivity, large specific surface area and exceptional chemical stability such as graphene, carbon nanotube and carbon sponge in catalysts preparation is proved to be a promising method to improve catalytic activity of metal catalysts and reduce the metals loading <sup>[36]</sup>. These supporting materials have been used to prepare nickel-based catalysts for UEO. Graphene oxide (GO), obtained from graphite via modified Hummers method, can be reduced together with Ni<sup>2+</sup> cation via electroreduction to form graphene supported Ni catalyst for UEO <sup>[33]</sup>. The current density of graphene supported Ni is observed to be much larger than that of pure Ni without graphene, attributed to the large active surface areas and perfect electro transfer of graphene sheets, as well as the synergistic contribution of Ni and graphene sheets. Lu Wang *et al.* applied active carbon and multi-walled carbon nanotubes (MWCNT) as supporting materials to form Ni-WC/C and Ni-WC/MWCNT catalysts <sup>[37]</sup>. Results showed that electrochemical surface areas (ESA) of Ni-WC and Ni-WC/MWCNT are  $113.87 \text{ m}^2 \text{g}^{-1}$  and  $77.22 \text{ m}^2 \text{g}^{-1}$ , respectively. The current densities of Ni-WC/MWCNT are over 3 times higher than those of the Ni-WC/C. Ke Ye *et al.* electrodeposited Ni on carbon sponge to prepare highly porous Ni@carbon sponge. This low-cost catalyst possesses superior porous network microstructures, and reveals lower onset oxidation potential and higher peak current density for UEO compared to Ni/Ti flat electrode.

#### 4. Advantages of DUFC for wastewater treatment

Combination of wastewater treatment and energy production is an attractive issue in sustainable development currently<sup>[38]</sup>. Industrial urea plants will produce wastewater containing 2 Kt urea per day, and the urea from human urine is about 120 times of that number, accounting for about 80% of N, 50% of P and 10% of the COD in municipal wastewater <sup>[9, 39]</sup>. Annually wastewater treatment consumes about 3% of all electrical power produced in the United States<sup>[12b, 40]</sup>. Capture energy from urine before piping to waste water treatment plants (WWTPs) will significantly cut loads of WWTPs and reduce the consumption of energy for wastewater treatment.

Typical technology of directly producing electricity from wastewater is the microbial fuel cells (MFCs), using electro-microorganism as biocatalyst and contaminants as fuels <sup>[12b, 38a]</sup>. Recently, MFCs with urine as anode fuel were successfully established to generate electricity, achieving power densities from 4 to 400 mW m<sup>-2</sup> and columbic efficiencies around 40%, shown in Table 2. After MFCs treatment, the content of organic substrates in urine is reduced by 60 to 80%. However, MFCs are shown to work only based on the organic substrates in urine, but failed to directly utilize the urea<sup>[41]</sup>. This is because urea is not metabolisable into electricity with current biocatalysts. As a result, MFCs fuelled with urine cannot recover the main parts of energy in urine and perform poorly in nitrogen removal. In order to removal nitrogen from urine, MFCs need to combine other technologies such as precipitation and gas purge<sup>[42]</sup>. Besides, hydrolysis of urea into ammonia will lead to rise of pH to more than 9 via urease<sup>[42b]</sup>. The rise of pH is observed to limit the current density of MFCs, as biocatalysts of electro-microorganism usually live around neutral condition and will suffer from activity decline at high pH <sup>[43]</sup>.

On the contrary, DUFCs based on chemical catalysts such as nickel alloys can directly utilize urea as energy source. Thus the application of DUFCs in urine treatment is supposed to have a larger energy output and to remove the nitrogen simultaneously. Tao *et al.* firstly used human urine for DUFCs, with carbon black supported Ni as anode catalyst. The OCV reached 0.26 V, and power density reached  $1000 \text{ mW m}^{-2}$  at 0.15 V<sup>[1d]</sup>. They further developed a nano-sized nickel catalyst by a simple chemical-reduction method to improve cell performance to OCV of 0.59 V and power density of  $11 \text{ W m}^{-2}$  at 0.34 V <sup>[8a]</sup>. Compared to MFCs, which usually work at 20 to 400 mW m<sup>-2</sup>, the power density of DUFCs is almost 30 to 500 times larger. With the newly developed nickel-based catalysts such as nickel alloys, 3D nano-nickel and nickel on advanced supporting materials, the UEO is observed to have lower overpotential and larger current

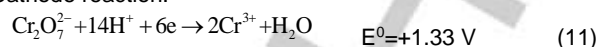
density. Reasonably these electrocatalysts will greatly improve the performance of DUFCS. The DUFCS as environmental technology for urine treatment in comparison with MFCs have three advantages: first, urea is direct electrooxidized to nitrogen gas to produce electricity; second, nickel-based chemical-catalysts are stable at high pH, so rise of pH will not limit current density; third, easier operation and much higher power density.

The membrane is also very important in DUFCS. Membrane is probable to suffer from loss of ion conductivity by urine, resulting in sub-standard power of DUFCS<sup>[10a, 44]</sup>. Related researches about urine-tolerant membrane need to be carried out for practical use.

The common cathode fuels in DUFCS are wet air or oxygen as electrons acceptors. Interestingly, a work by Binbin Yu *et al.* demonstrated that the oxygen in cathode can be replaced by contaminants as electrons acceptors<sup>[17]</sup>. They used urea as anode fuel, Cr(VI)-containing wastewater from chromium-slag leakage as cathode fuel, forming urea-Cr(VI) fuel cell. High toxic

Cr(VI) is reduced to less toxic Cr(III) with electricity generation. This kind of DUFCS has much higher OCV than that of DUFCS with O<sub>2</sub> as electron acceptor, as the redox potential of Cr(VI)/Cr(III) is 0.9 V higher than that of O<sub>2</sub> reduction.

Cathode reaction:



After 48 h, Cr(VI) removal efficiency is 98.6% with initial Cr(VI) concentration of 5.35 mM. This urea-Cr(VI) fuel cell achieves OCV of 1.59 V, and totally produce electric quantity of 20.5 C with 74.6% coulombic efficiency. While Cr(VI) is removed at cathode, the carbon and nitrogen can also be eliminated at anode via urine oxidation. Xu *et al.* claimed that about 78% of carbon and nitrogen in urine were removed by urine-Cr(VI) fuel cell, and simultaneously more than 90% of Cr(VI) was reduced with 4417 mAh electric quantity produced from per litre of human urine<sup>[44]</sup>. It indicates urine can be directly oxidized on Ni catalyst and treated together with high redox potential wastes.

**Table 2** Performance of DUFCS and MFCs in power output and contaminants removal with urine or urea as fuel.

Anode	Cathode	Fuel mix	membrane	output	efficiency	Ref.
microbes inoculated to carbon fibre	carbon fibre	fresh human urine/air	cation exchange membrane (VWR International)	4.93 mW m <sup>-2</sup>	22-67% of energy efficiency	Chris Melhuish <i>et al.</i> <sup>[45]</sup>
microbes inoculated to carbon cloth	Activated carbon coated carbon cloth	Fresh urine/air	membraneless single chamber	400 mW m <sup>-2</sup> at 2 A m <sup>-2</sup>	2.1% of coulombic efficiency, 85.4% of COD removal	Carlo Santoro <i>et al.</i> <sup>[46]</sup>
microbes inoculated to carbon veil	polyurethane-based conductive latex	fresh human urine/air	laboratory natural rubber latex glove	2 W m <sup>-3</sup>	-	Jonathan Winfield <i>et al.</i> <sup>[47]</sup>
microbes inoculated to carbon fibre	waterproof carbon fibre	fresh human urine/air	cation exchange membrane (CMI-7000S)	45 mW m <sup>-2</sup>	-	Majid Taghavi <i>et al.</i> <sup>[48]</sup>
microbes inoculated to carbon brush	micro porous layer coated carbon cloth	Fresh human urine/air	membraneless single chamber	OCV of 0.5 V, 0.1 mA under 1 kΩ	20-50% Phosphorous removal efficiency	Carlo Santoro <i>et al.</i> <sup>[49]</sup>
20 mg cm <sup>-2</sup> Ni on carbon black	20 mg cm <sup>-2</sup> Ag on carbon black	Human urine/wet air	anion-exchange resin-PVA membrane	OCV of 0.26 V, 1000 mW m <sup>-2</sup> at 0.15 V	-	Rong Lan <i>et al.</i> <sup>[1d]</sup>
20 mg cm <sup>-2</sup> nano-Ni on carbon black	20 mg cm <sup>-2</sup> MnO <sub>2</sub> on carbon black	Human urine/wet air	anion-exchange resin-PVA membrane	OCV of 0.59 V, 11 W m <sup>-2</sup> at 0.34 V	-	Shanwen Tao <i>et al.</i> <sup>[8a]</sup>
10 mg cm <sup>-2</sup> NiCo on carbon black	1 mg cm <sup>-2</sup> Pt on carbon black	Human urine/wet O <sub>2</sub>	anion exchange membrane (AMI-7001)	OCV of 0.28 V, 700 mW m <sup>-2</sup> at 0.15 V	-	Wei Xu <i>et al.</i> <sup>[10a]</sup>

10 mg cm <sup>-2</sup> Ni on carbon black	carbon cloth	1M urea in 1 M KOH/dichromate leakage	saturated KNO <sub>3</sub> solution blocked by the ceramic core	OCV of 1.59 V, 0.1 mA under 1 kΩ	98.6% of Cr(VI) removal, 74.6% of coulombic efficiency	Binbin Yu <i>et al.</i> <sup>[17]</sup>
8 mg cm <sup>-2</sup> Ni on carbon black	carbon cloth	Human urine/300 ppm Cr(VI) with 0.25 M H <sub>2</sub> SO <sub>4</sub>	One anion exchange membrane and one cation exchange membrane	OCV of 1.1 V, 1.25 W m <sup>-2</sup> at 0.65 V, electric quantity of 4417 mAh from a liter of human urine.	>90% of Cr(VI) removal, about 78% of carbon and nitrogen removal efficiency obtained at the same time	Wei Xu <i>et al.</i> <sup>[44]</sup>

## 5. Conclusions

Urea as a safe and sustainable energy storage material for fuel cells gains increasing attention in recent years. The state-of-the-art DUFCS achieve OCV of 0.6 V and power density of 13 mW cm<sup>-2</sup> with nickel-based catalysts. Although DUFCS' performance has been greatly improved, it is still not comparable with other types of low-temperature fuel cells. One main reason is that anode reaction of three-electron oxidation of urea is sluggish and limits current density of DUFCS. Novel nickel-based catalysts for UEO have seen reduction of overpotential by 40 to 100 mV and rise of current density by 2–10 times in recent years. On the other hand, DUFCS with noble-metal-free catalysts can function as an environmental technology to treat urine with electricity production. DUFCS based on anion exchange membrane which conducts hydroxide ions can provide an alkaline environment, thus makes it able to use non-noble metal catalysts such as nickel to remove the need of Pt-based catalysts<sup>[50]</sup>. However commercial anion exchange membrane has low anionic conductivity when compared to that of cation exchange membrane such as Nafion membrane<sup>[51]</sup>. Other challenges including insufficient stability (pH>14, temperature>60°C), fuel crossover and conductivity reduction due to the formation of CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> will also lead to a large performance drop<sup>[52]</sup>. Further work on tailoring the membrane is likely to result in DUFCS that are capable of commercial applications in wastewater treatment.

## Acknowledgements

The authors thank EPSRC urea fuel cell projects (EP/F028083/1 and EP/H029400/1) for funding. One of the authors (Xu) gratefully acknowledges the China Scholarship Council (CSC) for financial support.

**Keywords:** Electrocatalysis • Energy transfer • Environmental chemistry

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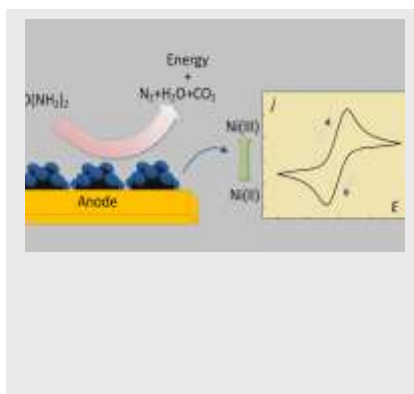
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**Entry for the Table of Contents** (Please choose one layout)

Layout 1:

**MINIREVIEW**

Urea and urine can be directly used as fuels to produce power via membrane fuel cells. Urea is oxidized to nitrogen gas and carbon dioxide with the catalysis of oxidation-active Ni(III) species, which can be generated from the non-precious nickel based anode catalysts.

*Wei Xu, Zucheng Wu, Shanwen Tao\****Page No. – Page No.****Urea based fuel cells and electrocatalysts for urea oxidation**

Layout 2:

**MINIREVIEW***Wei Xu, Zucheng Wu, Shanwen Tao\****Page No. – Page No.****Urea based fuel cells and electrocatalysts for urea oxidation**

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