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Preparation of nano-sized nickel as anode catalyst for direct urea and urine fuel cells

Rong Lan, Shanwen Tao*

Department of Chemical and Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK

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ABSTRACT

Nano-sized nickel with primary particle size of 2–3 nm has been successfully prepared for use as efficient anode catalysts in urea and urine fuel cells. XRD, SEM and TEM were used for characterisation of nano-sized nickel. Based on the previous communication, the performance of urea and urine fuel cells has been further improved when the relative humidity at the cathode was 100%. A maximum power density of 14.2 mW cm^{-2} was achieved when 1 M urea was used as fuel, humidified air as oxidant. The performance of urine fuel cells operating above room temperature was also reported for the first time and a power density of 4.23 mW cm^{-2} was achieved at 60 °C indicating potential application in urea-rich waste water treatment.

1. Introduction

The Nobel laureate for chemistry in 1996, Prof. Richard E Smalley identified energy and waste water as the first two of the top ten problems to face humanity in the next 50 years [1].

Hydrogen economy is promising but on-board hydrogen storage remains a significant obstacle. Alternatively, hydrogen can be stored in light chemicals such as methanol, ammonia or urea. Urea is a low-cost industrial product widely used as inexpensive fertiliser and a major component of municipal waste water and human/animal urine. Offering high energy density and effectively containing 10 wt% hydrogen, urea is an indirect H_2 storage material and possible alternative energy vector (Table 1) [2,3]. Key advantages of urea versus fuels such as hydrogen and methanol favoured in polymer electrolyte membrane fuel cell (PEMFC), are that it is a non-toxic non-flammable solid easily transported in bulk without pressurisation and can be used as a fuel by simply adding water. AdBlue®, a 32.5% urea solution is commercially available as a NO_x reduction additive for selective catalytic reduction (SCR) catalysed diesel vehicles and is widely available across the world providing an existing fuel distribution infrastructure.

There is a wide global availability of urea. It is more efficient to generate electricity directly from urea or AdBlue. During urea synthesis, large volumes of wastewater of varying urea concentration are formed and often purified by energy demanding electrochemical processes creating a barrier to industrial application [4]. High levels of urea exist in municipal waste water; de-nitrification technologies are expensive and inefficient [5]. It has been proposed to generate hydrogen from urine or urea-rich waste water through electrolysis but this requires energy input [6]. Using a urea fuel cell we reported to generate electricity from urea-rich waste water providing power and clean water, offering an attractive alternative to de-nitrification or electrolysis.

In addition to AdBlue urea solution; urea is naturally present in urine and in this case, urine is not a polluting waste, but a potential energy source. Urine fuel cell has the potential to power electrical vehicles [7]. Urea fuel cells could also be used for waste water treatment or in applications such as manned spaceship where water supply is limited.

In a previous communication, we have reported direct urea and urine fuel cells based on alkaline membrane electrolyte [7]. In our experiments, it was found that catalysts with small particle size are essential in order to achieve good performance. In this paper, the preparation and characterization of nano-sized nickel (2–3 nm) and the urea/urine fuel cell performance based on this catalyst are presented. For comparison, fuel cell performance based on a commercial fine nickel catalyst is also reported. It should be noted that Cr doped Ni was used as anode in previous report [7]. In order to compare with commercially available nickel, undoped nickel was used as anode catalyst in this paper. In our experiments, no significant difference in catalytic activities was observed between undoped and Cr-doped nickel. Only room temperature performance of a urine fuel cell was displayed in the previous com-

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* Corresponding author. Tel.: +44 141 548 2361; fax: +44 141 548 2539.
E-mail address: shanwen.tao@strath.ac.uk (S. Tao).

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Table 1
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 (700 bar)	0.039	100	0.039	5.6
Liquid H_2	0.071	100	0.071	10.1
NH_4OH (28%)	0.89	4.9	0.045	6.40
Liquid NH_3	0.747	17.6	0.13	15.6
$CO(NH_2)_2$	1.335	10.07[a]	0.134	16.9

[a] Effective density including hydrogen from water molecules for hydrolysis.

munication, here the improved performance of a direct urine fuel cell at elevated temperatures is also presented.

2. Experimental

2.1. Preparation of nano-sized nickel

Nano-sized nickel was prepared from $NiCl_2{\cdot}6H_2O$ (Alfa, 99.3%) and KBH_4 (Alfa, 98%) [8] but with the addition of sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) (Alfa, 99%). 5 wt% KBH_4 solution was dropwisely added into the mixed aqueous solution of $NiCl_2$ and $Na_3C_6H_5O_7$ aqueous solution. The formed precipitate was filtered and washed with deionised water for 3–5 times until the residual Cl^- ions cannot be detected by 0.01 M $AgNO_3$ solution. The precipitate was dried at room temperature or 100 °C overnight before being used as anode catalysts for fuel cells. In our previous experiments, nano-sized nickel dried at room temperature was used while nickel dried at 100 °C was used in experiments reported here. No obvious difference in performance was observed between the nickel powers dried at room temperature or 100 °C but higher drying temperature will remove most of water for easier quantification.

2.2. Materials characterisation of nano-sized nickel

X-ray data were collected on a Bruker-AXS (D8 Advance) diffractometer, controlled by DIFFRACTplus TM, in the Bragg-Brentano reflection geometry with a Ni-filtered Cu Kα source (1.5405 Å), fitted with a LynxEyeTM detector. Absolute scans in the 2θ range of 5–85° with step size of 0.009° and time step of 61.6 (123.2 s for sample at x = 0.4125) were used during data collection.

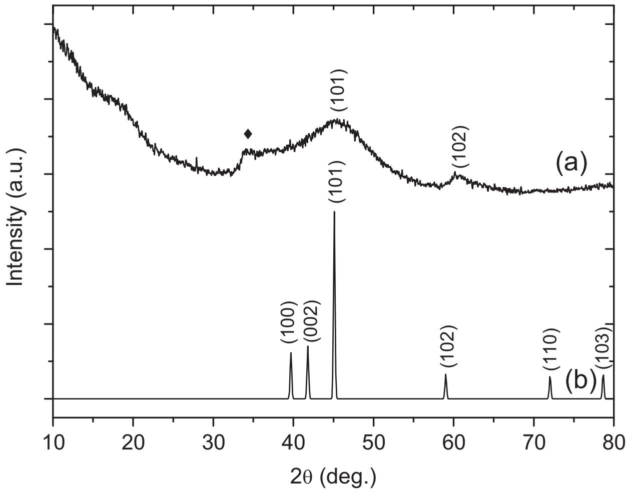

Fig. 1. XRD pattern of nano-sized nickel prepared by a precipitate method (a) and the simulated pattern (b). (♦) Unknown peak.

SEM pictures were taken with the use of a Quanta 3D FEG scanning electron microscope (FEI Company) with charges of 10 kV and 10 pA.

The microstructures were examined by a high resolution transmission electron microscopy (HRTEM, JEOL JEM-2011) at a voltage of 200 kV.

2.3. Fuel cell fabrication and measurements

Two types of cells were fabricated in our experiments.

For Cell A, a commercial fine nickel powder (Alfa, 99%) was also used as an anode catalyst and was mixed with carbon (Carbot Vulcan XC-72R) at weight ratio 50/50 to be used as anode.

The blend 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 1/2. 5 g PVA was dissolved in 30 ml de-ionised water and stirred at 85 °C for 2 h 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. The dried membrane was stored in 1 M KOH solution and was washed by deionised water for several times before used as electrolyte for fuel cells. The thickness of the membrane was around 100 μm.

20 wt% MnO_2/C was prepared from $KMnO_4$ (Avacado, 99%), $Mn(CH_3COO)_2{\cdot}4H_2O$ (Aldrich, 99.99%) and carbon (Cabot Vulcan XC-72R) by a co-precipitation method [9]. The loading of MnO_2 at cathode and Ni at anode were ~20 mg cm^{-2}. The catalyst ink was prepared by mixing the catalyst with the AER–PVA gel (AER to PVA weight ratio 1:2 as described above) and de-ionised water and stirred at room temperature for a few hours. The loading of AER was around 3 mg cm^{-2}.

The catalyst inks were cast on carbon paper (E-Tek, Torory 090) before attaching to the membrane electrolyte assembly.

For Cell B, the nano-sized nickel dried at 100 °C was mixed with carbon (Carbot Vulcan XC-72R) at a 50/50 weight ratio to be used as anode. The rest of the cell is the same as Cell A.

1 M urea solution was prepared from urea (Alfa Aesar, ACS grade) and de-ionised water. Commercial AdBlue (32.5% urea solution) was supplied by a local garage. Human urine was also used as fuel for fuel cell tests. The fuel solutions were pumped into the anode side by a peristaltic pump (Watson Marlow 323D). Wet air was supplied to the cathode with controlled relative humidity (RH) 100% at the operating temperature. The cell area was 1 cm^2. Fuel cell tests were carried out using a Solartron 1250 Frequency Response Analyser which was coupled to a 1287 Electrochemical Interface controlled by Z-plot electrochemical impedance software and CorrWare/CorrView for automatic data collection.

3. Results and discussion

After the prepared nickel was dried at 100 °C overnight, X-ray diffraction (XRD) analysis was carried out. As shown in Fig. 1a, only a few broad peaks appear in the RD pattern indicating for-

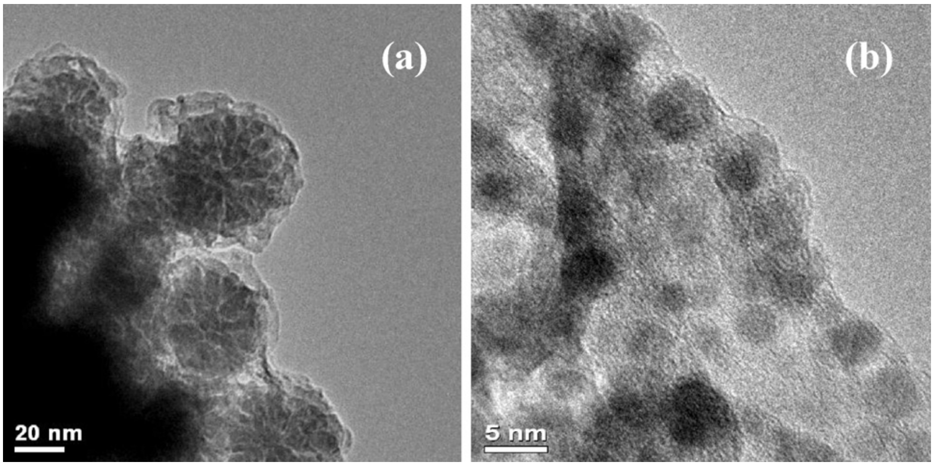

Fig. 2. HR-TEM pictures of the nano-sized nickel particles.

mation of nano-particles. The structure of metallic nickel has been well documented. Typically nickel exhibits two structures, cubic structure (SG $Fm\bar{3}m$ (2 2 5)) with lattice parameters $a = 3.524$ Å, $V = 43.76$ Å^3 [10] or hexagonal structure (SG $P6_3/mmc$ (1 9 4)) with lattice parameters $a = 2.622$ Å, $c = 4.321$ Å, $V = 25.73$ Å^3 [11]. Both cubic and hexagonal nickel have the strongest diffraction peak at $2\theta \sim 45^\circ$. The observed strongest diffraction at $2\theta \sim 45^\circ$ (Fig. 1a) indicates the formation of nickel. The small peak at $\sim 60^\circ$ indicates that the obtained nickel belongs to hexagonal rather than cubic because the later does not has a diffraction peak in the range of 2θ 55–75°. The small peak at $2\theta \sim 35^\circ$ cannot be indexed from the known nickel containing compounds. A simulated XRD pattern for hexagonal nickel is shown together (Fig. 1b) for comparison. Obviously both (1 0 1) and (1 0 2) peaks shift to higher angles in the diffraction in the prepared nano-sized nickel indicating lattice contraction. Lattice contractions in metallic nanoparticles are very common which is believed to be due to surface tension [12]. This phenomenon becomes significant on small nano particles.

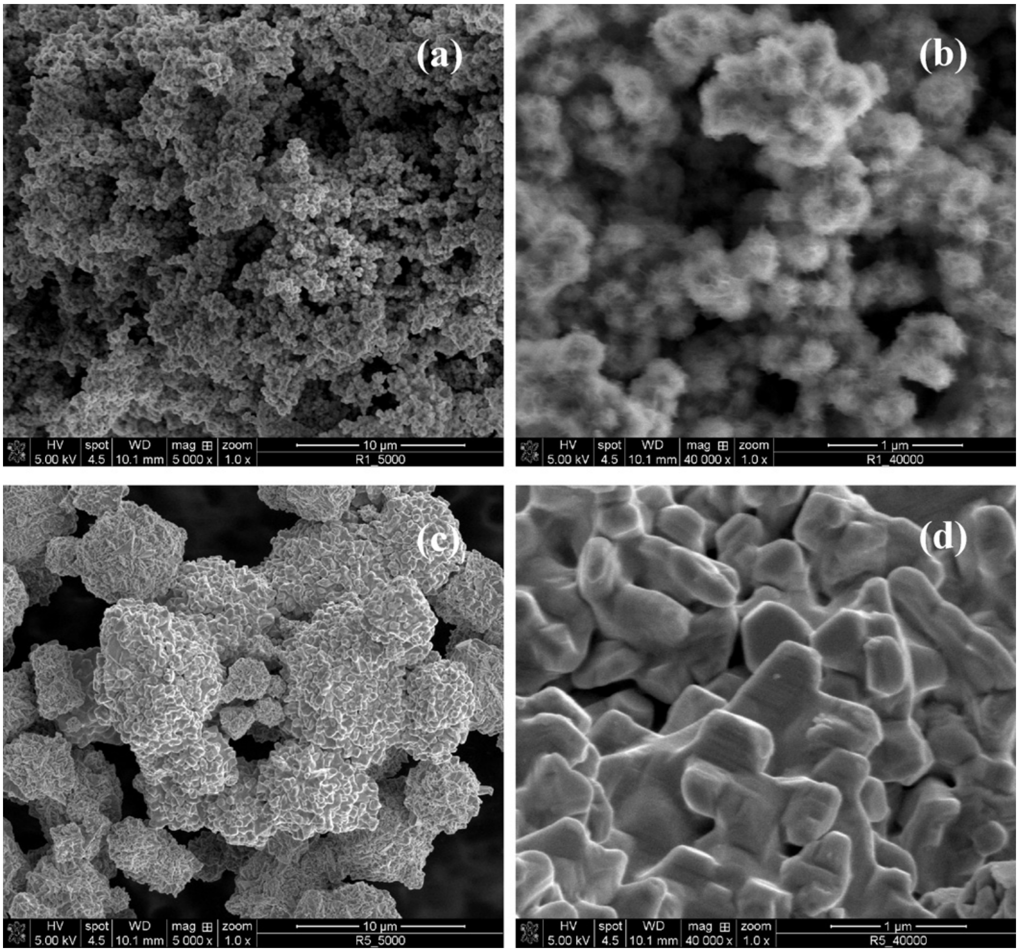

Fig. 3. SEM pictures of nano-nickel (a and b) and commercial nickel (c and d) at magnification factor of 5000 (a and c) and 40,000 (b and d) times, respectively.

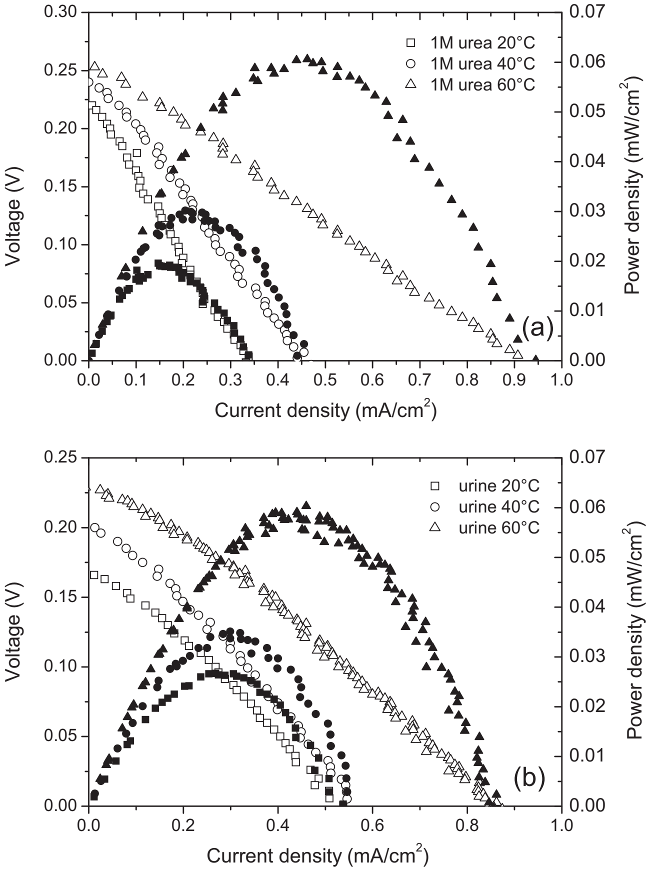

Fig. 4. Urea (a) and urine (b) fuel cell performance using a commercial nickel as an anode catalyst.

High resolution transmission electron microscopy (HRTEM) observation confirmed at the primary particle size is about 5 nm (Fig. 2a) but in some area, a particle size of 2–3 nm (Fig. 2b) was also observed. Nano-sized nickel has been prepared by different methods using $NaBH_4$ [13], hydrazine [14,15] or lithium as reducing agents [16]. Nickel with a particle size of ~10 nm was prepared by a reduction using $NaBH_4$ as a reducing agent [13] which is larger than that the nickel synthesised in our lab. The possible reason is the difference in reducing agents, solution concentration and the speed when adding reducing agents into the $NiCl_2$ solution. Nickel with an average particle size of 4.6 nm has been prepared using the microemulsion method [17]. However, the synthesised nano-sized nickel was dispersed in the microemulsion, hence it could not be directly used as catalytic material for fuel cells. To the best of our knowledge, nickel with the smallest particle size (~2 nm) was reported by Alonso et al. [16] through reduction of $NiCl_2$ by metallic lithium, but this contained significant amounts of unreacted $NiCl_2$. In this report, nano-sized nickel with comparable particle size prepared by a relatively easier method.

The SEM pictures of the prepared nanosized nickel are shown in Figs. 3a and b. The secondary particle size of the prepared nickel is about 0.2 μm although smaller secondary particle at ~50 nm was observed at the edge of the big particles when observed by TEM (Fig. 2a).

As shown in Figs. 3c and d, the commercial nickel has secondary particle size of 4–10 μm which is much larger than the prepared nano-sized nickel. It is expected that the prepared nano-sized nickel will have much larger specific area which would be an ideal catalyst for fuel cells.

Fig. 4 shows the urea and urine fuel cell performance of Cell A in which the commercial nickel was used an anode catalyst. At room temperature, an OCV of 0.22 V with an maximum current density of 0.34 mA cm^{-2} was achieved when 1 M urea was used as the fuel (Fig. 4a). This is lower than the reported OCV (0.46 V) and maximum current density (1.6 mA cm^{-2}) when nano-sized nickel was used as anode [7]. However, an OCV of 0.65 V and maximum current density of 6 mA cm^{-2} for 1 M urea (Fig. 5a) was observed in our new experiments with nano-sized nickel catalyst. The enhanced performance is due to the well controlled relative humidity at the cathode. The relative humidity (RH) of the cell was measured at 100% RH in new experiment while RH was not controlled in previous study. High RH at the cathode is definitely required to achieve good performance because water is a reactant at the cathode in order to form OH$^-$ ions.

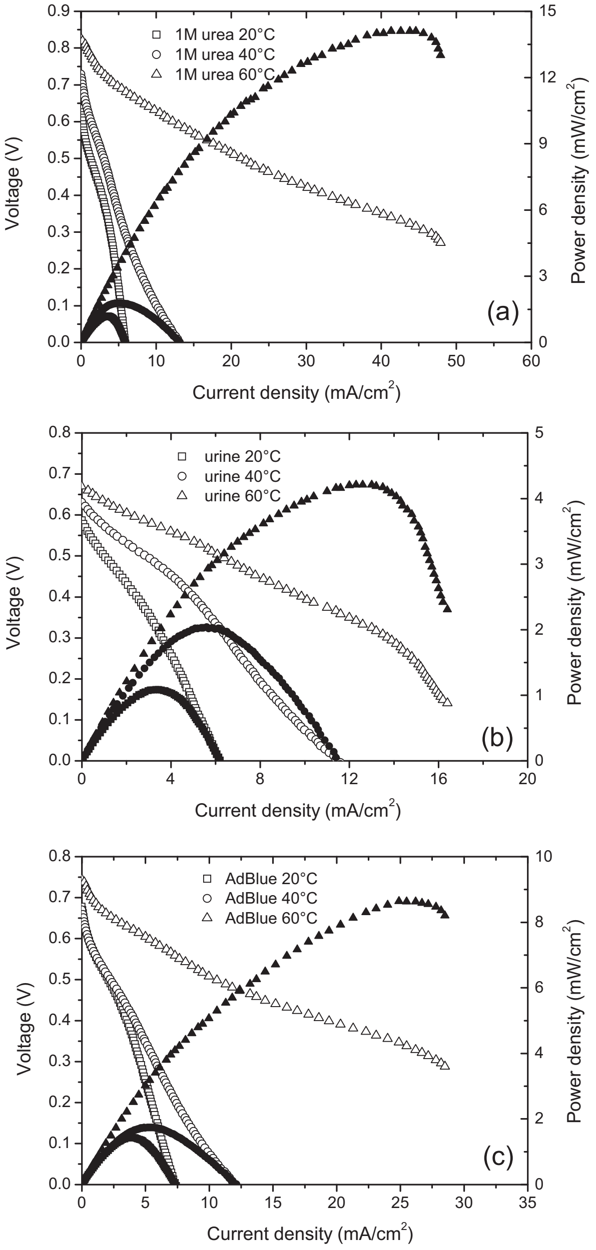

Fig. 5. Urea (a) and urine (b) and AdBlue (c) fuel cell performance using a nano-sized nickel as an anode catalyst.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

The performance of urea fuel cell is better at higher temperature but the power density is still relatively low (Fig. 4a). Comparable

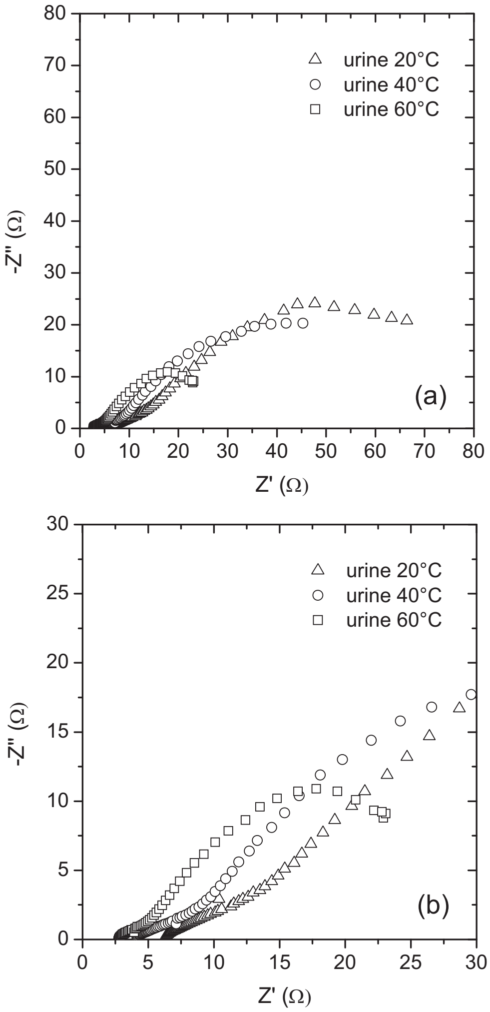

Fig. 6. a.c. impedance of urine fuel cells at different operating temperatures (a) and enlarged plot at lower resistance (b).

performance has been achieved when urine was used as fuel in the fuel cell (Fig. 4b) indicating that urine could be a good fuel for renewable power generation. Commercial nickel can be used as an anode catalyst in urea/urine fuel cells but the catalytic activities are not ideal.

As shown in Fig. 5, much better performances have been achieved when nano-sized nickel was used as an anode catalyst. It was found that the OCVs increase at higher working temperatures. This is believed to be due to the better catalytic activity of the electrodes. At 60 °C, an OCV of 0.83 V was achieved which is closer to the theoretical OCV at 60 °C (1.14 V). A maximum power density of 14.2 mW cm^{-2} at a current 43 mA cm^{-2} was observed at 60 °C. When urine was used as the fuel, the performance is comparable with 1 M urea at 20 and 40 °C but lower at 60 °C (Fig. 5b). Comparable performances between 1 M urea and urine were also observed in the previous study when the cell was operated at room temperature. The urea concentration in urine is about 2.5 wt% which is about half of that in 1 M urea (~6 wt%). The effect of urea concentration on urea fuel cells becomes significant at higher operating temperature when a large current/power density is achieved which means more fuels are required to be converted into electricity.

A maximum current density of 4.23 mW cm^{-2} at current density 12.6 mA cm^{-2} was observed for urine fuel cells when operating at 60 °C. A power of 42 W m^{-2} can be achieved when this urine fuel cell is used for waste water treatment. At the moment, research on microbiofuel cells for waste water treatment is very popular and promising [18]. The development of direct urine can provide an alternative solution to treatment for urea-rich waste water.

AdBlue, the commercial available urea solution was also tested in Cell B. As shown in Fig. 5c, an OCV of 0.75 V was observed at 60 °C, which is between those for 1 M urea and urine. It appears that the OCV is not only related to the catalysts in electrode, but also related to the fuel concentration. Slight lower OCV was observed for AdBlue (~5 M urea) than 1 M urea which is not usual and needs further investigation. A maximum power density of 8.65 mW cm^{-2} at current 25.6 mA cm^{-2} was observed when the operating temperature was 60 °C. For the tested three fuels, the best performance was exhibited with 1 M urea solution. Relatively lower concentration urea solution exhibits higher performance which was also observed in our previous experiments, was attributed to the large size of the molecule urea but cannot rule out the other possibilities [7]. Further optimisation to achieve a higher power density is required for transport applications.

The a.c. impedance spectra of urine fuel cells are shown in Fig. 6. It was found that the major resistance of the cell is due to the electrode polarisation (R_p) which were 86, 68 and 25 Ω cm^2 at 20, 40 and 60 °C, respectively when measured at open circuit voltage. The series resistances (R_s) which include the ohmic resistance of the membrane, electrodes, electrode/membrane interfaces and other contact resistance were 6, 4 and 2.8 Ω cm^2 at 20, 40 and 60 °C, respectively. Both R_s and R_p need to be reduced for practical application. For stationary applications such as waste water treatment, high power density is not required. Reasonably low overall resistance can be achieved on reduction of R_p through electrode optimisation by tailoring the microstructure and composition.

4. Conclusions

It was also found that nano-sized nickel is a key material to achieve better performance for urea and urine fuel cells. Nano-sized nickel with primary particle size 2–3 nm was successfully synthesised and used as an anode catalyst for fuel cells. Much higher performance has been achieved compared to cells using commercial fine nickel powers an anode catalyst.

Based on the previous communication, the performance of urea and urine fuel cells has been further improved when the relative humidity at the cathode was 100% while RH was not controlled in previous report. A maximum power density of 14.2 mW cm^{-2} (or 142 W m^{-2}) was achieved when 1 M urea was used as fuel, humidified air as oxidant. A power density of 4.23 mW cm^{-2} (or 42 W m^{-2}) is achieved at 60 °C for direct urine fuel cell, which makes it promising for urea-rich waste water treatment. Fuel cell performance was improved at higher operating temperatures due to decrease in both series and polarisation resistances. a.c. impedance measurement indicates that the major resistance of the cell is from the electrodes. Although the power densities of urea and urine fuel cells have been improved but certainly further development is required for stationary power generation and transport applications.

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