

Materials and Methods

Electrode Preparation

All chemicals and supplies were high purity (> 99.9%) and supplied from Alfa Aesar or Fisher Scientific. For anodic catalyst selection, 5 cm² titanium foil (0.127 mm thick) was used for working electrode substrates. Nickel foil (5 cm² 0.127 mm thick) was used for nickel oxyhydroxide modified nickel electrode (NOMN) substrates. Titanium wire (0.25 mm diameter) was connected to the working electrode substrates by cutting a small 1 mm slit in the foils and penetrating the Ti wire through the electrode. Pliers and a hand press were used to secure the connection. After constructing the anodes, the electrodes were rinsed with acetone and HPLC-grade ultrapure water. They were dried in an oven, and the electrode weights were recorded in order to determine catalyst loadings. Platinum foil counter (25 cm²) was used for both electroplating and testing the anodes. The Pt-foil cathode was constructed similarly to the anodes.

Catalyst Deposition

Table S1 shows catalyst plating conditions. The concentration of each metal in the bath was 160 mg L⁻¹. All of the salts were 99.99% pure from Alfa Aesar. Deposition potentials were experimentally determined using cyclic voltammetry using the setup in Figure S2. All electrodes in this study were plated potentiostatically with this same setup. A 2.5 cm stir bar at 60 rpm kept the bath solutions mixed during experimentation minimizing concentration gradients. Koslow Scientific supplied the Ag/AgCl reference electrode (+0.2224 V versus SHE) supported by a home-made Luggin capillary filled with its respective electrolyte. The tip of the Luggin capillary was placed 1 mm from the center of the working electrode. Platinum foil (0.01 cm thick, 99.999% pure from ESPI Metals) acted as the anode for plating except in the case of Ni, which utilized Ni foil (0.127 mm thick). The Ni electrode was plated using the common Watts bath (1). All of the plating solutions prepared here were solvated with ultrapure high performance liquid chromatography (HPLC) water.

Table S1. Electrocatalyst plating conditions

| Metal | Anode (foil) | Electrolyte | Salts | Temperature (°C) | Plating Potential (V versus Ag/AgCl) |
|-------|--------------|-----------------------------------|---|------------------|--------------------------------------|
| Rh | Pt | 1 M HCl/HPLC | RhCl ₃ ·3H ₂ O | 78 | -0.12 |
| Pt | Pt | 1 M HCl/HPLC | H ₂ PtCl ₆ ·6H ₂ O | 78 | -0.12 |
| Pt-Ir | Pt | 1 M HCl/HPLC | H ₂ PtCl ₆ ·6H ₂ O + IrCl ₃ ·3H ₂ O | 78 | -0.12 |
| Ni | Ni | 0.5 M B(OH) ₃ /HPLC | NiSO ₄ ·7H ₂ O + NiCl ₂ ·6H ₂ O | 45 | -0.80 |

Activation

A variety of procedures can be employed to activate a nickel electrode to the NOMN form (2-4). The activation solution used here consisted of nickel sulfate (0.05 M), sodium acetate (0.10 M) and sodium hydroxide (0.005 M). The activation was affected by holding the nickel electrode at 6.25 A m⁻² galvanostatically with a stainless steel counter electrode at 33°C. Polarity switching was employed such that the nickel electrode was used as the anode and cathode twice each for one minute. The same

nickel electrode was then held as the anode and cathode for two minutes each, before two hours of further activation with the nickel kept as the anode.

Product Analysis

GC

The gaseous products at each electrode were collected separately using a Hoffman electrolysis apparatus (Fisher Scientific) filled with 0.33 M urea and 5 M KOH. A potential of 1.5 V was applied with an Arbin BT2000 potentiostat for 22 hours to allow for sufficient gas production. The anode was a 20 cm² Ni foil (99.99% pure) that was deposited with 34.0 ± 0.1 mg of Ni and activated to form a NOMN electrode. The cathode was a 25 cm² Pt foil (99.999% pure). A 10 mL gas sample was extracted from each column and injected into the GC (SRI 8610 multi-gas) sample loop to ensure removal of any residual gases. Finally, 0.1 mL from the sample loop was then injected onto Haysep and mol sieve columns with a TCD detector.

Urea determination

Six urea standards of different concentrations were prepared in the range of 0.10 to 0.33 M urea in 7 M KOH. The solutions were sealed in 250 mL brown plastic bottles and heated at 70°C for 22 hours. The bottles were then allowed to cool to room temperature for 5.5 hours. Each bottle was then opened and allowed to equilibrate with air for exactly one minute before extracting 1 mL with a volumetric pipet and diluting to 100 mL. A 45 mL aliquot of each diluted solution was treated with 1 mL pH adjusting solution and tested with an ammonia ISE (Ion-selective electrode, Orion 9512 Ammonia Electrode) for determination of ammonia concentration in ppm. These results were compiled to create a calibration curve for urea determination (Figure S3). An exponential curve fits the data points with R² value of 0.9966, meaning that 99.7% of the variation in NH₃ concentration can be explained by the variation in urea concentration with the exponential relationship.

Supporting Figures

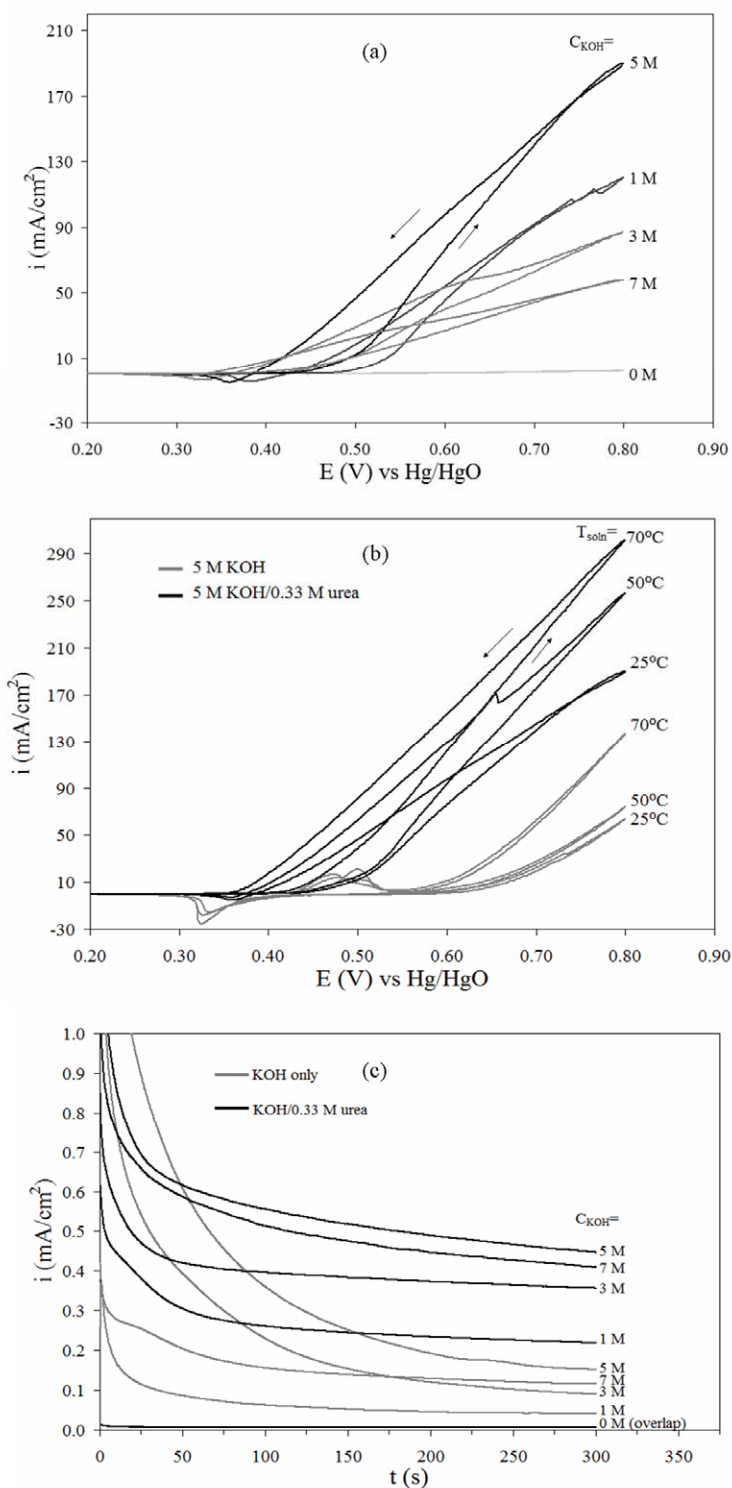


Figure S1. Operating conditions effects on electrooxidation of urea. Effect of (a) KOH concentration on CV behavior, (b) Temperature on CV behavior, and (c) KOH concentration on potentiostatic performance.

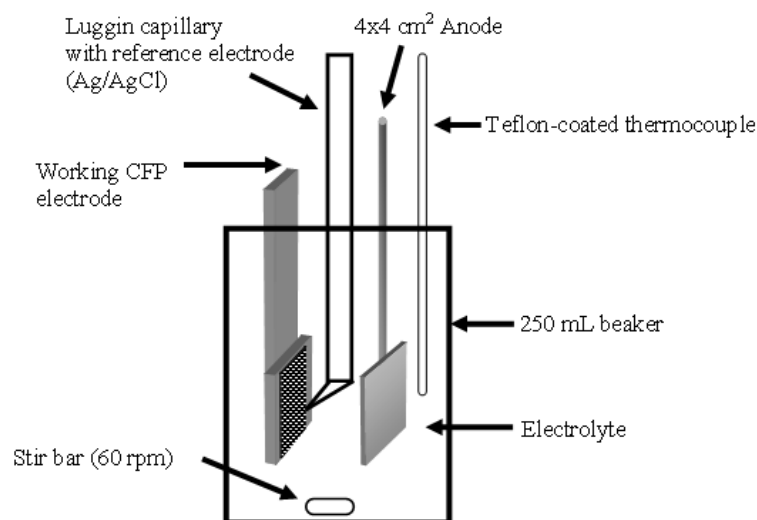


Figure S2. Plating setup. A Luggin capillary was used for cyclic voltammetry plating potential determination and was removed for electrodeposition.

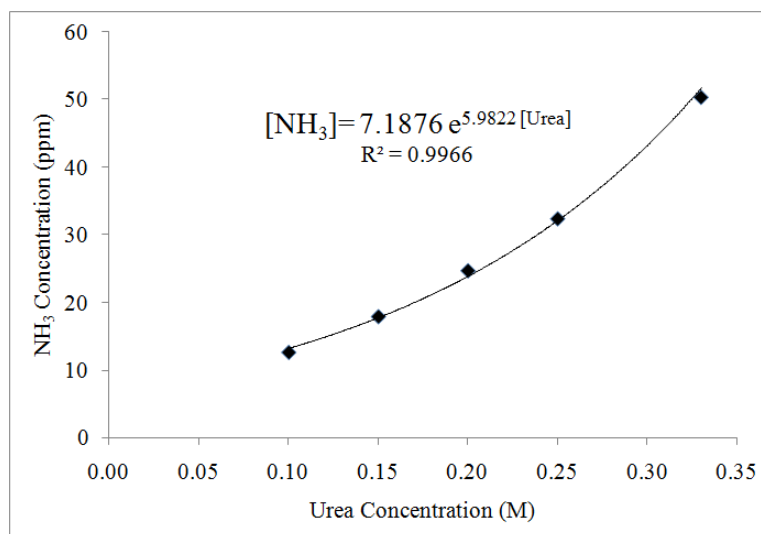


Figure S3. Calibration Curve for determination of urea concentration.

Urea versus Urine

In order to demonstrate that the oxidation of urea is similar to that of human urine, a cyclic voltammetry comparison was made using 3 different electrolytes. First, a baseline comparison in 1 M KOH was made followed by a solution of 1 M KOH with 0.33 M urea. Finally, a solution consisting of 1 M KOH and human urine was tested and compared. The anode was 2 cm x 2 cm 100-mesh Ni gauze that was sandblasted with a 2 cm x 2.5 cm 0.4 mg/cm² Pt on carbon paper cathode. The CV was conducted at room temperature with a 10 mV/s sweep rate from 0 to 0.8 V versus Hg/HgO reference electrode. It can be concluded that human urine oxidizes similarly to a solution of synthetic urine composed of urea.

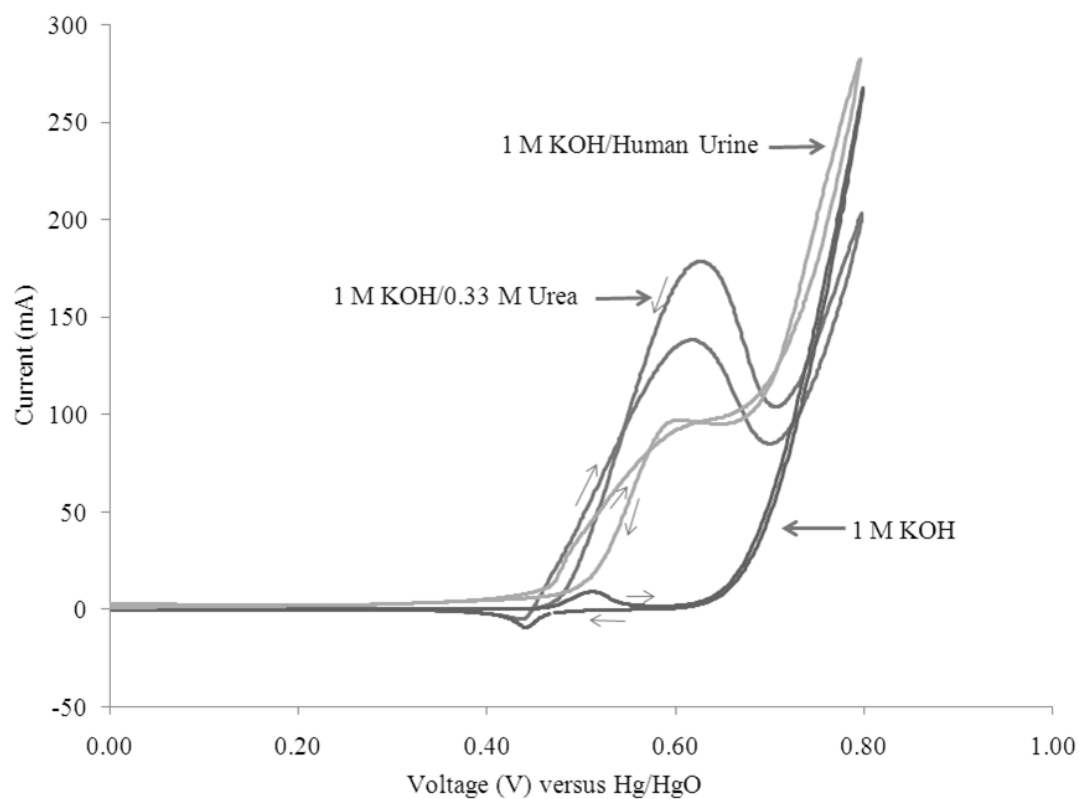


Figure S4. Cyclic voltammogram comparison of oxidation of synthetic urine (as urea) to that of human urine.

References

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2. A. S. Vaze, S. B. Sawant, V.G. Pangarkar, *J. Appl. Electrochem.*, 1997, **27**, 584-588.
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