

## Urea-based Fuel Cells on Paper with Micro-Watt Power Generationto Drive Low Power Circuits

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## Abstract

This work demonstrates the application of a urea-powered paper-based fuel cell (PFC) with Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) as the oxidant to drive a flexible electronic circuit (ring oscillator (RO)), for the first time. Herein, the electrochemical performance of membraneless PFCs is studied by employing different non-precious electrodes, such as, Nickel-mesh, Toray carbon paper(CP) and Nickel Cobalt nanoparticles supported on reduced Graphene Oxide loaded on the CP (NiCo@rGo@CP). A single-PFC with Ni-Co@rGo@CP as electrodes delivers a peak power density (P<sup>max</sup>) of 55 µW cm<sup>-2</sup>, maximum current density (J<sup>max</sup>) of 371 µA cm<sup>-2</sup> and an open-circuit voltage (OCV) of 0.7 V at 3 M urea. A membrane-based PFC assembled onto an anion exchange membrane with Ni-Co@rGo@CP electrodes, delivers a P<sup>max</sup> of approx 70 µW cm<sup>-2</sup>, J<sup>max</sup> of  $\approx$  500 µA cm<sup>-2</sup> and an OCV of 0.7 V at 3 M urea. Subsequently, a stack of two membrane-based PFCs delivers an OCV of  $\approx$  1.4 V for 400 seconds. Finally, this stack is employed as a power source to drive a RO. The measured frequency and peak-to-peak voltage are 37.52 kHz and 1.04 V, respectively. This demonstration opens a window to implement self-contained flexible electronic system using PFC as power source with minimal e-waste.

## 1. Introduction

The evolving landscape of circuits and systems developed using emerging flexible technologies demands for compatible power sources with inherent flexibility, such as thin film batteries [1, 2]. These batteries encounter limitations, in terms of spatial requirements and restricted flexibility. Moreover, for development of disposable point-of-care (POC) digital devices (digital pregnancy test kits, glucometers, uric acid meters) integrated with flexible electronics, the use of thin-film batteries can lead to significant e-waste generation which can impact the human health and environment [8]. The primary use of these batteries in these devices is to drive their micro-electronic circuits and power the visual display (LCD). Typically these require, low-scale (µW to few mW) of power for their functioning. This implicates that the energy stored in the batteries will be under utilized, if they are employed in the above mentioned POC devices, which consume low-scale power for their operation and are meant for a few uses. To this end, paper-based fuel cells (PFCs) are being explored as prospective power sources for low-scale powering applications, besides being a clean-energy source, as paper is biodegradable. The PFCs have several advantages associated with them, such as, easy availability, flexibility, porosity and low-cost [3, 4]. The porous nature of the paper facilitates the self-pumping of the fluids in the paper by the virtue of the capillary forces existing in the network of the cellulosic fibres of the paper [5, 6]. Thus eliminating the need for ancillary pumping mechanisms [7] and making them suitable for the development of portable power sources. Additionally, if the micro-electronic circuits are implemented on flexible substrates and can be driven by PFCs, this integration of the PFC-power source and flexible electronic circuits can lead to the development of flexible and disposable versions of the existing battery-operated diagnostic devices. This can aid in the upliftment of healthcare in low-resource settings by providing quick, easy and affordable diagnosis of common health conditions. So far, methanol [10], hydrazine hydrate [11], hydrogen gas (generated in-situ) [7], formic acid [5], formate [12] and hydrogen peroxide [13, 14] have been employed as fuels in different

PFCs. The typical range of the reported peak power density is 0.5 mW cm<sup>-2</sup> to 100 mW cm<sup>-2</sup> [7]. While, these PFCs have demonstrated promising cell performances, their integration with analytical systems would be more advantageous, if the fuel is bio-compatible with the system. For instance, developing PFCs as a power source for analytical devices, wherein the sample for the analysis serves as the fuel for driving the fuel cell (power source). Merino-Jimenez et. al have reported the working of a self-powered minimalist glucometer, wherein a microbial PFC drives the whole device with the sample (blood) serving as the fuel [15]. In this context, urine is an important biological fluid that contains vital bio-markers such as urea. To this end, urea-based PFCs can play a significant role in the development of self-powered electrochemical sensors for urine based analysis. Therefore, urea can be considered as a promising fuel as it can be sourced from human urine [16, 17], which is commonly used as a sample/ reagent for performing diagnostic analysis in healthcare. Urea has an energy density of 16.9 MJ L<sup>-1</sup> while being nontoxic, non-flammable, easy to store and transport (solid form) [18]. It is also commonly found in industrial effluents/ waste water of fertilizer plants [11-12]. The application of urea as a fuel has been investigated in direct urea-based fuel cells (DUFC), wherein power density upto 38.15 mW cm<sup>-2</sup> has been achieved at 0.5 M urea at room temperature [19]. Generally, anion exchange membranes are employed in DUFCs to facilitate the transportation ionic (OH<sup>-</sup>) species in membrane-based systems. However, introducing an appropriate electrolyte, such as, NaOH and KOH, which contain OH<sup>-</sup> ions, into the fuel (urea) aids in the ion migration and imparts ionic conductivity in membraneless systems. Recently, the development of PFCs powered by urea [20, 21] and urine [22] has been investigated elaboratively by researchers. However, there are only two reports highlighting the practical demonstration of these fuel cells by powering the display of a digital pregnancy test kit [20, 22]. While the results obtained in these works are highly encouraging, the use of noble-metals, such as AgNO<sub>3</sub> and Pt in the PFCs, limits their practical feasibility, as multiple such cells consisting of the noble metals need to be coupled to obtain the desired voltage (>1 V). However, the use of these noble metal catalysts can compromise the vision of the development of cost-effective and affordable paper-based energy devices. Nevertheless, these findings clearly validate the idea of developing PFCs as a disposable, on-board power source in analytical systems. Further, studies relevant to the practical ability of the PFCs to drive an existing (micro) electronic system on a flexible substrate are quite limited [15].

Therefore, in order to develop cost-effective PFCs, it has to be ensured that the electrode is free of prtecious metals. Pt, Pd, Ag and their bimetallic alloys with other metals, such as Ni, have shown good electrocatalytic activity towards urea electro-oxidation [23–25]. Alternatively, non-noble metals, such as nickel (Ni) and cobalt (Co) have shown good catalytic activity towards the electrochemical oxidation of urea [26–28]. Further, doping Ni with Co can enhance the active sites and reduce the onset potential [29], thereby improve the electrocatalytic activity of Ni-Co composite catalysts. The incorporation of a suitable carbon-based support, such as, rGo can further improve the overall electrnoic conductivity, surface area and dispersion of the catalysts [30, 31]. Hence Ni-Co catalysts supported on rGo can be suitable for the electrochemical oxidation of urea and subsequently, serve as electrodes in urea-powered PFCs. Keeping in view the advantages of PFCs as a power source, urea as a fuel, Ni-Co supported on rGo as composite catalysts and integration of PFCs to drive flexible electronic circuits; the present work reports the

development and characterization of urea-powered PFCs with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidant. Membraneless and membrane-based configurations of the PFC have been employed with different electrodes, such as, CP, Ni-mesh and Ni-Co@rGo for the comparison of the electrochemical performance of the cells. The PFCs with Ni-Co@rGo electrodes delivered the maximum power density at 3 M urea. The practical utility of the PFC was demonstrated by employing it as a power source to drive an 11-stage ring oscillator (RO) implemented using oxide TFTs on a polyimide substrate, for the first time. RO circuit is ubiquitous in all electronic systems like analog to digital converters (ADCs) [32], signal processing units [33] communication systems [34], PLLs [35] and microprocessors [36]. This demonstration and integration of the PFC with flexible RO highlights their ability to be implemented as a power source in flexible electronic systems.

# 2. Experimental

# 2.1. Chemicals

Urea (NH<sub>2</sub>CONH<sub>2</sub>), 30 wt% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O), cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O), isopropyl alcohol (IPA), graphite powder, hydrazine hydrate, sodium hydroxide (NaOH), were procured from Merck (Sigma Aldrich. Acetone, ethylene glycol and toluene were purchased from Finnar. Whatman filter paper (ashless, grade 42) was used as the scaffold for PFCs. Toray carbon paper (CP), Nickel mesh (Ni-mesh) and anion exchange membrane were purchased from Sainergy Fuel Cell. Ultrapure water was obtained from Millipore system. Oxide-based RO fabricated on a 30  $\mu$ m thick polyimide substrate using a commercial fab-in-a-box process. The thin film deposition process used in fabrication consists of a combination of physical vapour deposition and atomic layer deposition. More details on the fabrication can be found in [37, 38].

# 2.2. Instrumentation and Characterization methods

The electrochemical measurements were carried out using an electrochemical analyzer,

CHI604E, CH Instruments. The measurement of the electrochemical performance of the PFCs was done via chronoamperometry (I vs t) and chronopotentiometry (V vs t), while the catalysts rGo and Ni-Co@rGo were characterized via cyclic voltammetry (CV). The structural characterization of the as-prepared catalysts, rGo and Ni-Co@rGo were done via Zeiss Scanning Electron Microscope (SEM). The frequency response and peak-to-peak voltage measurement of the RO were performed using a Mixed Signal Oscilloscope-MSO2012B, Tektronix.

## 2.3. Cell construction and assembly

A schematic and photograph of the membraneless PFC and membrane-based PFC are shown in Fig. 1 (a), (b) and (c),(d), respectively. The membraneless U-shaped PFCs were constructed by using Whatman filter paper as the substrate.

As a first step, the paper was cut into a rectangular shape strip of dimensions 7 cm X2 cm. A gap of dimensions 3.5 cm X 0.5 cm is introduced at the center of the paper strip, giving it a Ushape. This strip was then placed on a glass slide. The electrodes (CP, Ni-mesh, Ni-Co@rGo@CP) used in the experiments have a geometric area of 0.25 cm<sup>2</sup> and were placed each side of the Ushape strip to serve as the anode and cathode. Stainless steel plate (SS) served as the current collector. This cell assembly was referred as the membraneless PFC.

The membrane-based PFC was constructed by simply replacing the glass slide with an anion exchange membrane as the base of the cell, while keeping the arrangement of all the other components same. 1 M NaOH with x M urea (x = 1, 2, 3, 4, 5) and 30 wt%  $H_2O_2$  served as the anolyte and catholyte, respectively, in all the experiments. Each experiment consumed 30–40 µL of anolyte and catholyte, which were dropped manually near the electrodes using a hand held micropipette.

# 2.4. Synthesis of rGo and Ni-Co@rGo

Graphene oxide (Go) was synthesized according to the Hummer's method and subsequently rGo was synthesized following a procedure reported elsewhere [39]. First, a homogeneous dispersion was obtained by ultrasonication of Go in DI water (1 mg/ml) for 1 hour at a temperature less than 50 °C. The dispersion was then mixed with 2 mL of hydrazine hydrate and pH was adjusted to 10. The solution was kept in a hot air oven at 90 °C for 24 hours. Later, the as-prepared flakes of rGo were washed several times with ethanol and DI water. Finally, this was left for drying in a hot air oven at 60 °C for 24 hours. The final product obtained in the form of flaky black powder was referred as rGo. The Ni-Co@rGo nanocomposite was synthesized following an approach reported elsewhere [40]. First a solution was prepared by dispersing 50.0 mg of GO, 49.9 mg of NiCl<sub>2</sub>.6H<sub>2</sub>O, and 50.0 mg of CoCl<sub>2</sub>.6H<sub>2</sub>O in 150 mL of ethylene glycol (EG), keeping the molar ration of Ni:Co = 1:1. This solution was then subjected to ultrasonication for 1 hour to form a uniform dispersion. The resultant dispersion was subjected to a temperature of 110 °C in an inert (argon) atmosphere, resulting in an yellow-coloured solution. Further, a solution of 25 mL of hydrazine hydrate dissolved in NaOH (1 g) was added continuously, followed by 45 minutes of refluxing at 110 °C. The black product formed was then centrifuged, washed with copius amounts of water and ethanol to remove impurities. Finally, the product is dried in a vacuum oven at 45 *о*С.

The final black-coloured product thus obtained was referred as Ni-Co@rGo. To prepare the catalyst ink, 5 mg of catalyst was taken in 5 ml of DI water and sonicated for uniform dispersion. The catalyst ink was then drop-casted onto Toray Carbon paper and Glassy Carbon electrode, which are subsequently dried for 4–5 hours.

# 2.5. Fabrication of the Ring Oscilator

The RO was fabricated on a 30 µm thick polyimide substrate using a fab-in-a-box process with a-IGZO as the semiconductor [41]. The schematic and the microphotograph of the fabricated RO are shown in Fig. 1 (e) and (f), respectively.

## 3. Results and Discussions

# 3.1. Structural and Electrochemical Characterization of rGo and Ni-Co@rGo

The surface and morphological properties of rGo and the Ni-Co@rGo composite was analysed by SEM and the corresponding micrographs are presented in Fig. 3 (a), (b) and (d), (e) respectively. The images obtained for rGo at low and high magnification, Fig. 3 (a) and (b), respectively, show agglomerated, flaky and rough surface structure, indicating the expanded graphite layers in rGo. The rough surface morphology present in rGo is due to the exfoliated sheets which occurs during the oxidation of graphite to Go. The presence of C and O is shown in the EDX analysis Fig. 3 (c) of the rGo samples. The presence of oxygen could be due to the residual O-atoms which were not completely removed during the reduction of Go. The growth of the bimetallic Ni-Co nanoparticles on to the sheets of rGo is depicted in the micrographs Fig. 3 (d) and (e). It can be inferred from the micrographs that the agglomerated nanoparticles have a spherical, bead-like structure and adhere to the surface of the rGo in a non-uniform pattern. The average diameter of the bimetallic nanoparticles is  $\approx$  50 nm. The EDX analysis Fig. 3 (f) confirms the presence of C, O, Ni and Co in the Ni-Co@rGo compsoite. Fig. 3. The electrochemical characterization of CP, Ni-mesh and Ni-Co@rGo was studied by CV and the voltammograms are shown in Fig. 2. The working electrodes were CP, Ni-mesh with an electrode area of 0.25 cm<sup>2</sup>, each and Ni-Co@rGo drop casted onto GCE with an electrode area of 0.071 cm<sup>2</sup>. Pt rod and Ag/ AgCl served as the counter and reference electrodes, respectively. The analyte consisted of 1 M urea and 1 M NaOH.

The potential was swept, forward and reverse, between 0 V to 0.8 V at a scan rate of 50 mV/s. The CP based working electrode shows minimal catalytic activity with a total peak current density of  $\approx$  5 mA cm<sup>-2</sup>.

The voltammogram of Ni-mesh shows a broad oxidation peak at 0.5 V and a reduction peak at 0.4 V, which can be attributed to the formation of the surface-adsorbed intermediates, NiOOH and Ni(OH)<sub>2</sub>. In alkaline media, OH<sup>-</sup> ions get adsorbed to the surface of the nickel-based electrode and form Ni(OH)<sub>2</sub>, which further undergoes oxidation to form NiOOH. During the reverse sweep, NiOOH gets reduced back to Ni(OH)<sub>2</sub> [42]. The NiOOH intermediate species, wherein, Ni exists in the +3 oxidation state, primarily facilitates the electro-oxidation of urea [31].

The voltammogram of Ni-Co@rGo shows two well-defined oxidation-reduction peaks at 0.35 V and 0.2 V, respectively, wherein, the onset potentials of the formation of NiOOH and urea oxidation overlap with each other at  $\approx 0.3$  V, which typically occurs at 0.356 V [43] in alkaline medium. This has also been observed in the CV profiles obtained in this work, as shown in Fig. 2. This indicates that the NiOOH species were able to successfully catalyze the electro-oxidation of urea. The increase in the current density towards the attainment of the switching potential, i.e., at 0.8 implicates the diffusion of the OH<sup>-</sup> ions from the bulk solution towards the electrode surface, which still has available area to form more

surface adsorbed intermediate hydroxide species. In addition, the incorporation of Co in the composite enables reduction in the onset potential of conversion of Ni(OH)<sub>2</sub> to NiOOH by adding surface defects on Ni and thus providing more active sites on Ni [29] to aid in the urea electro-oxidation. In addition to this Co also enhances the overall electronic conductivity of the composite, which leads to the increase in the current density, as depicted in the CV profiles obtained for Ni-Co@rGo (2. Further, it has been reported that Co can aid in the suppression of the undesired oxygen evolution reaction [44]. An oxidation peak current density of  $\approx$  90 mA cm<sup>-2</sup> obtained with Ni-Co@rGo as the working electrode explains its good catalytic activity towards the electro-oxidation of urea, which were employed as the one of the sets of electrodes in the proposed PFCs in this work. These PFCs could deliver the maximum OCV, current density and power density were obtained as compared to other electrodes (CP and Ni-mesh).

# 3.2. Electrochemical Performance Measurement of the urea-powered PFC

The cell geometry and the assembly of the membraneless and membrane-based PFCs are presented in Fig. 1 (a) and (c). The analyte containing variable concentrations of urea with 1 M NaOH, and the catholyte consisting of 30 wt%  $H_2O_2$  are self-absorbed into the PFC when dropped (manually) near the anode and cathode, respectively. The electro-oxidation of urea is a 6e<sup>-</sup> release process and occurs at the anode in accordance to equation 1 [45], as shown below:

$$CO(NH_2)_2 + 6OH^- \rightleftharpoons N_2 + 5H_2O + CO_2 + 6e^-, E_o = -0.75V$$
 (1)

The electrons produced at anode travel through the external circuit (connecting wires) and react with  $H_2O_2$  (oxidizing agent, catholyte) to furnish  $OH^-$  ions, as per equation. 2 [46].

$$H_2O_2 + 2e^- \rightleftharpoons 2OH^-, E_0 = 1.04V$$
(2)

The overall theoretical cell potential is  $\approx 1.79$  V, which is seemingly promising in order to generate electrical energy from the above mentioned fuel-oxidant (urea-H<sub>2</sub>O<sub>2</sub>) pair. However, the experimental open-circuit voltage (OCV) of the urea-powered PFCs was found to be to be much lower than the theoretical OCV, as can be seen in Fig. 4(a)-(d). It is noteworthy that the OCVs are significantly lower than the theoretical OCV across all the PFCs due to the prevalent overpotential losses [20] arising due to sluggish reaction rates. Another important reason that can be highlighted here, is the low fuel utilization in the paper-based fuel cells. Paper is anisotropic due to the random arrangement of the fibres of cellulose and this impacts rate of transportation of reacting species towards the electrodes as well as the removal of the by-products away from the electrodes. The above mentioned reasons are majorly responsible for the low OCV of the PFCs. Prior to evaluating the electrochemical performance of the PFCs, the OCVs were measured across different cells at varying urea concentrations (1 M - 5 M) in 1 M NaOH. Herein, three different electrodes, i.e., CP, Ni-mesh and Ni-Co@rGo@CP, were employed in the membrane-based PFC. The OCV for

each case recorded for a period of 200 seconds at 1 µA current input. The lowest OCV was recorded for the PFC with CP-electrode, which varied from 0.4 V to 0.5 V, as shown in Fig. 4 (a) at different urea concentrations. The rest of the cells delivered nearly same OCV varying between 0.7 to 0.6 V at different urea concentrations. It was observed that all the PFC (except the PFC in Fig. 4(a)) delivered the maximum OCV of at 3 M urea concentration, consistently. The cell voltage was nearly stable across all cell configurations upto 4 M urea but experiences a dip in the voltage at 5 M urea. Ideally the cell voltage is expected to increase with increasing fuel concentration, according to the Nernst equation, given by equation 3.

$$E = E_{o} - \frac{RT}{nF}$$

where R is the universal gas constant, F is the Faraday constant, n is the amount of electrons transferred in mol, T is the absolute Kelvin scale temperature, and Q is the reaction quotient [47]. However, at higher urea concentrations (4 M and 5 M) the phenomenon of fuel cross over (mixing of the anolyte and catholyte) is more apparent in the present configuration of the PFCs, since there is no physical barrier between the electrodes. The separation between the electrodes is ensured by the slit between them, which cannot eliminate the fuel cross-over totally. Inferior, OCV was also observed at low urea concentrations (1 M) which can be attributed to low fuel availability. The membrane-based PFC with Ni-Co@rGo@CP delivered consistent and stable OCV at 2 M, 3 M and 4 M urea, as shown in Fig. 4 (d).

(3)

The electrochemical performances of the PFCs were investigated with the current-voltage (IV), i.e., polarization studies. The IV studies were carried out via chronopotentiometry, by stepping up the current density from  $\approx 2 \,\mu\text{A cm}^{-2}$  to its limiting (maximum) value and subsequently measuring the resulting voltage for 50 seconds, each time. As shown in Fig. 4, the cell voltage was stable in the first 50 seconds for all the configurations. The membraneless PFC with CP electrodes (anode and cathode), Fig. 4 (a), delivered a ( $P^{max}$ ) of 7  $\mu$ W cm<sup>-2</sup> and ( $J^{max}$ ) of 78  $\mu$ A cm<sup>-2</sup>. This indicates that the carbon paper-based electrode has no to minimal activity towards urea electrooxidation. When this was replaced with Ni-mesh as the electrodes (Fig. 4 (b)), the ( $P^{max}$ ) and ( $J^{max}$ ) increased to 45  $\mu$ W cm<sup>-2</sup> and 275  $\mu$ A cm<sup>-2</sup>, respectively. This can be attributed to the proven better electrocatalytic activity of Ni towards urea electrooxidation [26]. Next, Ni-Co@rGo composite nanotsructured catalysts were synthesized and loaded onto CP to serve as the electrodes (Fig. 4 (c)). The ( $P^{max}$ ) and ( $J^{max}$ ) delivered in this case were 55  $\mu$ W cm<sup>-2</sup> and 371 µA cm<sup>2</sup>, respectively. The enhancement in the cell performance is mainly due to the combined effects of Ni-Co nanoparticles and rGo, wherein doping Ni with Co, provides more active sites and rGo improves the surface area of the catalyst. Finally, the PFC was assembled onto an anion exchange membrane, with Ni-Co@rGo@CP electrodes resulting into a membrane-based PFC (Fig. 4 (d)). The ( $P^{max}$ ) and ( $J^{max}$ ) obtained from the membrane-based PFC were 70  $\mu$ W cm<sup>-2</sup> and 500  $\mu$ A cm<sup>-2</sup>, respectively, which were the highest among all the configurations. This is due to the fact that the anion exchange membrane facilitates the migration of OH<sup>-</sup> ions within the system and therefore the cell

performance improves in comparison to the membraneless PFCs. In addition to this, it can be seen from the IV-curves that maximum power density is attained at 3 M urea across all PFC configurations.

Further, the change in cell performance w.r.t urea concentration is consistent in all the PFCs. This implicates that the cell performances are reproducible. The inferior cell performance at 4 M and 5 M urea is possibly due to fuel cross over. This was also observed during OCV measurement studies, as shown in Fig. 4. The initial drop in the OCV is due to the sluggish kinetics which contribute to activation overpotential losses in the cell(s). This can be observed in the PFC performances, shown in Fig. 5 (b)-(d), where the activation losses are prevalent upto  $\approx 50 \ \mu A \ cm^{-2}$ . The electrochemical performance exhibited by the urea-powered PFCs, indicates that they can be used for harvesting energy from human urine as well, which is a good source of urea. This further suggests that urea/ urine powered PFC can serve as the power source in analytical devices for performing urine-based analysis and thereby rendering a selfpowered device which is capable of generating power from the sample (urine) itself. It is worth to note that this work is almost the first demonstration of an urea powered PFC with non-nobel metal based electrodes. Since the membrane-based PFC with Ni-Co@rGo@CP electrodes exhibited the best performance, it was employed for the demonstration of the practical utility of the PFC for driving flexible electronic circuits. Prior to this, a stack of two membrane-based PFCs was prepared by connecting them in series, in order to obtain the desired voltage (> 1 V) for driving the flexible electronic circuits. The stack delivered a nearly stable OCV of 1.4 V for a period of 400 seconds. The corresponding result is shown in Fig. 6 (a). Similarly, the limiting current density of the stack was also measured w.r.t time as shown in Fig. 6 (b). Initially, the stack delivered a  $J^{max}$  of 500  $\mu$ A cm<sup>-2</sup>, which is in-line with the performance of the single PFC (Fig. 5 (d)). However, after 100 seconds the current density of the stack starts declining due to the consumption of the fuel/ oxidant at the anode/ cathode. Nevertheless, the membrane-based PFC stack possessed the desirable range of OCV and current density for driving flexible electronic circuits (RO). The measurements and subsequent response of the circuits driven by the PFC have been discussed in the next section 3.3.

Urea Concentration	$V_{DD}(V)$	$V_{PP}(V)$	f (kHz)
(M)			
1	1.20	0.80	22.25
2	1.30	1.00	30.79
3	1.41	1.04	37.52
4	1.25	0.88	27.23
5	1.16	0.74	22.48

Table 1: Performance comparison of the proposed comparator

An 11-stage RO fabricated on a flexible wafer was driven the stack of two PFCs to demonstrate the PFC driving capability, as shown in Fig. 7. This setup shows the two-PFC stack, a multi meter measuring the

DC output voltage of the PFC stack, an RO (at wafer level) placed on a probe station and an oscilloscope showing the measured response of the RO. Fig. 8(a) to (e) show the RO response when it is driven by the PFC stack with x M urea concentration (where x = 1 to 5). Table 1 presents voltage generated by the PFC stack ( $V_{DD}$ ), RO output voltage peak to peak ( $V_{PP}$ ) value and frequency of oscillation (f) for different urea concentration levels. This has been also presented in Fig. 9, which can serve as the calibration curve between the measured frequency and urea concentration. A maximum f of 37.52 kHz and  $V_{PP}$  of 1.04 V were obtained at 3 M urea concentration. As it is expected from the functionality of the RO, f and  $V_{PP}$  are proportional to the  $V_{DD}$  generated by the stack of two PFCs under same loading condition. It can be noticed from Table 1 and Fig. 9, the whole setup can also be used as a sensor and readout circuit as the variation in the urea concentration is converted in to frequency. This setup opens a window for self-powered flexible POC devices to sense different bio-signals.

## 4. Conclusions

This work demonstrates the development of urea-powered PFCs and the experimental characterization of flexible electronics circuits driven by these PFCs under ambient conditions. Out of all the various cell configurations, the membrane-based PFC with Ni-Co@rGo@CP electrodes could deliver a ( $P^{max}$ ) of 70 µW cm<sup>-2</sup> with an OCV of  $\approx 0.7$  V. Activation overpotential losses and low fuel utilization in paper-based systems are generally responsible for low-scale (µW) power densities. A stack of two membrane-based PFC with Ni-Co@rGo@CP as electrodes could deliver a nearly stable OCV of 1.4 V and current density of 500 µA cm<sup>-2</sup> for 400 seconds. This stack could successfully drive an 11-stage RO, which was designed using a-IGZO TFT technology on a flexible polymeric substrate. The measured oscillating frequency and peak-to-peak voltage were 37.52 kHz and 1.04 V respectively at 3 M urea concentration. This demonstration evidently elucidates the serviceability of the urea-powered PFC with non-noble metal-based electrodes, as a power source for driving flexible electronic circuits and portable diagnostic/ sensing devices which employ these kinds of circuits that require low-scale power. When coupled together with appropriate sensing components, this can lead towards the development of self-powered flexible sensing systems driven by PFCs, powered by urea (a commonly occurring component in urine) for urine-based analysis.

# Declarations Author Contribution

SK: Experimental, Technical Investigations, Writing, Data Collection and analysis.SL: Writing, data Interpretation, data analysis, technical Investigation. SS: Experimental, Technical Investigations, Writing, data Interpretation,PG: Writing, data analysis, technical Investigation.

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## Figure 1

(a) Schematic and (b) Photograph of the urea-powered membraneless PFC. (c) Schematic and (d) Photograph of the urea-powered membrane-based PFC. Anode, Cathode: Ni-Co@rGo@CP. Anolyte: x M Urea (x= 1-5) + 1 M NaOH, Catholyte: 30 wt%  $H_2O_2$ . Current Collector: Stainless steel plate (SS) (e) Schematic and (f) Micro-photograph of the fabricated 11-stage RO.



Cyclic Voltammetry studies in 1 M urea and 1 M NaOH with Working electrodes: CP, Ni-mesh and Ni-Co@rGo@GCE, Counter electrode: Pt Rod, Reference Electrode: Ag/AgCl. Potential Scan rate: 50 mV/s. GCE: Glassy Carbon Electrode.



Scanning Electron Micrographs of (a) Reduced Graphene Oxide (rGo) and (b) selected area for EDX analysis of rGo (c) EDX analysis of rGo,Scanning Electron Micrographs of (d) Nickel-Cobalt nanoparticles supported on Reduced Graphene Oxide (Ni-Co@rGo), (e)selected area of Ni-Co@rGo selected for EDX analysis (f) EDX analysis of Ni-Co@rGo.



Cell open-circuit voltage measurement w.r.t time at 1  $\mu$ A current for Membraneless PFC with anode and cathode as (a) CP (b) Ni-mesh (c) Ni-Co@rGo@CP and (d) Membrane-based PFC with anode and cathode as NiCo@rGo@CP. Anolyte: 1 M urea+ 1 M NaOH. Catholyte: 30 wt% H<sub>2</sub>O<sub>2</sub>.



Polarization studies of Membraneless-PFC with(a) CP (b) N-mesh (c) Ni-Co@rGo@CP and (d) Membranebased PFC with anode and cathode as Ni-Co@rGo@CP. Anolyte: 1 M urea+ 1 M NaOH. Catholyte: 30 wt%  $H_2O_2$ .



(a) Cell open-circuit voltage measurement w.r.t time at 1  $\mu$ A current and (b) Limiting current density w.r.t time at 0.1 V operating voltage for the stack of two Membrane-based PFC. Anode and Cathode: Ni-Co@rGo@CP.

Anolyte: 3 M urea+ 1 M NaOH. Catholyte: 30 wt%  $H_2O_2$ .



Test set-up demonstrating the characterization of a 11-stage RO on a flexible substrate driven by a proposed stack of two-membrane-based urea-powered-PFC.



The circuit response from experimental characterization, when it is driven by the stack of twomembranebased PFCs at (a) 1 M (b) 2 M (c) 3 M (d) 4 M and (e) 5 M urea. Oxidant: 30 wt%  $H_2O_2$ . Anode, Cathode: Ni-Co@rGo@CP.



Frequency vs urea concentration calibration curve based on the frequency response of 11-stage RO driven by stack of PFC, anolyte: x M Urea + 1 M NaOH (x=1:5), Oxidant: 30 wt%  $H_2O_2$ . Anode, Cathode: Ni-Co@rGo@CP.