Paper based hydrazine monohydrate fuel cells with Cu and C composite catalysts

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Abstract

Self-pumping fuel cells supported on filter papers are constructed by using hydrazine monohydrate as a fuel and potassium permanganate as the oxidant. Cost effective catalysts, namely, Cu nanoparticles (NPs), functionalized multiwalled carbon nanotubes (f-MWCNTs) and Cu-NPs@f-MWCNTs composite are synthesized and loaded onto carbon cloths, which are employed as the electrodes. The cells are operated at room temperature. The Cu-NPs@f-MWCNTs composite contained 75% and 25% of Cu-NPs and f-MWCNTs, respectively. The morphology of the composite comprises of Cu-NPs flanked to the tubular structures of f-MWCNTs, which resulted in improved electrocatalytic activity, compared to pristine Cu-NPs (which tend to aggregate severely) and pristine f-MWCNTs. The electrocatalytic activities of Cu-NPs@f-MWCNTs and Cu-NPs are comparable and superior to f-MWCNTs for hydrazine oxidation. Multiple cells with different catalyst combinations at the anode and cathode are electrochemically characterized. The cell with Cu-NPs@f-MWCNTs composite at the anode and with f-MWCNTs at the cathode produced the highest power density of 3.57 mW/cm² at 0.89 V. For this catalyst combination, the cell retained an open circuit voltage between 1.85 V - 1.74 V for more than ten minutes of operation. Although the cell current density declined over time, it could be recovered to its original value by replenishing the cell with fresh anolyte and catholyte streams.

Keywords:

1. Introduction

Advances in nano-technology have led to the miniaturization of portable electronic and sensing devices, and hence to low power requirements. Some of these devices require power only in the range of nano to milli watts, and some do not require a continuous power supply. For instance, in biomedical and environmental monitoring, sampling rates of once every few minutes or even slower are adequate [1]. Low power consuming disposable biomedical and health monitoring systems require one-time electrical input for a few seconds to a few minutes. The use of batteries in these disposable devices is therefore highly uneconomical. Paper based fuel cells composed of low cost components are apt for fulfilling this one-time low power requirement, for they are not only cheap but also easily disposable.

While the early designs of fuel cells targeted high power density applications, fuel cell research has been witnessing a growing number of reports on the development of laminar flow membrane-less fuel cells, which are applicable in low power consuming systems. While the laminar flow cell eliminates the need of having a physical electrolyte membrane between the electrodes [2], their drawback is that they rely on precise manufacturing techniques, which are cumbersome. The ion transport in these systems is achieved by mixing the fuel and oxidant with appropriate electrolytes to form the anolyte and catholyte. Use of laminar flow fuel cells in sensing devices with filter paper supports for anolyte and catholyt transport have been recently demonstrated [3]. Filter papers can self transport the anolyte and catholyte to the respective electrodes and the mixing of these streams is confined to the liquid-liquid interface formed due to the laminar flow. However, cell performance deteriorates with time owing to eventual anolyte and catholyte cross over [4]. But this disadvantage is insignificant in view of the short duration of application of the cell. The self

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transport properties of paper eliminate the need for any metering devices for supplying the anolyte or catholyte to the electrodes. However, the identification of a fuel-oxidant pair capable of delivering high standard cell potential is critical to the performance of these cells. Since the anolyte/catholyte transport is achieved due to the inherent capillary effect of paper, the formation of the diffusion barrier layer and the rate of transport will depend on the viscosity and density of the fluids employed. The electrochemical performance is mainly decided by the electro-catalytic activity of the electrodes and the redox couple chosen. A large reduction potential difference between the fuel and oxidant is desirable for obtaining a high open circuit potential.

The anolyte and catholyte should possess high ionic conductivities for facile transport of the cations from the anode to the cathode or anions from the cathode to the anode. For instance, a laminar flow fuel cell with HCOOH as the fuel and H₂SO₄ saturated with O₂ as the oxidant was successfully demonstrated [5], where H₂SO₄ acted as the medium for the transport of H⁺ ions. In another example of paper based fuel cell using CH₃OH as fuel, KOH was used as the electrolyte phase for the transport of OH⁻ ions, which were formed at the cathode [3]. In these examples the electrolyte phase facilitates the transport of ions to the respective electrodes. Thus higher conductivities of the resulting anolyte and catholyte will result in lower Ohmic resistances and improved cell performances. A paper based Y-shaped cell with pencil stroked graphite electrodes and with HCOOH as fuel and O₂ (from air) as the oxidant was also reported in the literature [6]. Here also H₂SO₄ was used as the electrolyte. Without specifying the active electrode area, authors reported a maximum power density of ∼30 mW/cm², which appears to be surprisingly high for electrodes without any catalyst [6].

Among fuels such as CH₃OH, C₂H₅OH, HCOOH, H₂O₂ and hydrazine monohydrate (N₂H₄.H₂O), the latter is a promising candidate for application to laminar flow paper based fuel cells. The oxidation of hydrazine monohydrate leads to the formation of N₂ and H₂O, both of which are harmless to the environment. Moreover, hydrazine based fuel cells can operate at low temperatures and deliver high power densities [7, 8]. One downside of using hydrazine is that, it is hazardous when handled in pure form. Therefore, it is generally stored in aqueous solutions or in solid form as hydrazone. Although not for laminar flow based systems, the working of hydrazine-hydrogen peroxide fuel cells at low temperatures has also been demonstrated [7, 8]. Typically, Pt has been used as the electro-catalyst in these systems. Replacing expensive noble metals with other electro-catalysts has always received considerable attention.

Inexpensive non-noble metals, especially Cu has been successfully used in different forms and structures for electrochemical oxidation of hydrazine [9, 10, 11]. A Cu-based nanostructured anode [12], (Cu-Ni nanostructured catalyst), where a Cu-foam is electroplated using a Ni-salt [13] or Cu nanocubes grown on graphene paper [14], have shown high catalytic activity towards hydrazine oxidation, with long-term stability of the fuel cell. At the same time, the catalyst support also plays a major role in deciding the electro-catalytic activity of the metal. Therefore, combining Cu nanostructures on carbon supports, such as functionalized multi-walled carbon nanotubes (f-MWCNTs), single walled carbon nanotubes (SWCNTs) and graphene can improve it’s electro-catalytic activity. Stand-alone Cu nanoparticles (Cu-NPs) tend to agglomerate, but when dispersed on a support such as f-MWCNTs or graphene paper, this problem is overcome, which otherwise leads to a decrease in active surface area, and hence low activity. Apart from this, Cu-MWCNTs hybrid microstructures have also been fabricated by calcination and H₂ reduction method [15]. The aforementioned carbon nanostructures have been used as support materials for Pd, Ni, and Ag [16, 17]; however, not for application in laminar flow fuel cells operating at room temperature.

Keeping in view (i) the merits of laminar flow paper based fuel cell (low cost, self transport, room temperature operation and ease of construction), (ii) the ability of C-Cu nanocomposites to serve as cheap but effective electrocatalysts, and (iii) hydrazine monohydrate as an “easy to use” fuel, in this work, a hydrazine monohydrate (fuel)- KMnO₄ (oxidant) based paper supported fuel cell is demonstrated and characterized in terms of its electrochemical properties. Here, KMnO₄ is used as the oxidant because of its faster reduction kinetics compared to O₂. The cell functions at room temperature and the filter paper forms the backbone of the cell, which maintains the flow of the anolyte and catholyte due to its intrinsic transport properties. Pristine carbon cloth and carbon cloth loaded with Cu-NPs, f-MWCNTs, and composites of Cu-NPs and f-MWCNTs, are used as electrodes.

The rest of the paper is organized as follows: The experimental method is presented in section 2, wherein the procedure for preparing the catalysts and construction of the paper based fuel cell are also discussed. The results are discussed in section 3, and concluding remarks are given in section 4.
2. Experimental methods

2.1. Chemicals

Hydrazine monohydrate (N$_2$H$_4$.H$_2$O, 99%), Cupric sulfate (CuSO$_4$.5H$_2$O, 99%), potassium permanganate, (KMnO$_4$, 98.5%), polyethylene glycol (PEG-9000), sodium borohydride (NaBH$_4$, 98%) nitric acid (HNO$_3$, 69%) and sodium hydroxide pellets (NaOH, 99%) were purchased from Merck, while L-ascorbic acid (99.7%) was purchased from Sisco research labs. Sulfuric acid (H$_2$SO$_4$, 90%) was purchased from Fisher Scientific, and MWCNTs were purchased from Sigma Aldrich. Whatman filter paper (ashless, 40) served as the medium for the transport of anolyte and catholyte.

2.2. Preparation of catalysts and electrodes

2.2.1. Cu nanoparticles (Cu-NPs)

Copper nanoparticles (Cu-NPs) were prepared following a procedure described elsewhere [18], which is briefly outlined below. 0.01 M of CuSO$_4$.5H$_2$O and 0.02 M polyethylene glycol (PEG) (capping agent) were dissolved in deionized water and stirred vigorously. This was followed by drop-wise addition of 0.02 M ascorbic acid and 0.1 M NaOH to the above solution under continuous stirring. Finally, 0.1 M NaBH$_4$, the reducing agent, was added to complete the reaction and the solution was stirred for 10 minutes. The final solution containing Cu-NPs was dark green in color, which was centrifuged and washed with distilled water to isolate the final product and was dried in a vacuum oven at 85°C for 12 hours. 5 mg of Cu-NPs were dispersed in 1 ml of tetrahydrofuran (THF), sonicated for 20 minutes and deposited onto the electrodes (carbon cloth) by drop casting using a pipette.

2.2.2. Functionalized multiwalled carbon nanotubes (f-MWCNTs)

Multiwalled carbon nanotubes (MWCNTs) were first functionalized by dispersing and sonicating them in HNO$_3$ and H$_2$SO$_4$ (volume ratio of 1:3). This solution was then refluxed at 80°C, followed by filtering and washing with copious amounts of distilled water till the solution neutralized. The filtrate was then dried in a hot air oven at 60°C for 2 days. The resulting product is referred to as f-MWCNTs. 2 mg of f-MWCNTs in 0.5 ml of toluene was prepared by sonication, and deposited on carbon cloth by drop casting and dried in air prior to use as electrodes.

2.2.3. Cu-NPs@f-MWCNTs composite

For the preparation of the Cu-NPs@f-MWCNTs composite, f-MWCNTs were added in-situ to a solution of 0.01 M of CuSO$_4$.5H$_2$O, 0.02 M PEG, 0.02 M ascorbic acid and 0.1 M NaOH, and this mixture was stirred for a few minutes. A 0.1 M NaBH$_4$ solution was then added to this solution and was stirred for 10 minutes. Once the reaction was complete, the product was isolated from the solution by subsequent washing with distilled water and acetone, followed by drying in a vacuum oven at 85°C for 24 hours. The resulting product is referred to as Cu-NPs@f-MWCNTs composite. Approximately, 5 mg of the composite catalyst powder was then dispersed in 1 ml of toluene, and sonicated for 1 hour and then deposited onto the electrodes (carbon cloth) by drop casting.

2.3. Construction of paper based fuel cells

The paper cell was assembled by placing two 7 cm long paper strips, with a width of 0.7 cm each, separated by a 0.4 cm × 3.5 cm slit in between and connected to each other at a distance of 3.5 cm from point ‘B’ (see Fig. 1). The electrodes were placed on each of the lateral strips and were connected externally by using steel plate as current collectors. The area of the electrode used was 0.35 cm$^2$ for each one. A schematic of the cell assembly is shown in Fig. 1. The anolyte was prepared by mixing N$_2$H$_4$.H$_2$O with NaOH (4 M) and the catholyte was prepared by mixing KMnO$_4$ (1 M) and H$_2$SO$_4$ (4 M). An absorbing pad was placed at one end of the assembly to absorb the excess fluids. The anolyte and catholyte were discharged manually using a pipette near the electrodes.
2.4. Characterization techniques

Electrochemical measurements, such as chronopotentiometry, chronoamperometry and electrochemical impedance spectroscopy were done using an Autolab PGSTAT 302N with a frequency response analyzer. The measurements were performed using a NOVA 1.6 software. Cu-NPs and Cu-NPs@f-MWCNTs composite were characterised by a UV-Vis-NIR spectrophotometer (Shimadzu UV-3600). The morphology and the structure of Cu-NPs, f-MWCNTs and Cu-NPs@f-MWCNTs composite were investigated by field emission scanning electron microscopy (FE-SEM, Carl Zeiss Supra 40) and X-ray powder diffraction (XRD, PANalytical, XPertPRO) instrument with Cu-Kα (λ = 1.5406 Å). Transmission electron microscope (Philips TEM CM 200), resolution 2.4 Å, was used for characterizing the catalysts by transferring a thin layer of the samples to carbon coated copper grids. The composition of the composite was estimated using thermogravimetric analysis, Pyris 1 TGA, PerkinElmer, under helium atmosphere, at a temperature ramp of 10°/min. Raman spectra of functionalized MWCNTs (f-MWCNTs) and Cu-NPs@f-MWCNTs composite were recorded using a Bruker Senterra Raman Spectrometer, at λ=532 nm.

3. Results and discussion

3.1. Structural features of Cu-NPs, f-MWCNTs and Cu-NPs@f-MWCNTs

Prior to studying the electrochemical characterization of the paper based fuel cells, the structural characterization of the catalysts is performed. Fig. 2(a) shows the absorption spectra for Cu-NPs and the Cu-NPs@f-MWCNTs composite. The Cu-NPs show a broad peak in the visible region with a λmax at 573 nm, which is due to the surface plasmon resonance (SPR) effect of the metal NPs. Upon inclusion of the f-MWCNTs, as in the Cu-NPs@f-MWCNTs composite, this peak is red shifted by 6 nm to 579 nm, due to the increased refractive index of the composite, induced by the f-MWCNTs.

In Fig. 2(b), the XRD patterns of Cu-NPs, Cu-NPs@f-MWCNTs composite and f-MWCNTs are shown. The f-MWCNTs show a featureless diffractogram indicating that the CNTs are amorphous. Cu-NPs show three peaks at 2θ= 43.3°, 50.44° and 74.125°, which agree well with the (111), (200) and (220) planes of the face centered cubic (fcc) lattice of Cu, in accordance with PDF: 892838. The XRD pattern of the Cu-NPs@f-MWCNTs composite also shows
the same three diffraction peaks of Cu with no additional feature, indicating that crystalline Cu-NPs are dispersed in an amorphous f-MWCNTs matrix.

Figure 2: (a) Diffuse reflectance UV-Vis spectra of Cu-NPs and Cu-NPs@f-MWCNTs composite. (b) XRD patterns of f-MWCNTs, Cu-NPs and the Cu-NPs@f-MWCNTs composite.

Raman spectra for f-MWCNTs and Cu-NPs@f-MWCNTs composite are compared in Fig. 3. In pristine f-MWCNTs, the D-band (due to defects) is observed at 1347 cm$^{-1}$ and the G-band (due to sp$^2$ hybridized carbon atoms with a graphitic structure) is observed at 1594 cm$^{-1}$. The profiles of the D-band and the G-band alter slightly ongoing from f-MWCNTs to the composite, but the position remains unchanged.

The $I_D/I_G$ ratio increases from 0.8 in f-MWCNTs to 1.1 in the Cu-NPs@f-MWCNTs composite. The $I_D/I_G$ ratio is calculated based on the percentage areas under the curve for D-band and G-band. For f-MWCNTs, the D-band percentage area under the curve is 0.445 and for G-band, it is 0.554. Hence, the calculated $I_D/I_G$ ratio for f-MWCNTs is 0.803. Similarly for Cu-NPs@f-MWCNTs, the percentage areas under the curve for the D-band and the G-band are 0.54 and 0.46, respectively. Hence the $I_D/I_G$ ratio is 1.1.

The FE-SEM images of Cu-NPs, f-MWCNTs and Cu-NPs@f-MWCNTs composite are shown in Fig. S1 (see supplementary material). The images of Cu-NPs, given in Fig. S1 (a) and (b) shows aggregated interlinked particles and the dimensions of the aggregates are of the order of a few hundred nanometers and they have no definite shapes. The images of the f-MWCNTs (Fig. S1 (c) and (d)), show a fibrillar morphology, comprising of a densely packed network of intertwined nanotubes. The nanotubes form bundled clusters. The low magnification image of the Cu-NPs@f-MWCNTs composite (see Fig. S1(e)) shows a mixed morphology, wherein the aggregates of Cu-NPs coat the fiber like shapes of f-MWCNTs uniformly. The discrete but entwined nanotubular structures observed for the
f-MWCNTs, are not distinctly visible for the composite. From the undulating contours of the image, it is perceived that the aggregated particles of Cu tend to envelope the f-MWCNTs.

![Figure 3: Raman spectra of f-MWCNTs and Cu-NPs@f-MWCNTs composite catalysts.](image)

Fig. 3: Raman spectra of f-MWCNTs and Cu-NPs@f-MWCNTs composite catalysts.

Fig. 4 (a) and (b) show the TEM images for Cu-NPs at low and high magnifications, respectively. The particle size varies from 8 to 30 nm (based on a couple of micrographs). The particle dispersion and size distribution are non-uniform, due to the agglomeration among the NPs. Fig. 4 (c) shows the selected area electron diffraction (SAED) pattern of Cu-NPs. A spotty concentric ring pattern is observed, and the bright spots are indexed to the (220) and the (111) planes corresponding to inter planar spacing of 0.13 and 0.24 nm of Cu, as per PDF: 892838. The micrographs of f-MWCNTs (Fig. 4 (d) and (e)) reveal highly entangled and tubular structures, characteristic of f-MWCNTs. The
length of the nanotubes extend to several microns and the outer diameters lie in the range of 14-20 nm. The corresponding SAED pattern shows concentric diffuse rings devoid of spots, thus, re-affirming the almost amorphous nature of the CNTs. One of the rings indexed to the (002) plane of graphitic carbon, corresponding to an inter planar distance of 0.34 nm. The TEM micrographs of the Cu-NPs@f-MWCNTs composite (Fig. 4(g) and (h)), show aggregates of Cu-NPs attached to the tangled network of the tubular structures of f-MWCNTs. From the micrographs, it is evident that a reasonably good mixing of Cu-NPs with f-MWCNTs is achieved in the composite. The corresponding SAED pattern shows spots assigned to the (220) and (111) planes of Cu with a fcc lattice and the ring due to the (002) plane of graphitic carbon, thus confirming the formation of the composite.

3.2. Electrochemical performances of paper based fuel cells

A mixture of \( \text{N}_2\text{H}_4, \text{H}_2\text{O} \) and \( \text{NaOH} \) formed the anolyte and a mixture of \( \text{KMnO}_4 \) and \( \text{H}_2\text{SO}_4 \) formed the catholyte. The half cell reaction at the anode is given by

\[
\text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^- \quad (E^0 = -1.21 \text{ V}).
\]

and the half cell reaction at the cathode is given by

\[
2\text{Na}^+ + \text{SO}_4^{2-} + \text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \quad (E^0 = 1.51 \text{ V}).
\]

The overall reaction is given by

\[
5\text{N}_2\text{H}_4 + 32\text{H}^+ + 4\text{MnO}_4^- + 8\text{Na}^+ + 4\text{SO}_4^{2-} + 20 \text{OH}^- \rightarrow 5\text{N}_2 + 36\text{H}_2\text{O} + 4\text{Mn}^{2+} + 4\text{Na}_2\text{SO}_4 \quad (E^0 = 2.72 \text{ V}).
\]

These reactions are very much similar to the \( \text{N}_2\text{H}_4 \) fuel cell reported by Yang et al., [17]. Instead of \( \text{KMnO}_4 \), they used \( \text{H}_2\text{O}_2 \) as the oxidant. Its worth noticing that in these cells, the electrolyte phase also participates in the electrochemical reactions. The oxidation of the fuel and reduction of the oxidant is caused by the electrolyte phase rather than the oxidizing or reducing agent. To identify the fuel concentration for the best cell performance, three different \( \text{N}_2\text{H}_4, \text{H}_2\text{O} \) concentrations (4 M, 6 M and 8 M) are investigated (without using any catalysts). The catholyte concentration is kept constant in all the experiments at 1 M \( \text{KMnO}_4 \) and 4 M \( \text{H}_2\text{SO}_4 \). The voltage-current density and power density-current density curves are shown in Fig. S2 (supplementary material). A fuel concentration of 6 M delivers better performance compared to 4 M and 8 M. At lower concentrations, the slower oxidation kinetics limits the cell performance, whereas at higher concentrations, the anolyte cross over from the anode to the cathode becomes prominent. Anolyte/Catholyte cross over is a time dependent phenomenon and since a new cell was used for each experiment, the effect of anolyte/catholyte cross over is observed only during the later stages of the experiment, i.e., when the cell becomes more and more polarized. A still image showing the cross diffusion of anolyte and catholyte is show in Fig. S3 (see supplementary material), which clearly shows that the diffusion is faster at higher fuel concentration (8M) as compared to lower concentration (4M).

Besides optimizing the fuel concentration, the position of the electrodes is also varied from the end of the slit ‘E’, to determine the best electrode position for cell performance. Placing the electrodes too close to the junction ‘E’ decreases the diffusion path for the ions, but, increases the fuel and catholyte cross over effects. Placing the electrodes too far from the junction ‘E’ leads to an increase in the diffusion path and hence the Ohmic resistance increases. After a number of experiments, the electrode position is fixed at 0.5 cm from the junction ‘E’. The effect of electrode position on the cell performance is shown in Fig. S4 (supplementary material). For all the results presented in this study the \( \text{N}_2\text{H}_4, \text{H}_2\text{O} \) concentration is fixed at 6 M and the electrodes were placed at 0.5 cm from the point ‘E’.

To further augment the cell performance, Cu-NPs, f-MWCNTs, and Cu-NPs@f-MWCNTs composites are used as catalysts. Depending upon the activity of the catalysts used, oxidation is expected to be either a charge transfer limited process or a mass transport limited process [10]. Metallic catalysts promote the oxidation process by forming complexes with hydrazine. The stability of the complexes is determined by the charge transfer between the catalyst (metal) surface and the species in the solution (anolyte). For example, in an alkaline medium, Cu undergoes oxidation.
Cu + 2OH⁻ → Cu(OH)₂ + 2e⁻, \hspace{1cm} (4)

Cu(OH)₂ ↔ CuO + H₂O. \hspace{1cm} (5)

These species such as Cu(OH)₂, CuO are capable of bonding with N₂H₄ to form intermediates via electron/charge transfer and these reactions influence the overall oxidation process. Compared to other metal catalysts, such as Ag and Au, Cu has a higher onset potential of -0.75 V, for hydrazine oxidation [12].

Figure 5: Cell performances using (a,b) Cu-NPs, (c,d) f-MWCNTs, (e,f) Cu-NPs@f-MWCNTs at different wt% of Cu-NPs and f-MWCNTs, and (g,h) Cu-NPs@f-MWCNTs composite, f-MWCNTs and Cu-NPs as catalysts in different electrode combinations at 6 M N₂H₄, H₂O + 4 M NaOH as the anolyte. The catholyte is 1 M KMnO₄ + 4 M H₂SO₄. (a,c,e,g) show voltage versus current density and (b,d,f,h) show power density versus current density curves. A- Anode is plain carbon cloth, C- Cathode is plain carbon cloth and no catalyst implies that anode and cathode are plain carbon cloths. In (e,f) the wt% of Cu-NPs to f-MWCNTs is 1.2:1 in (1) and 3:1 in (2).
Fig. 5(a) and (b) show the cell performance using Cu-NPs. The role of the Cu-NPs is investigated by loading it at both and at either of the two electrodes. Since \( \text{H}_2\text{SO}_4 \) is used in the catholyte, the cell under-performs whenever the catalyst is used at the cathode. Cu reacts easily with \( \text{H}_2\text{SO}_4 \), leading to unwanted reactions and this decreases the cell performance. Using Cu-NPs only at the anode gave a maximum power density of 2.68 mW/cm\(^2\) at an operating voltage of 0.93 V, implying that Cu-NPs favor the oxidation of hydrazine at the anode more than the reduction of \( \text{KMnO}_4 \) at the cathode.

The electrochemical activity of f-MWCNTs is also investigated in a similar way. Functionalization of MWCNTs is important because non-functionalized MWCNTs are hydrophobic and secondly, they tend to aggregate by the virtue of van der Waals forces, which leads to interaction of the particles in the vicinity of each other. This reduces the effective surface area and limits their activity. Functional groups such as -COOH or -OH limits the interaction between the particles and makes the MWCNT hydrophilic. The presence of oxygen containing functional groups in the nanotubes allows the formation of intermediates in the electro-oxidation process. Moreover, MWCNTs are inert towards \( \text{H}_2\text{SO}_4 \) and can be considered as a continuous chain of carbon atoms linked together; thus giving rise to a 1-D structure. In this case it is easier for a mobile electron to jump from one atom to the neighboring atom, thereby facilitating the electron transport. When f-MWCNTs are used at both the electrodes, it leads to a relative increase of 42% in peak power density compared to the use of Cu-NPs at both the electrodes. The use of Cu-NPs at the anode alone gives better performance as compared to its use at both the electrodes. The use of f-MWCNTs in all cases leads to similar performance, although slightly better when used at both the electrodes. Its use at the cathode alone leads to much better performance compared to the use of Cu-NPs at the cathode alone. This leads to the conclusion that Cu-NPs act as good electro-catalyst for hydrazine oxidation and f-MWCNTs act as good electro-catalyst for \( \text{KMnO}_4 \) reduction. Therefore, an even better performance can be achieved by using Cu-NPs at the anode and f-MWCNTs at the cathode. A combination of Cu-NPs at the anode and f-MWCNTs at the cathode leads to 92% and 35% increase in the power densities compared to the sole use of Cu-NPs (Fig. 5(b)) and sole f-MWCNTs (Fig. 5 (d)) respectively, at both electrodes.

The Cu-NPs@f-MWCNTs composite also offers promising cell performance. The structure of the composite shows a mixed morphology of aggregates of Cu-NPs attached to the f-MWCNTs. To decide on the wt% of Cu-NPs and f-MWCNTs in the composite, experiments are performed using two different compositions on the anode and the results are shown in Fig. 5(e) and Fig. 5(f). Blank carbon cloth is used as the cathode. The wt% of Cu and f-MWCNTs in the composites is estimated by TGA, and it is deduced that in one case the composite is composed of 75% of Cu and in the other case 45%. The composite having higher Cu content lead to slightly better performance compared to the one with lower Cu content. The synergistic effect between the two increases the effective surface area for the electrochemical reactions and also assists in better conductivity of electrons. Fig. 5(g) and (h) shows the performance of the cell using Cu-NPs@f-MWCNTs composite. Using the composite catalyst at both electrodes resulted in a cell performance, which is lower than that of the cell with only Cu-NPs at the anode (Fig. 5(a) and (b)). However, when the composite at the cathode is replaced with only f-MWCNTs, the cell delivered the best performance, of all combinations studied. This cell produces a power density 3.58 mW/cm\(^2\) at 0.89 V. Table 1 shows a performance comparison of different anode and cathode combinations studied in the present work.
Table 1: Performance comparison of different anode and cathode combinations studied.

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<th>Cathode</th>
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<td>12</td>
<td>Cu-NPs@f-MWCNTs</td>
<td>Cu-NPs@f-MWCNTs</td>
<td>2.16</td>
</tr>
</tbody>
</table>

Figure 6: Cyclic voltammograms showing oxidation of a solution of 6 M $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ in 4 M NaOH using Cu-NPs, f-MWCNTs, and Cu-NPs@f-MWCNTs composite, as the working electrodes, Ag/AgCl/KCl as the reference electrode and a Pt rod as the counter electrode.

To understand the electrochemical oxidation of hydrazine at the anode, cyclic voltammograms are recorded with electrodes based on f-MWCNTs, Cu-NPs, and Cu-NPs@f-MWCNTs as working electrodes in an alkaline solutions of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, with Pt as counter electrode and Ag/AgCl/KCl as the reference electrode. The results are shown in Fig. 6. For the f-MWCNTs there is no well-defined oxidation peak at any voltage. However, a very broad peak is visible around 0.2 - 0.3 V (vs Ag/Ag$^+$). This indicates that f-MWCNTs have a mild catalytic activity towards hydrazine. This can also be justified from the polarization curves (Fig. 5d), where the peak power density increases from 1.16 (without any catalyst) to 1.98 mW/cm$^2$. For Cu-NPs, the oxidation peak at ~0.32 V is relatively well-defined as compared to f-MWCNTs and hence they have a better catalytic activity towards hydrazine oxidation. The oxidation pick position matches well with a previously reported value of 0.26 V (versus Ag/Ag$^+$) for hydrazine oxidation at a Cu electrode [19]. With Cu-NPs, the peak power density increases to 2.67 mW/cm$^2$. In the case of Cu-NPs@f-MWCNTs, the oxidation peak is observed at 0.27 V (versus Ag/Ag$^+$), which is prominent and sharp as compared to f-MWCNTs and Cu-NPs. The peak power density for this case is 2.63 mW/cm$^2$ and it is comparable to that of Cu-NPs. The above results indicate that Cu-NPs and Cu-NPs@f-MWCNTs show good electrocatalytic activity towards hydrazine oxidation at the anode.
Figure 7: Electrochemical impedance spectra (EIS) recorded at 0.9 V with an ac voltage amplitude of 10 mV for 4 fresh cells at (a) 4 M (b) 6 M (c) 8 M N₂H₄.H₂O concentrations with 4 M NaOH in each case, and (d) comparison of Nyquist plots for different fuel concentrations (inset image for cell at 6 M N₂H₄.H₂O). Cu-NPs@f-MWCNTs-carbon cloth is used at the anode and f-MWCNTs-carbon cloth is used at the cathode. The catholyte is a mixture of 1 M KMnO₄ and 4 M H₂SO₄.

The electrochemical impedance spectra recorded at 0.9 V are shown in Fig. 7. The frequency is scanned from 1 MHz to 0.1 Hz with an amplitude of 10 mV. The only variable in the experiments is the concentration of N₂H₄.H₂O (fuel) in the anolyte, and for each anolyte concentration, the experiment is repeated four times, each time using a newly constructed cell. Fig. 7 shows that even under the same experimental conditions, there is a significant variation in the spectra, particularly at 4 M concentration. Ideally, the impedance spectra must be recorded at steady state conditions. However, performance degradation of the cell (discussed in the later section) does not allow recording of the spectra at steady state conditions, and the data at low frequency becomes scattered. There are also other uncertainties associated with the experiment such as the anisotropy of the paper, which may lead to different diffusion rates from cell to cell. Nevertheless, the high frequency intercept of the Nyquist plots give some indication about the Ohmic resistance offered by the system. Nothing much can be concluded on the polarization resistance because of the distortion of data at low frequency. It appears from the trend of Nyquist plot that the polarization resistance is lower at 6 M compared to 4 M and 8 M fuel concentrations in the anolyte. The corresponding cell performances are shown in Fig. S5 in the supplementary information. The scattering of the data is highest for 4 M case, which is similar to what is observed in the Nyquist plots (Fig. 7). It can also be observed that the IV curves are almost overlapping for 6 M and 8 M cases. Although the electrolyte concentration (NaOH and H₂SO₄) are maintained constant at the anode and the cathode, the Ohmic resistance increases with increase in N₂H₄.H₂O concentration. The complete data set is shown in Table 2.
along with the standard error (defined as $\sigma/\sqrt{n}$, where $\sigma$ is the standard deviation in the Ohmic resistance obtained as $n = 4$).

Table 2: Ohmic resistance and its standard error for different cells obtained from the impedance analysis.

<table>
<thead>
<tr>
<th>Fuel concentration in anolyte</th>
<th>$R_{\text{ohm}}$(Ω-cm$^2$)</th>
<th>Cell-1</th>
<th>Cell-2</th>
<th>Cell-3</th>
<th>Cell-4</th>
<th>Average</th>
<th>Standard Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 M</td>
<td>117.8</td>
<td>111.2</td>
<td>101.3</td>
<td>97.8</td>
<td>107.1</td>
<td>4.57</td>
<td></td>
</tr>
<tr>
<td>6 M</td>
<td>110.6</td>
<td>101.1</td>
<td>116.3</td>
<td>128.8</td>
<td>114.2</td>
<td>5.78</td>
<td></td>
</tr>
<tr>
<td>8 M</td>
<td>165.8</td>
<td>157.1</td>
<td>170.2</td>
<td>169.4</td>
<td>165.6</td>
<td>3.0</td>
<td></td>
</tr>
</tbody>
</table>

To cross-verify the trend in the Ohmic resistance observed in the Nyquist plots, we have performed, current interruption method. The current interruption method also resulted in the same trend in Ohmic resistance, i.e., resistance increases with increase in the fuel ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$) concentration in the anolyte and the results are shown in Table 3.

Table 3: Ohmic resistance and its standard error for different cells obtained from the current interrupt method.

<table>
<thead>
<tr>
<th>Fuel concentration in anolyte</th>
<th>$R_{\text{ohm}}$(Ω-cm$^2$)</th>
<th>Cell-1</th>
<th>Cell-2</th>
<th>Cell-3</th>
<th>Cell-4</th>
<th>Average</th>
<th>Standard Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 M</td>
<td>102.5</td>
<td>123.2</td>
<td>80.8</td>
<td>79.4</td>
<td>96.5</td>
<td>10.3</td>
<td></td>
</tr>
<tr>
<td>6 M</td>
<td>124.3</td>
<td>120.8</td>
<td>133.3</td>
<td>144.5</td>
<td>130.7</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>8 M</td>
<td>152.6</td>
<td>157.5</td>
<td>137.5</td>
<td>147.0</td>
<td>148.6</td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>

These two methods give the Ohmic resistance of the working cell, however they do not aid in identifying the source of increase in resistance. Since the only variable is the concentration of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, it should be anticipated that the increase in resistance is due to the decrease in conductivity of the anolyte with increase in concentration of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. To verify this hypothesis, we have measured the resistance of the anolyte and catholyte by using three electrode configuration. Ag/AgCl/KCl is is used as the reference electrode, Pt is used as the counter electrode and FTO plate as the working electrode. The three electrode system is placed in the solution of the anolyte or catholyte, and impedance anaysis is performed to obtain the Ohmic resistance. The results obtained are shown in Table 4.

Table 4: Ohmic resistance of the anolyte and the catholyte.

<table>
<thead>
<tr>
<th>Medium</th>
<th>$R_{\text{ohm}}$(Ω-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH (4 M)</td>
<td>104.4</td>
</tr>
<tr>
<td>NaOH (4 M) + $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (4 M)</td>
<td>340.3</td>
</tr>
<tr>
<td>NaOH (4 M) + $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (6 M)</td>
<td>354.2</td>
</tr>
<tr>
<td>NaOH (4 M) + $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (8 M)</td>
<td>377.2</td>
</tr>
<tr>
<td>KMnO$_4$ (1 M) + H$_2$SO$_4$ (4 M)</td>
<td>99.0</td>
</tr>
</tbody>
</table>

Clearly, the resistance of the anolyte increases with increase in the concentration of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$. This indicates that the increase in Ohmic resistance observed in the Nyquist plot (Fig. 7) is due to the decrease in the ionic conductivity of the anolyte on increasing the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ concentration.
3.3. Stability of cell performance

Figure 8: Stability of cell performance: (a) regeneration of current density (at \( \sim 0.9 \) V), and (b) chronopotentiometry (at 1 \( \mu \)A). Cu-NPs@f-MWCNTs on carbon cloth is used at the anode and f-MWCNTs is used at the cathode. The anolyte is a mixture of 6 M \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) and 4 M \( \text{NaOH} \), and the catholyte is a mixture of 1 M \( \text{KMnO}_4 \) and 4 M \( \text{H}_2\text{SO}_4 \).

Although the filter paper can self transport the anolyte and catholyte from their reservoirs, in our experiments, the reaction is initiated by discharging 3-4 drops each of the anolyte and the catholyte near the respective electrodes. While a large portion of the fuel and the oxidant is absorbed by the filter paper, a relatively small portion participates in the electrochemical reactions. Once these are consumed, the cell current density declines. However, as shown in Fig. 8(a), the current density can be recovered nearly to its initial value by replenishing the cell with fresh drops of the anolyte and the catholyte. There are several reasons for the drop in cell current with time, such as anolyte and catholyte cross overs, dilution effect due to the reaction products etc. Fig. 8(b) shows the decay of open circuit voltage as a function of time. The aforementioned effects are also responsible for the decrease in OCV over time. Since the decrease in OCV observed over a period of nearly 11 minutes occurs by only 0.1 V (Fig. 8(b)) and since the current density after decay, is restored to its original value upon fuel and oxidant replenishment, it is obvious that this cell is most suitable for providing stable electrical power input for a short duration of time for low power consuming devices.

4. Concluding remarks

Paper based fuel cells operating at room temperature are developed with \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) as the fuel and \( \text{KMnO}_4 \) as the oxidant. Carbon cloth and carbon cloth loaded with the following catalysts: Cu-NPs, f-MWCNTs and a Cu-NPs@f-MWCNTs composite are used as the electrodes. Cu-NPs are having particle sizes in the range of 8-30 nm and the Cu-NPs@f-MWCNTs composite consists of Cu-NPs tethered to the fibrillar structures of f-MWCNTs. Among all the cells studied by varying catalyst combinations at the cathode and the anode, the best cell performance is obtained with Cu-NPs@f-MWCNTs at the anode and with f-MWCNTs at the cathode. The cell delivered a maximum power density of 3.57 mW/cm\(^2\) at 0.89 V. In this configuration, the synergistic effects of the two materials, (i) the high electrocatalytic activity of Cu-NPs towards hydrazine monohydrate, and their stability in an alkaline medium (at the anode), and (ii) the high effective surface area (that allows high loading of electrochemically accessible Cu-NPs) and the good electronic conductivity of f-MWCNTs, and their stability in both alkaline and acidic media (at anode and cathode), came to the fore, manifesting in the best fuel cell performance. Electrochemical impedance analysis of the cells also showed the least Ohmic resistances for the 4 M case, compared to other fuel concentrations. This cell with Cu-NPs@f-MWCNTs at the anode and f-MWCNTs at the cathode, we obtained (i) an almost invariant OCV, for over 10 minutes of operation, and (ii) a current density that restored to its original magnitude of c.a. 4.5 mA/cm\(^2\) from a decayed value, upon replenishing the fuel and oxidant (at 0.9 V). The combination of low cost Cu and carbon nanotubes based catalysts, filter paper based scaffolds for the flow of fluids, and carbon cloth as the electrodes applied
to this cell, clearly demonstrated the potential of this fuel cell for applications in systems that require power for short duration.

**Supplementary material**

FE-SEM images of catalysts, polarization plots for different fuel concentrations, photos showing the crossover as a function of concentrations and polarization plots for different electrode positions.

**References**