**Scalable screen-printing manufacturing process for graphene oxide platinum free alternative counter electrodes in efficient dye sensitized solar cells.**

D. Kishore Kumar1[[1]](#footnote-1), Sanjay Kumar Swami2, Viresh Dutta3, Baixin Chen1, Nick Bennett1, and H. M. Upadhyaya4

*1Energy Conversion Lab (ECL), Institute of Mechanical Process and Energy Engineering (IMPEE), School of Engineering and Physical Sciences, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, UK*

*2CSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi, 110012-India*

*3Photovolatic Lab, Centre for Energy Studies, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India*

*4Advanced Materials Centre, School of Engineering, London South Bank University, 103, Borough Road, London- SE10AA, UK*

**Abstract**

The graphene oxide paste (GO) was prepared by mixing α-terpineol and ethyl cellulose, and GO films was prepared by screen printing on fluorine doped Tin oxide (FTO) glass substrates to validate as an alternative counter electrode material to platinum in dye sensitized solar cells (DSSC). The graphene oxide films were characterised by X-Ray Diffraction, Scanning Electron Microscopy, Raman spectroscopy and the catalytic properties of films were being investigated by cyclic voltammetry and electrochemical Impedance measurements. The DSSC fabricated by coupling TiO2 films soaked in N719 dye with GO as counter electrode exhibited photoconversion efficiency of 5.58% under standard one Sun illumination, whereas platinum based device showed photoconversion efficiency of 7.57%. The present study suggests that graphene oxide counter electrodes can be considered as a promising alternative to platinum, with further optimisation, which clearly has advantages in terms of its abundance and low cost processing towards industrial prospects.

**Keywords:** Graphene oxide, low cost, counter electrode, screen printing, DSSC

1. **Introduction**

In dye sensitised solar cells (DSSCs), the counter electrode (CE) plays an important role. The important activities of the CE are to act as the catalyst for the redox I-/I3- electrolyte and also to transfer the electrons from the external circuit into the electrolyte.[[2]](#endnote-1) Platinum (Pt) is known as best the catalyst because of its catalytic behaviour, conductivity and stability.[[3]](#endnote-2) Hence, Pt is most widely used as CE in DSSC. But a major disadvantage of Pt is that it is expensive and not so abundant.[[4]](#endnote-3) The redox couple is highly corrosive and it reacts with Pt to form iodide compounds of platinum which are soluble in the electrolyte.[[5]](#endnote-4) These two difficulties are the limiting factors in the commercialization of DSSC. Several researchers have focused on developing alternatives to platinum which are cheap and possess all features of platinum in terms of performance of DSSCs. Among them carbon based materials have gained much attraction due to their excellent catalytic activity, stability, conductivity and earth-abundance. Two-dimensional one atom thick graphene has attracted attention after its application in field effect transistors (FETs). In the structure of graphene, the carbon atoms are arranged in a honey comb lattice.[[6]](#endnote-5) It possesses excellent electrical conductivity,[[7]](#endnote-6) electron mobility,[[8]](#endnote-7) high mechanical strength,[[9]](#endnote-8) and is chemically stable with a high surface area.[[10]](#endnote-9) These properties make graphene a potential alternative to platinum as the CE in DSSC. The electrical conductivity of graphene helps to decrease the charge transfer resistance (RCT). Kaniyoor *et al.* reported that the RCT of thermally exfoliated graphene films was 11.7 Ω cm2 where the platinum in the form of film was 6.5 Ω cm2.6 Zhang *et al.* experimental results supported the Kaniyoor *et al.* results where the photoconversion efficiency is comparable with Pt.[[11]](#endnote-10)

Along with graphene, other forms of graphene such as graphene oxide (GO) and reduced graphene oxide (rGO) are also investigated as CE by many groups. Graphene composites with polymer and metal sulfides have also been studied.12,26,28 The best photo-conversion efficiencies (PCE) of graphene and its related materials as CEs are listed below in Table 1.

**Table 1:** Photovoltaic performances of DSSCs fabricated with graphene and its related materials.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No** | **Material** | **VOC**  **(V)** | **JSC (mA cm-2)** | **FF**  **(%)** | **η (%)** | **Area**  **(cm2)** | **Preparation of CE** | **Ref.** |
| 1 | Functionalised graphene | 0.64 | 13.16 | 60.0 | 5.0 | 0.39 | Spin coating | [[12]](#endnote-11) |
| 2 | rGO | 0.70 | 15.01 | 57.0 | 6.0 | - | Spin coating | [[13]](#endnote-12) |
| 3 | Graphene/Pedot:PSS | 0.72 | 12.96 | 48.0 | 4.5 | 0.07 | Spin coating | [[14]](#endnote-13) |
| 4 | Graphene | 0.54 | 14.3 | 65.3 | 5.7 | - | Electrophoretic | [[15]](#endnote-14) |
| 5 | rGO/CNT | 0.78 | 12.86 | 61.0 | 6.2 | 0.2 | Electrophoretic | [[16]](#endnote-15) |
| 6 | Graphene nanosheets | 0.75 | 17.0 | 53.6 | 6.8 | 0.2 | Screen printing | [[17]](#endnote-16) |
| 7 | rGO | 0.78 | 12.82 | 72.0 | 7.2 | - | Doctor-blade | [[18]](#endnote-17) |
| 8 | rGO foam | 0.75 | 14.34 | 45.0 | 4.8 | 0.2 | Spin coating | [[19]](#endnote-18) |
| 9 | rGO | 0.56 | 14.32 | 25.0 | 2.0 | 0.25 | Sputtering | [[20]](#endnote-19) |
| 10 | Graphene | 0.60 | 12.08 | 39.0 | 2.8 | - | Spraying | [[21]](#endnote-20) |
| 11 | Graphene  Nanosheets | 0.75 | 12.66 | 57.2 | 5.4 | - | Electro spray | [[22]](#endnote-21) |
| 12 | rGO | 0.69 | 15.57 | 52.0 | 5.6 | 0.25 | Electro spray | [[23]](#endnote-22) |
| 13 | GO+CNT+N | 0.77 | 16.23 | 54.0 | 6.7 | - | Spin coating | [[24]](#endnote-23) |
| 14 | Pt+rGO | 0.67 | 10.08 | 60.0 | 4.0 | 0.16 | Srop casting | [[25]](#endnote-24) |
| 15 | rGO-Cu2S | 0.71 | 14.45 | 69.0 | 7.1 | - | Spray coating | [[26]](#endnote-25) |
| 16 | N+GO | 0.71 | 13.14 | 48.0 | 4.5 | - | Drop casting | [[27]](#endnote-26) |
| 17 | SnS2+rGO | 0.77 | 15.18 | 63.0 | 7.5 | 0.25 | Drop casting | [[28]](#endnote-27) |
| 18 | Ru+GO | 0.77 | 16.13 | 67.0 | 8.3 | - | Doctor blade | [[29]](#endnote-28) |
| 19 | MoS2/rGO/CNT | 0.76 | 14.59 | 67.0 | 7.5 | 0.16 | Electrophoretic deposition | [[30]](#endnote-29) |
| 20 | Graphene + Au | 1.01 | 18.27 | 77.0 | 14.3 | - | Drop casting | [[31]](#endnote-30) |
| 21 | CoS/MoS2 | 0.74 | 16.50 | 61.0 | 7.5 | 0.25 | Doctor blade | [[32]](#endnote-31) |
| 22 | CoS2/rGO | 0.70 | 16.35 | 67.0 | 7.7 | - | Spray | [[33]](#endnote-32) |
| 23 | MoS2/rGO | 0.66 | 17.20 | 60.0 | 6.8 | 0.25 | Doctor blade | [[34]](#endnote-33) |
| 24 | Grap/Bi8La10O27 | 0.75 | 16.36 | 67.0 | 7.1 | 0.25 | Doctor blade | [[35]](#endnote-34) |
| 25 | MoS2/SnS2 | 0.73 | 15.99 | 65.0 | 7.6 | 0.25 | Doctor blade | [[36]](#endnote-35) |
| 26 | PEDOT/rGO | 0.73 | 15.82 | 67.0 | 7.8 | - | Electrodeposition | [[37]](#endnote-36) |
| 27 | PVP/Grap | 0.86 | 14.80 | 70.0 | 8.9 | 0.16 | Dip coating | [[38]](#endnote-37) |
| 28 | CoSe/Grap | 0.75 | 17.96 | 68.8 | 9.3 | - | Doctor blade | [[39]](#endnote-38) |
| 29 | Ta/Co-N-C | 0.65 | 18.11 | 68.0 | 8.0 | 0.16 | Spray | [[40]](#endnote-39) |
| 30 | GO/Co-macro | 0.76 | 17.34 | 57.0 | 7.5 | 0.126 | Drop casting | [[41]](#endnote-40) |
| 31 | Co3O4-WC-CN/rGO | 0.77 | 16.27 | 59.0 | 7.4 | 0.10 | Screen printing | [[42]](#endnote-41) |
| 32 | N-S-GN | 0.74 | 16.86 | 74.0 | 9.4 | 0.16 | Drop casting | [[43]](#endnote-42) |
| 33 | WOx/WS2/C | 0.72 | 15.48 | 69.5 | 7.7 | - | Doctor blade | [[44]](#endnote-43) |
| 34 | CoInS4 | 0.77 | 17.65 | 65.0 | 8.8 | 0.3 | Hydrothermal | [[45]](#endnote-44) |
| 35 | In2S3-C-Au | 0.8 | 16.88 | 66.0 | 8.9 | 0.25 | Doctor blade | [[46]](#endnote-45) |
| 36 | SrRuO3/GQD | 0.76 | 15.62 | 68.0 | 8.0 | 0.16 | Spin coating | [[47]](#endnote-46) |
| 37 | Co3O4/rGO | 0.76 | 15.70 | 67.7 | 8.1 | 0.25 | Doctor blade | [[48]](#endnote-47) |
| 38 | rGO-NiCo2S4 | 0.75 | 16.40 | 66.1 | 8.1 | 0.2 | Doctor blade | [[49]](#endnote-48) |
| 39 | CoNi-N-carbon | 0.70 | 18.53 | 58.0 | 7.6 | 0.25 | Doctor blade | [[50]](#endnote-49) |
| 40 | Pt-Zn | 0.72 | 15.76 | 70.3 | 8.0 | - | Drop casting | [[51]](#endnote-50) |
| 41 | Carbon fiber | 0.75 | 15.66 | 75.5 | 8.9 | 0.2 | Spin coating | [[52]](#endnote-51) |

From the literature, it is evident that graphene, functionalised graphene and graphene composites can be used as CEs in DSSC. The current state of art of graphene CE based DSSC is 14.3%.30 Different techniques such as drop casting,26 spin casting,12 sputtering,18 electro-spray,21 doctor blade,27 screen printing,15 and electrophoretic deposition,28 are practised in the fabrication of graphene based CEs. The photoconversion efficiencies of DSSC fabricated with graphene oxide CE is much smaller compared to pristine graphene CE. Graphene and reduced graphene oxide (rGO) has more active sites for the redox activity of I-/I3- compared to rather than GO. The photoconversion parameters of GO-CE devices are mentioned in Table 2.

**Table 2:** Photovoltaic characteristics of DSSCs fabricated with graphene oxide as CE.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S.No.** | **material** | **VOC (V)** | **JSC (mA cm-2)** | **FF (%)** | **η(%)** | **Area (cm2)** | **preparation** | **Ref.** |
| 1 | GO | 0.39 | 0.43 | 17 | 0.03 | 0.2 | Drop casting | [[53]](#endnote-52) |
| 2 | GO | 0.72 | 8.11 | 46 | 2.6 | 0.6 | Spray | [[54]](#endnote-53) |
| 3 | GO | 0.59 | 4.19 | 26 | 0.6 | 0.16 | Dispersion | [[55]](#endnote-54) |
| 4 | GO | 0.66 | 16.35 | 33 | 3.6 | - | Spin coating | [[56]](#endnote-55) |
| 5 | GO | 0.78 | 14.37 | 40 | 4.5 | - | Dye plasma reduction | [[57]](#endnote-56) |
| 6 | GO | 0.71 | 14.02 | 38 | 4.0 | - | Spin coating | [[58]](#endnote-57) |
| 7 | GO | 0.32 | 4.92 | 49 | 0.8 | 0.42 | Drop casting | [[59]](#endnote-58) |

In most of the reports, the CEs are prepared by spin casting, drop casting, spray deposition and electrophoretic deposition mainly. Until now only one report is available of screen printing and in that work, the CE was made with graphene nanosheets,16 whereas, there are no reports available on screen printing of GO.

In this work, we report the preparation of GO paste by grinding GO powder and ethyl cellulose using α-terpineol. The GO films are prepared with the screen printing technique and used as a counter electrode in dye sensitised solar cells.

1. **Experimental section**

**2.1 Synthesis of Graphene oxide**

Graphene oxide (GO) is synthesized with the modified Hummer’s method.[[60]](#endnote-59) Graphite flakes and NaNO3 are added to the conc. H2SO4 and refluxed for 30 min at 0 °C. KMnO4 is added in small fractions to this mixture such that the temperature of the solution is maintained below 30 °C and after refluxing for 6 h, diluted H2O2 is added to neutralize the unreacted KMnO4. The final solution is repeatedly washed with 1 M HCl and followed by de-ionised (DI) water. After drying at 60 °C overnight, GO is re-dispersed in DI water and subjected to sonication for ten min and centrifuged at 4000 rpm to remove unexfoliated GO.

**2.2 Fabrication of GO CEs**

The FTO glass substrates (TEC8, Pilkington, UK) were cleaned with soap solution, followed by rinsing with DI water and again cleaned with DI water by ultrasonication and then with acetone and finally with iso-butyl alcohol . To a mixture of 20 mg GO and 5 mg of ethyl cellulose, a few drops of α-terpineol were added and grinded well. Thus obtained GO paste was used to prepare GO films on FTO substrates by screen printing with intermittent heat treatment of 120 °C for 2 min. The screen printing was repeated for five successive layers. After screen printing, the GO were subjected to a heat treatment cycle with 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and finally at 500 °C for 15 min. The heat treated GO films were then ready to be used as CE in DSSC. GO paste was prepared without adding ethyl cellulose and GO films are prepared as described earlier. The GO films prepared with the paste contains GO and α-terpineol are termed as GO-a and the films prepared with the paste contains GO, α-terpineol and ethyl cellulose are termed as GO-b.

**2.3 Device fabrication**

The FTO coated glass substrates (TEC8, Pilkington, UK) were cleaned ultrasonically in a three stage process - first in soap solution followed by acetone and iso-propanol and finally dried with N2 gas. After cleaning, a layer of TiO2 film of thickness around 30-50 nm is deposited by the immersion of FTO glass substrates in 40 mM TiCl4 solution for 30 min at 80 °C. This step was repeated to ensure complete formation of the TiO2 film over the FTO substrates. After TiCl4 treatment, the FTO substrates were subjected to screen printing. The thickness of the film was 8 µm for the TiO2 transparent paste (Dyesol) and 4 µm with light scattering TiO2 paste (Dyesol). Now the TiO2 films were subjected to a cycle of annealing temperatures, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min, and 500 °C for 15 min.[[61]](#endnote-60) After cooling, the TiO2 films were again immersed in a 40 mM TiCl4 solution for 30 min at 80 °C. Then the TiO2 films were washed with DI water and subjected to a heat treatment at 450 °C for 30 min. After cooling, the samples were immersed in a 0.3 mM N719 ethanolic dye (Dyesol) solution for 24 h. GO films on FTO substrates were used as the CE. The cells were coupled using 25 µm thick Surlyn (Solaronix) as a spacer between the photoelectrode and CE. The electrolyte was injected from the hole drilled in the counter electrode using vacuum suction to ensure complete filling. The electrolyte contained 0.1 M iodine (I2), 0.05 M lithium iodide (LiI), 0.5 M *tert*-butyl pyridine and 0.6 M 1-butyl-3- methylimidazolium iodide (BMII) in the mixture of acetonitrile and valeronitrile (85:15).[[62]](#endnote-61) The active area of the device is set to 0.25 cm2 during the J-V measurements.

**2.4 Characterisation techniques**

The crystallinity and phase purity of the GO samples were characterised by X-ray diffraction (Bruker D8 Advance diffractometer) using Cu-Kα radiation. The morphology of the GO was investigated using transmission electron microscopy (JEM-2100) at an operating voltage of 200 kV. The chemical structures of GO were analysed by XPS in ultrahigh vacuum (UHV) using a multipurpose surface analysis system (Axis Ultra DLD) at an operating pressures of <10-10 mbar using a conventional X-ray source (XR-50, Monochromatic Al). Photovoltaic properties were measured by a computer-controlled digital source meter (Keithley 2400) under simulated one sun illumination at AM 1.5G (100 mA cm-2) from a solar simulator (92250 A, Newport, USA). The electrochemical impedance spectroscopy (EIS) is carried out using Metrohm Autolab in the frequency range of 0.1 Hz to 1 MHz with amplitude of 0.050 V under dark conditions. The cyclic voltammetry measurements are recorded using a Metrohm cyclic voltammetry instrument.

1. **Results and discussions**

**3.1 X-ray diffraction and Raman Spectrum**

The X-ray diffraction (XRD) pattern of the synthesized GO is shown in Fig. 1(a). The GO XRD pattern is recorded from 5 ° to 35 ° with scan rate of 3 ° min-1. The presence of peak 2θ = 9.48 ° confirms the formation of GO.[[63]](#endnote-62) Raman spectroscopy is a powerful tool to characterise the graphene and its graphene related materials signature spectrum. In Fig. 1(b), the peak at 1351 cm-1 is related to the D-band which corresponds to the A1g mode and represents the vibrations of the carbon atoms with dangling bonds of disordered graphite. The presence of a G-band at 1592 cm-1 corresponds to the E2g mode of graphite which in turn is related to the vibration of sp2 bonded carbon atoms.[[64]](#endnote-63)

****

**Fig. 1:** a) X-ray diffraction data, and b) Raman spectra of a graphene oxide.

**3.2 TEM micrographs**

Fig. 2 presents the TEM images of GO. The TEM micrographs of GO exhibited the translucent nature to electrons with a two dimensional layered structure and with silk veil waves, which is a signature feature of single or several layered GO sheets. The dark regions occur owing to the aggregation of GO.



**Fig. 2:** TEM micrographs of graphene oxide exhibiting two dimensional layered structure.

**3. 3 Cyclic voltammetry**

The catalytic activity of the GO electrode was tested using a cyclic voltammetry. The measurement was carried in a three electrode system using Ag/AgCl as an auxiliary electrode where the GO film acts as a working electrode and platinum wire as a reference electrode. The electrolyte contains 0.01 M LiI, 1.0 mM I2 and 0.1 M lithium perchlorate (LiClO4) in acetronitrile (de-gassed-free from dissolved oxygen). Fig. 3 shows the cyclic voltagrams of GO and Pt electrodes. Both the GO and the Pt exhibited almost similar characteristic reduction and oxidation peaks shown in Fig. 3. At the extreme left, the peaks are associated with oxidation of I- to I3- and at the extreme right the peaks correspond to a reduction of I3- to I-. The peak current density and peak to peak separation (Epp) were two key parameters to understand the catalytic activity of the counter electrodes. The Epp of GO electrode was 0.494 V and Epp of Pt electrode was 0.6350 V. The smaller Epp value indicates a better catalytic activity of the electrode. The cathodic peak current density of GO electrode was -2.07 x 10-3 mA cm-2 and Pt electrode was -1.31 x 10-3 mA cm-2 whereas, the cathodic peak potential of GO was 0.071 V and the cathodic peak potential of Pt was -0.054 V. The anodic peak current density of GO was 2.55 x 10-3 mA cm-2 and Pt was 1.47 x 10-3 mA cm-2 whereas, the anodic peak potential of Pt was 0.581 V and anodic peak potential of GO electrode was 0.565 V. The cathodic peak current density of GO was shifted towards negative values which indicates the higher resistance of GO films than Pt.[[65]](#endnote-64)



**Fig. 3:** Cyclic voltammetry scans of GO and Pt CE measured at the scan rate of 0.050 V s-1 in 0.01 M LiI, 1.0 mM I2 and 0.1 M LiClO4 electrolyte in acetonitrile.

**3.4 X-ray Photon spectroscopy (XPS)**

The composition of the GO films are analysed by XPS (Fig. 4). Graphene oxide was dispersed on silicon wafer using ethanol and dried. It is found that GO contains 69.82% of carbon, 21.36% of oxygen, 8.81% of nitrogen (the presence of nitrogen in the atmosphere) and 0.01% other impurities. The C-1 band is observed at 285.04 eV which is correlated with the binding energy of the C-C bonding of graphene.[[66]](#endnote-65)



**Fig. 4:** X-ray photoelectron spectroscopy of Graphene oxide film.

**3.5 Photovoltaic performances of DSSCs**

The photocurrent density-voltage (J-V) measurements of the DSSC fabricated with GO-a are shown in Fig. 5. The DSSCs assembled with GO-a as CE exhibited an open circuit voltage (VOC) = 0.6 V, the short current density (JSC) = 3.08 mA cm-2 and fill factor (FF) of 16 % with photoconversion efficiency = 0.29 %. The devices prepared with GO-a CE resulted in poor performance in terms photoconversion parameters.



**Fig. 5:** J-V measurements of GO-a CE based DSSC.

The J-V measurements of the DSSC fabricated with GO-b and Pt are shown in Fig. 6. The photoconversion parameters of GO-b based devices are VOC = 0.66 V, JSC = 11.83 mA cm-2, FF = 71.5 % and PCE = 5.58 %., whereas, the Pt CE based exhibited VOC = 0.65 V, JSC =14.87 mA cm-2 and FF = 78.1 % with PCE of 7.57%. The GO-CE exhibited much higher cathodic current density when compared with the Pt-CE. This could be seen from the cyclic voltammetry measurement shown in Fig. 3. However, the photovoltaic parameters of GO-b CEs are comparable with those for Pt-CEs. The photoconversion efficiencies of the DSSC made with GO-a, GO-b and Pt CEs are tabulated in Table 3.



**Fig. 6** J-V measurements of GO-b CE and Pt CE of the DSSCs.

The electrocatalytic performance of the GO depends on the defects and oxygen vacancies. This is attributed to the limited active sites for the I-/I3- electrocatalysis.[[67]](#endnote-66) The GO film adhesion to the FTO substrate also plays an important role in the device behaviour. The GO-a film adhesion to the FTO substrate is poor due to the absence of organic binders and as a result the photovoltaic parameters are very low especially the fill factor. But the GO-b films prepared using paste containing organic binders exhibited excellent photovoltaic parameters and all the photovoltaic parameters are comparable with Pt CE except for the short circuit current density. Ethyl cellulose acts as binder molecule in the paste preparation. The GO-b films prepared with ethyl cellulose increases the adhesion of the GO films and doesn’t undergo deformation by the addition of iodine/triiodide redox electrolyte whereas, the GO-a films prepared without binders, undergoes deformation with the addition of electrolyte and decreases the electrocatalytic activity of the counter electrode.

**Table 3:** Photovoltaic parameters of DSSC with GO-a, GO-b and Pt CEs.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **S.No** | **VOC (V)** | **JSC (mA cm-2)** | **FF (%)** | **η (%)** |
| GO-a1 | 0.61 | 2.49 | 7.9 | 0.1 |
| GO-a2 | 0.59 | 2.44 | 14.0 | 0.2 |
| GO-a3 | 0.59 | 2.60 | 13.8 | 0.2 |
| GO-a4 | 0.57 | 3.08 | 16. 3 | 0. 3 |
| GO-b1 | 0.66 | 11.83 | 71.5 | 5.6 |
| GO-b2 | 0.65 | 11.43 | 73.6 | 5.5 |
| GO-b3 | 0.66 | 11.5 | 71.9 | 5.3 |
| GO-b4 | 0.65 | 11.78 | 70.7 | 5.4 |
| GO-b5 | 0.65 | 11.47 | 72.8 | 5.4 |
| GO-b6 | 0.64 | 11.11 | 74.2 | 5.2 |
| Pt-1 | 0.63 | 14.21 | 80.7 | 7. 3 |
| Pt-2 | 0.64 | 14.26 | 79.9 | 7.3 |
| Pt-3 | 0.65 | 14.87 | 78.1 | 7.57 |

**3.6 Impedance spectra of DSSCs with different CEs**

To promote and explore catalytic properties of CEs, Tafel polarization experiments were carried out on GO and Pt in a symmetrical cell assembly with iodine electrolyte (Fig. 7). Scan rate used for Tafel polarization was 0.010 V s-1. In the Tafel zone the intersection of the tangents to the cathodic branch at zero potential ordinate is J0, which is exchange current density. J0 is the inversely proportional to RCT from the equation:

J0= RT/nFRCT  (1)

Where R is the gas constant, T is the temperature, n is the number of electron involved in the reaction and F is the Faraday’s constant. Highest J0 infers a low value of RCT. The value of J0 for GO is lower than the value of J0 for Pt CE. This supports the observation that GO shows the lower catalytic behaviour compared to Pt CE for iodine electrolyte.

****

**Fig. 7:** Tafel plot for GO and Pt CE.

The electrocatalytic properties of the CEs are investigated using electrochemical impedance spectroscopy (EIS) analysis. The Nyquist plots of DSSC presented in Fig. 8 are recorded in the frequency of 106 to 10-1 Hz with an amplitude voltage of 0.050 V in the dark. The RCT at the interface of the CE is represented by the semi-circle in the high frequency region (first semi-circle) and also decides the CE’s catalytic action in the I3- reduction.[[68]](#endnote-67),[[69]](#endnote-68) From Fig. 8, it is evident that GO CE exhibited high resistance (first semi-circle) compared to Pt CE which resulted in a low current density.



**Fig. 8:** The Nyquist plots of GO-b and Pt CE based DSSC.

The dummy cell impedance measurements of GO electrodes and Pt electrodes are performed using HCH instrument at voltages 0.7 V and 0.0 V with an amplitude of 0,05 V from 1 MHz to 0.1 Hz. The corresponding EIS plots are fitted with the equivalent circuit model shown in the fig. 9. The Rct of platinum electrodes is 0.42 ohms with applied voltages 0.7 V whereas, the Rct of GO electrodes is 52.26 ohms. From the results, it is evident that the electrocatalytic activity of GO is lesser than Pt.



Fig. 9 Electrochemical impedance of the dummy cells a) GO b) Pt

1. **Conclusions**

We explored the possibility of preparation of screen printed GO films as counter electrodes in DSSC. The cell prepared with GO-a counter electrode exhibited photoconversion efficiency of 0.3% while GO-b counter electrode exhibited photoconversion efficiency of 5.6%. Addition of ethyl cellulose binder resulted in improved adhesion and exhibited better photoconversion efficiency. Although considerable improvement of the efficiency is observed in GO-b films using screen printing method, the EIS studies performed on these electrodes reveals higher resistance in compared to Pt electrode. For this reason, to make this research commercial viable further research is required to bridge the gap in efficiency to make it comparable to that for Pt CE.

**Acknowledgements**

The authors thank the EPRSC-DST APEX consortium grant number EP/H040218/1 for the financial support. S.K.S. thanks the Dept. of Science and Technology (DST), New Delhi, India for Inspire Faculty award [DST/04/2015/002272].

**Declaration of interests:**

The authors declare no competing interests.

**References**

1. Corresponding author: D. Kishore Kumar, Energy conversion lab, Institute of Mechanical Process and Energy Engineering, School of Engineering and Physical Sciences, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS, Scotland, UK. Email id: [nanokishore@gmail.com](mailto:nanokishore@gmail.com) [↑](#footnote-ref-1)
2. C. K. Hong, H. S. Ko, E. M. Han, K. H. Park, *Int. J. Electrochem. Sci.* 10 (2015) 5521-5529. [↑](#endnote-ref-1)
3. A. Esmaeilifar, S. Rowshanzamir, M.H. Eikani, E. Ghazanfari, *Energy* 35 (2010) 3941- 3957. [↑](#endnote-ref-2)
4. C. Sealy, *Mat. Today* 11 (2008) 65-68. [↑](#endnote-ref-3)
5. E. Olsen, G. Hagen, S. E. Lindquist, *Sol. Energy Mater. Sol. cells* 63 (2000) 267- 273. [↑](#endnote-ref-4)
6. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science* 306 (2004) 666-669. [↑](#endnote-ref-5)
7. A. Kaniyoor, S. Ramaprabhu, *J. Appl. Phys.* 109 (2011) 124308 (6pp). [↑](#endnote-ref-6)
8. X. Du, I. Skachko, A. Barker, E. Y. Andrei, *Nat. Nanotechnol*. 3 (2008) 491-495. [↑](#endnote-ref-7)
9. D. G. Papageorgiou, I. A. Kinloch, R. J. Young, *Prog. Mat. Sci.* 90 (2017) 75-127. [↑](#endnote-ref-8)
10. A. Peigney, C. Laurent, E. Flahaut, R. R. Bacsa, A. Rousset, *Carbon* 39 (2001) 507-514. [↑](#endnote-ref-9)
11. D. W. Zhang, X. D. Li, H. B. Li, S. Chen, Z. Sun, X. J. Yin, S. M. Huang, *Carbon* 49 (2011) 5382- 5388. [↑](#endnote-ref-10)
12. J. D. Roy-Mayhew, D. J. Bozym, C. Punckt, I. A. Aksay, *ACS Nano* 4 (2010) 6203-6211. [↑](#endnote-ref-11)
13. S-J. Kim, H-S. Ko, G-H. Jeong, K-H. Park, J-J. Yun, E-M. Han, *Mol. Cryst. Liq. Cryst.* 598 (2014) 1-5. [↑](#endnote-ref-12)
14. W. Hong, Y. Xu, G. Lu, C. Li, G. Shi, *Electrochem. Commun.* 10 (2008) 1555-1558. [↑](#endnote-ref-13)
15. H. Choi, H. Kim, S. Hwang, Y. Han, M. Jeon, *J. Mater. Chem*. 21 (2011) 7548-7551. [↑](#endnote-ref-14)
16. G. Zhu, L. Pan, T. Lu, T. Xu, Z. Sun, *J. Mater. Chem.* 21 (2011) 14869-14875. [↑](#endnote-ref-15)
17. D.W. Zhang, X.D. Li, H.B. Li, S. Chen, Z. Sun, X.J. Yin, S.M. Huang, *Carbon* 49 (2011) 5382- 5388. [↑](#endnote-ref-16)
18. H. Zheng, C. Y. Neo, X. Mei, J. Qiu, J. Ouyang, *J. Mater. Chem.* 22 (2012) 14465-14474. [↑](#endnote-ref-17)
19. Y. Xue, J. Liu, H. Chen, R. Wang, D. Li, J. Qu and L. Dai, *Angew. Chem. Int. Ed.* 51 (2012) 12124-12127. [↑](#endnote-ref-18)
20. G. H. Guai, Q. L. Song, C. X. Guo, Z. S. Lu, T. Chen, C. M. Ng, C. M. Li, *Solar Energy* 86 (2012) 2041-2048. [↑](#endnote-ref-19)
21. G. Wang, W. Xing, S. Zhuo, *Electrochimica Acta* 66 (2012) 151-157. [↑](#endnote-ref-20)
22. S-Y. Jang, Y-G. Kim, D. Y. Kim, H-G. Kim, S. M. Jo, *ACS Appl. Mater. Inter.* 4 (2012) 3500- 3507. [↑](#endnote-ref-21)
23. A. G. Kannan, J. Zhao, S. G. Jo, Y. S. Kang, D-W. Kim, *J. Mater. Chem. A* 2 (2014) 12232- 12239. [↑](#endnote-ref-22)
24. J. Ma, C. Li, F. Yu, J. Chen, *J. Power Sources* 273 (2015) 1048-1055. [↑](#endnote-ref-23)
25. L. Wan, Q. Zhang, S. Wang, X. Wang, Z. Guo, B. Dong, L. Zhao, Z. Xu, J. Li, B. Wang, T. Luo, H. Xiong, *J. Mater. Sci.* 50 (2015) 4412-4421. [↑](#endnote-ref-24)
26. E. Bi, Y. Su, H. Chen, X. Yang, M. Yin, F. Ye, Z. Li, L. Han, *RSC Adv.* 5 (2015) 9075-9078. [↑](#endnote-ref-25)
27. L. Song, Q. Luo, F. Zhao, Y. Li, H. Lin, L. Qu, Z. Zhang, Phys. *Chem. Chem. Phys.* 16 (2014) 21820-21826. [↑](#endnote-ref-26)
28. B. Yang, P. Chen, X. Zuo, L. Zhou, X. Yang, G. Li, M. Wu, Y. Ma, S. Jin, K. Zhu, *Appl. Surf. Sci.* 353 (2015) 300- 306. [↑](#endnote-ref-27)
29. V-D. Dao, L. L. Larina, J-K. Lee, K-D. Jung, B. T. Huy, H-S. Choi, *Carbon* 81 (2015) 710-719. [↑](#endnote-ref-28)
30. J-Y. Lin, A-L. Su, C-Y. Chang, K-C. Hung, T-W. Lin, *ChemElectroChem* 2 (2015) 720-725. [↑](#endnote-ref-29)
31. K. Kakiage, Y. Aoyama, T. Yano, K. Oya, J. Fujisawa, M. Hanaya, *Chem. Commun.* 51 (2015) 15894-15897. [↑](#endnote-ref-30)
32. X.Wang, Y. Xie, Z. Cai, N. Xiong, Z. Xu, M. Li, Q. Feng, W. Zhou, K. Pan, *J. Alloys and Comp.* 739 (2018) 568-576. [↑](#endnote-ref-31)
33. H. Yuan, J. Liu, Q. Jiao, Y. Li, X. Liu, D. Shi, Q. Wu, Y. Zhao, H. Li, *Carbon* 119 (2017) 225-234. [↑](#endnote-ref-32)
34. X. Yuan, X. Li, X. Zhang, Y. Li, L. Liu, *J. Alloys and Comp*. 731 (2018) 685-692. [↑](#endnote-ref-33)
35. Y. Areerob, K-Y. Cho, W-C Oh, *New J. Chem.* 41 (2017) 9613-9622. [↑](#endnote-ref-34)
36. K. Zhang, J. Yao, X. Zuo, Q. Yang, H. Tang, G. Li, M. Wu, K. Zhu, H. Zhang, C*rystEngComm* 20 (2018) 1252-1263. [↑](#endnote-ref-35)
37. J. Ma, S. Yuan, S. Yang, H. Lu, Y. Li, *Appl. Surf. Sci.* 440 (2018) 8–15. [↑](#endnote-ref-36)
38. Y-C. Liu, P. Zhai, M-N. Lu, C-C. Lee, K. S. K. Reddy, Y. Tingare, C-Y. Yeh, T-C. Wei, *Energy Technol*. 5 (2017) 756-764. [↑](#endnote-ref-37)
39. V. Murugadoss, N. Wang, S. Tadakamalla, B. Wang, Z. Guo, S. Angaiah, *J. Mater. Chem. A* 5 (2017) 14583-14594. [↑](#endnote-ref-38)
40. J. Li, S. Yun, X. Zhou, Y. Hou, W. Fang, T. Zhang, Y. Liu, *Carbon* 126 (2018) 145-155. [↑](#endnote-ref-39)
41. C-H. Tsai, C-J. Shih, W-S. Wang, W-F. Chi, W-C. Huang, Y-C. Hu, Y-H. Yu, *Appl. Surf. Sci.* 434 (2018) 412–422. [↑](#endnote-ref-40)
42. L. Chen, W. Chen, E. Wang, *J. Power Sources* 380 (2018) 18-25. [↑](#endnote-ref-41)
43. Z. Yu, Y. Bai, Y. Wang, Y. Liu, Y. Zhao, Y. Liu, K. Sun, *Chem. Eng. J*. 311 (2017) 302–309. [↑](#endnote-ref-42)
44. Z. Shen, M. Wang, L. Liu, M. V. Sofianos, H. Yang, S. Wang, S. Liu, *Electrochimica Acta* 266 (2018) 130-138. [↑](#endnote-ref-43)
45. W. Hou, Y. Xiao, G. Han, *Angew. Chem. Int. Ed.* 56 (2017) 9146-9150. [↑](#endnote-ref-44)
46. S-q. Guo, L-c. Wang, C-g. Zhang, G-c. Qi, B-c. Gu, L. Liu, Z-h.Yuan, *Nanoscale* 9 (2017) 6837-6845. [↑](#endnote-ref-45)
47. T. Liu, K. Yu, L. Gao, H. Chen, N. Wang, L. Hao, T. Li, H. He, Z. Guo, *J. Mater. Chem*. A 5 (2017) 17848–17855. [↑](#endnote-ref-46)
48. T. Jiang, S. Yang, P. Dai, X. Yu, Z. Bai, M. Wu, G. Li, C. Tu, *Electrochimica Acta* 261 (2018) 143-150. [↑](#endnote-ref-47)
49. K. S. Anuratha, M. Ramaprakash, S. K. Panda, S. Mohan, S., *Ceramics International* 43 (2017) 10174-10182. [↑](#endnote-ref-48)
50. Z. Gao, L. Wang, J. Chang, C. Chen, D. Wu, F. Xu, K. Jiang, *J. Power Sources* 348 (2017) 158-167. [↑](#endnote-ref-49)
51. K-H. Bae, E. Park, V-D. Dao, H-S Choi, *J. Alloys and Comp.* 702 (2017) 449-457. [↑](#endnote-ref-50)
52. A. A. Arbab, M. H. Peerzada, I. A. Sahito, S. H. Jeong, *J. Power Sources* 343 (2017) 412-423. [↑](#endnote-ref-51)
53. M-H.Yeh, L-Y. Lin, L-Y. Chang, Y-A. Leu, W-Y Cheng, J-J. Lin, K-C. Ho, *Chem. Phys. Chem.* 15 (2014) 1175-1181. [↑](#endnote-ref-52)
54. R. Cruz, D. A. P. Tanaka, A. Mendes, *Solar Energy* 86 (2012) 716-724. [↑](#endnote-ref-53)
55. C-T. Hsieh, B-H. Yang, Y-F. Chen, *Diamond & Related Mater.* 27–28 (2012) 68-75. [↑](#endnote-ref-54)
56. H-S. Jang, J-M. Yun, D-Y. Kim, D-W. Park, S-I. Na, S-S. Kim, *Electrochimica Acta* 81 (2012) 301-307. [↑](#endnote-ref-55)
57. V-D. Dao, L. L. Larina, K-D. Jung, J-K. Lee, H-S. Choi, *Nanoscale* 6 (2014) 477-482. [↑](#endnote-ref-56)
58. H-S. Jang, J-M. Yun, D-Y. Kim, S-I. Na, S-S. Kim, *Surf. Coat. Tech.* 242 (2014) 8-13. [↑](#endnote-ref-57)
59. V-D. Dao, S-H. Jung, J-S. Kim, Q. C. Tran, S-A. Chong, L. L. Larina, H-S. Choi, *Electrochimica Acta* 156 (2015) 138-146. [↑](#endnote-ref-58)
60. W. S. Hummers, Jr., R. E. Offeman, *J. Am. Chem. Soc.* 80 (1958) 1339-1339. [↑](#endnote-ref-59)
61. M. Ojeda, D. K. Kumar, B. Chen, J. Xuan, M. M. Maroto-Valer, D. Y. C. Leung, H. Wang, *Chem. Select* 2, (2017) 702-706. [↑](#endnote-ref-60)
62. S. K. Swami, N. Chaturvedi, A. Kumar, N. Chander, V. Dutta, D. K. Kumar, A. Iuaturu, S. Senthilrasu, H. M. Upadhyaya, *Phys. Chem. Chem. Phys.* 16 (2014) 23993- 23999. [↑](#endnote-ref-61)
63. S. Bose, T. Kuila, A K. Mishra, N. Kim, J. H. Lee, *J. Mater. Chem.* 22 (2012) 9696-9703. [↑](#endnote-ref-62)
64. C. N. R. Rao, K. Biswas, K. S Subrahmanyam, A. J. Govindaraj, *Mater. Chem.* 19 (2009) 2457-2469. [↑](#endnote-ref-63)
65. I. A. Sahito, K. C. Sun, A. A. Arbab, M. B. Qadir, S. H. Jeong, *Electrochimica Acta* 173 (2015) 164-171. [↑](#endnote-ref-64)
66. H. J. Shin, K. K. Kim, A. Benayad, S. M. Yoon, H. K. Park, I. S. Jung, M. H.Jin, H. K. Jeong, J. M. Kim, J. Y. Choi, Y. H. Lee, *Adv. Funct. Mater.* 19 (2009) 1987-1992. [↑](#endnote-ref-65)
67. L. Kavan, J. Yum, M. Gratzel, *ACS Nano* 5 (2011) 165-172. [↑](#endnote-ref-66)
68. T-S. Oh, D. A. Boyd, D. G. Goodwin, S. M. Haile, *Phys chem. Chem. Phys.* 15 (2013) 2466-2472. [↑](#endnote-ref-67)
69. C-Y. Liu, K-C. Huang, P-H. Chung, C-C. Wang, *J. power sources,* 217 (2012) 152-157.

    **List of Figures**

    **Fig. 1:** a) X-ray diffraction data, and b) Raman spectra of a graphene oxide.

    **Fig. 2:** TEM micrographs of graphene oxide.

    **Fig. 3:** Cyclic voltammetry scans of GO and Pt CE measured at the scan rate of 0.050 V s-1 in 0.01 M LiI, 1.0 mM I2 0.1 M LiClO4 electrolyte in acetonitrile.

    **Fig. 4:** X-ray photoelectron spectroscopy of Graphene oxide film.

    **Fig. 5:** J-V measurements of GO-a CE based DSSC.

    **Fig. 6:** J-V measurements of GO-b CE and Pt CE of the DSSCs.

    **Fig. 7:** Tafel plot for GO and Pt CE.

    **Fig. 8:** The Nyquist plots of GO-b and Pt CE based DSSC.

    Fig. 9 Electrochemical impedance of the dummy cells a) GO b) Pt

    **List of Tables**

    **Table 1:** Photovoltaic performances of DSSCs fabricated with graphene and its related materials.

    **Table 2:** Photovoltaic characteristics of DSSCs fabricated with graphene oxide as CE.

    **Table 3:** Photovoltaic parameters of DSSC with GO-a, GO-b and Pt CEs. [↑](#endnote-ref-68)