

Original Research Article

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Waste water as a Photoelectrochemical Fuel Source for Biphasic Batteries using Liquid Crystals

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ABSTRACT

Keywords

Liquid crystals, N-methyl phenothiazine, Photogalvanic cell Fill factor, Power conversion efficiency, Photocurrent, Photopotential

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The power conversions was studied by producing a voltage-current plot for each system using N-methyl phenothiazine as an active photoagent prepared in the La phase of the crystalline liquid. The photopotential, photocurrent and power were generated by the photogalvanic cell, the conversion efficiency of cell was determined as 27.305%. A mechanism was proposed for the power production process using industrial run-off or other waste water supplies as electrochemical remediation power sources for waste water management which environmentally friendly and little cost to operate.

Introduction

Photogalvanic cells¹ work by creating high energy products where, the product is excited by a photon; the products, full of energy, release this electrochemically in the form of electricity a concentration change in the two form of redox couple allows the cell to develop a photovoltage.

However, a self-assembles lyotropic liquid

crystals^{2,3} was used to produce biphasic photogalvanic cells 'liquid crystal|liquid'⁴, study and optimize a series of photogalvanic cells in order to achieve the highest power conversion as well as study the mechanism for power production within the cell. Photogalvanic⁵ and photochemistry⁶ in general are well studied.

This study will try to produce a novel system and show how cells can be created using

water waste with very little cost to operate and environmentally friendly.

Materials and Methods

Electrochemical measurements

The electrochemical measurements were recorded using an Autolab PGSTAT30 potentiostat. In all cases, a three electrode system was employed, with nickel wire wound into a spiral serving as the counter electrode, and a silver/silver chloride was utilized as the reference electrode. The working electrode was a 3.0 mm diameter glassy carbon disc electrode (purchased from BASI,UK).

Reagents

All chemical reagents were purchased from Sigma-Aldrich.

Procedures

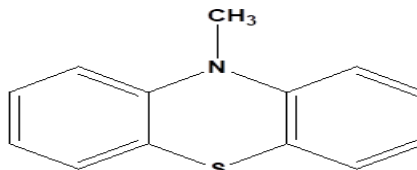
Formulation of normal lyotropic liquid crystals

Surfactant (Brij 35 or Triton X 100)^{7,8}/aqueous electrolyte (KCl) mixtures in the mass ratio required by the published phase diagrams were homogenised in the presence of the required amount of redox dopant and photosensitizers N-methylphenothiazine (NMP)⁹ through heating, to approximately 320 K, with stirring, so as to form the micellar isotropic phase, for about one hour. The samples were then allowed to cool, slowly to 294 ± 2 K.

System under investigation (Photo-biphasic batteries)

An indium tin oxide (ITO) cell was attached with tube then half filled it with then half filled with the NMP liquid crystal and the aqueous ZnCl₂ solution was then added on top of it¹⁰. It was decided that a two phases, liquid

crystal |liquid photogalvanic cell should be constructed and tested. The photoactive agent NMP was suggested for study and so several experiments were planned using this thionine like chemicals. This was suggested as its likeness to thionine as well as it never being studied for photocells before. Chloroform¹¹ was proposed as a mediator as it would act as an artificial pollutant.



N-methylphenothiazine

Results and Discussion

UV-Vis spectra of NMP in L_α phase and H₁ phase

The experimentally observed absorption for NMP maxima is π to π* peak at 352 nm (3.52 eV) in L_α 2.6628 and in H₁ phase the absorbance is 2.2190 (Figure 1). So it can be seen that the L_α phase observed higher absorbance than H₁. However, the energy band was calculated from the wavelength by using this formula¹²⁻¹⁴: Energy (E) = $\frac{h \times c}{\lambda}$, where, Energy (E) = band gap, planks constant (h) = 6.626 × 10⁻³⁴ Joules sec, velocity of light (C) = 2.99 × 10⁸ meter/sec and wavelength (λ) = absorption peak value. Also 1eV = 1.6 × 10⁻¹⁹ Joules (conversion factor).

Determination of NMP by differential pulse voltammetry (DPV)

The DPV¹⁵ exhibited anodic peak in about 0.523 V to the oxidation of NMP in L_α phase (Figure 2), also exhibited anodic peak in about 0.5532 V to the oxidation of NMP in H₁ phase (Figure 3). Surfactant changes the potential peak NMP and therefore the

charging current. The peak potential at L_{α} phase has lower than at H_1 phase. The height of the current wave of NMP in L_{α} phase was found to be higher than in H_1 phase. Therefore, the L_{α} phase was chosen for use in design of photogalvanic cell.

**Effect of variation of NMP concentration:
Zn | Zn²⁺,CHCl₃, NMP | ITO**

All cells measured in the same conditions (light intensity = 103.2μW/cm²/electrode area = 0.78 cm²/ZnCl₂=0.01 M). As we can see from Table 1 increasing in the concentration

of NMP there is increasing in the electrical output until reach the maximum point and then decrease.

On the lower concentration range of NMP; there is a limited number of photosensitized molecules to absorb the major portion of the light and therefore, a few number of electrons can reach the zinc electrode and a low electrical output was obtained. Table 2 shows the calculation of max power density, fill factor and power conversion efficiency for each cell.

Table.1 Effect of variation of photosensitizer NMP concentration

| NMP concentration | 0.01 M | 0.1 M | 1 M | 1.75 M | 2 M |
|--------------------|---------|---------|--------|--------|-------|
| Photopotential (V) | 0.481 | 0.803 | 0.792 | 0.850 | 0.550 |
| Photocurrent (μA) | 14.1815 | 14.872 | 27.647 | 14.705 | 10.41 |
| Power(μW) | 6.8210 | 11.9420 | 21.89 | 12.499 | 5.73 |

Table.2 Calculation of max power density, fill factor and power conversion efficiency for each cell (NMP)

| NMP concentration | Max Power Density | Fill Factor | Power Conversion efficiency |
|-------------------|--------------------------------|--------------|-----------------------------|
| 0.01 M | 8.743 μW/Cm ² | 0.226 | 8.472% |
| 0.1 M | 15.3102 μW/Cm ² | 0.256 | 14.835% |
| 1 M | 28.17 μW/Cm² | 0.242 | 27.305% |
| 1.75 M | 16.012μW/Cm ² | 0.245 | 15.516% |
| 2 M | 7.346 μW/Cm ² | 0.224 | 7.118% |

Table.3 Calculation of max power density, fill factor and power conversion efficiency for each cell (ZnCl₂)

| ZnCl ₂ concentration | Max Power Density | Fill Factor | Power Conversion efficiency |
|---------------------------------|--------------------------------|--------------|-----------------------------|
| 0.004 M | 2.4410 μW/Cm ² | 0.2419 | 2.3653% |
| 0.008 M | 4.4789 μW/Cm ² | 0.2507 | 4.3400% |
| 0.01 M | 28.17 μW/Cm² | 0.242 | 27.305% |
| 0.016 M | 3.4600μW/Cm ² | 0.2546 | 3.353% |
| 0.019 M | 2.2208 μW/Cm ² | 0.2428 | 2.15203% |

Fig.1 UV-Vis spectra of 0.1 M NMP in $L\alpha$ phase and H_1 phase

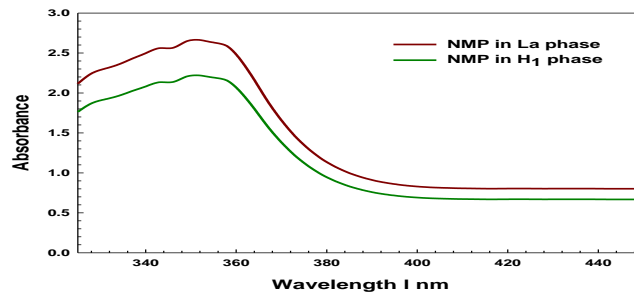


Fig.2 Differential pulse voltammograms of 0.1M of NMP, in $L\alpha$ phase, with scan rate 0.05 V/s

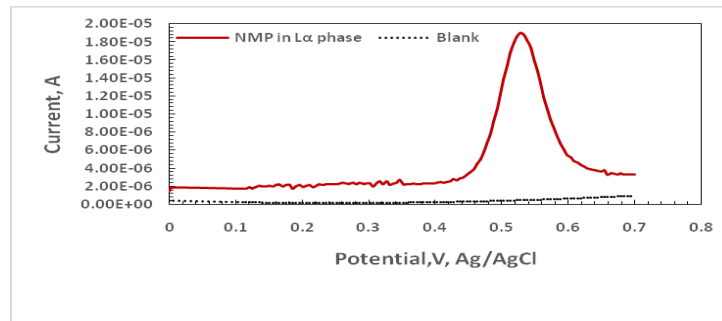


Fig.3 Differential pulse voltammograms of 0.1M of NMP, in H_1 phase, with scan rate 0.05 V/s

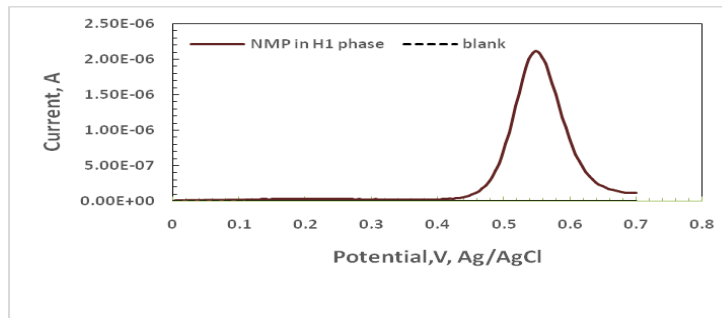


Fig.4 Effect of variation of $ZnCl_2$ concentrations on electrical output

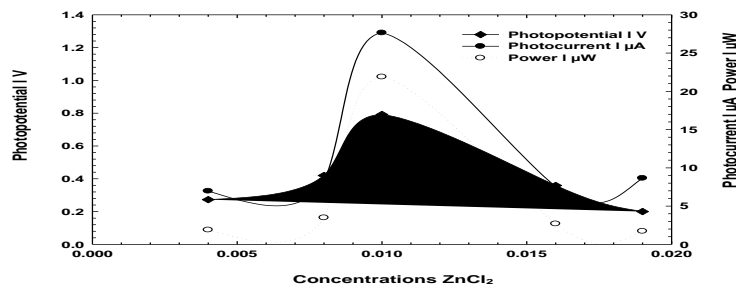
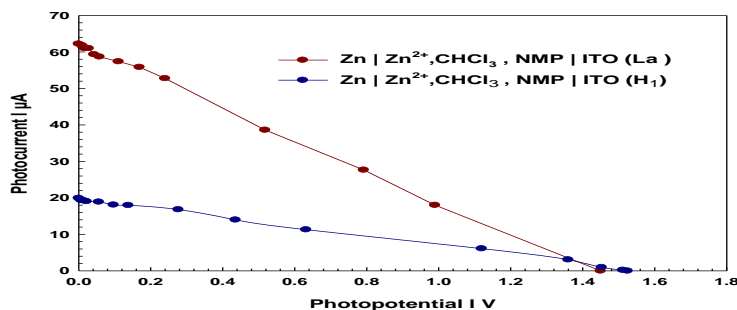


Fig.5 Current-voltage (i-v) curve of the cell (L_α, H₁)



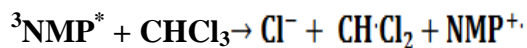
Effect of variation of reductant (ZnCl₂) concentration

With the increase in concentration of the reductant the photopotential and photocurrent were found to increase until they reach a maximum value. On further increase in concentration of reductant the decrease in electrical output of The cell was found. graphically the NMP-ZnCl₂ system represented graphically in Figure 4, however, table 3 shows the calculation of max power density, fill factor and power conversion efficiency for each cell.

Possible reaction mechanism

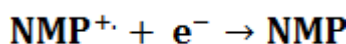
Using the analogues reaction¹⁶⁻¹⁸ outlined in the introduction section of this document by Girault a reaction mechanism can be postulated.

In the liquid crystal phase

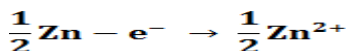


Where ¹NMP* is the excited singlet state and ³NMP* is the excited triplet state.

At the light electrode



At dark electrode



This shows how NMP can be used as the light harvester and the zinc electrode is sacrificial. The excited singlet state is the most likely to be produced on direct excitation however it will quickly relax into the less excited triplet state.

The effect of surfactant in PC

The use of Triton-X as a replacement to Brij-35 to see the effect of liquid crystal phases on the PC. From UV-Vis spectroscopy and DPV we can see the low absorbance and electrochemical properties this is probably due to the arrangement¹⁹ of molecules in H₁ phase it causes a lot of refraction and less absorbance than L_α phase of light. It can be seen Figure 5 is not an ideal situation as a lamellar phase with 8.864 % PC.

In conclusion this work has demonstrated that a photogalvanic cell can be constructed that can have high conversion rates, ≈ 27.305 %. Although the reaction mechanisms given cannot be fully verified it does seem to fit the empirical evidence. Namely that the stepwise reaction is far less efficient than the concerted, faster reaction. The ability for

power to be produced even when very little chloroform is present is a property that makes this type of cell of interest. A novel attempt at power production was attempted with the construction and optimization of a photogalvanic cell system. The study aimed to create a cell that could be produced using industrial run-off or other waste water supplies. A series of cells was produced with varying concentrations of NMP solutions and the power conversions studied by producing a voltage-current plot for each system. The photopotential, photocurrent and power generated by the photogalvanic cell were 0.792 V, 27.647 μ A and 21.89 μ W respectively. The determined conversion efficiency of cell was determined as 27.305% and fill factor was 0.242. A mechanism was proposed for the power production process.

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