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

Amal A. Altalhi*

Chemistry department, Faculty of science, Taif University, KSA

*Corresponding author

A B S T R A C T

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.

K e y w o r d s
Liquid crystals, N-methyl phenothiazine, Photogalvanic cell Fill factor, Power conversion efficiency, Photocurrent, Photopotential

Introduction

Photogalvanic cells\(^1\) 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 photogalvaine 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. Photogalvanic\(^5\) and photochemistry\(^6\) 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)/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) 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 it. It was decided that a two phases, liquid crystal | liquid photogalvanic cell should be constructed and tested. The photoreactive 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. Chloroform was proposed as a mediator as it would act as an artificial pollutant.

Results and Discussion

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

The experimentally observed absorption for NMP maxima is π to π* peak at 352 nm (3.52 eV) in Lα 2.6628 and in H₁ phase the absorbance is 2.2190 (Figure 1). So it can be seen that the Lα phase observed higher absorbance than H₁. However, the energy band was calculated from the wavelength by using this formula: Energy (E) = \frac{hc}{\lambda}

where, Energy (E) = band gap, planks constant (h) = 6.626×10⁻³⁴ Joules sec, velocity of light (C) = 2.99×10⁻⁸ 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 DPV exhibited anodic peak in about 0.523 V to the oxidation of NMP in Lα 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 \( \text{L}_\alpha \) phase has lower than at \( \text{H}_1 \) phase. The height of the current wave of NMP in \( \text{L}_\alpha \) phase was found to be higher than in \( \text{H}_1 \) phase. Therefore, the \( \text{L}_\alpha \) phase was chosen for use in design of photogalvanic cell.

**Effect of variation of NMP concentration:**

\( \text{Zn} | \text{Zn}^{2+}, \text{CHCl}_3, \text{NMP} | \text{ITO} \)

All cells measured in the same conditions (light intensity = 103.2\( \mu \text{W/cm}^2/\text{electrode area} = 0.78 \text{ cm}^2/\text{ZnCl}_2=0.01 \text{ M} \)). 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 (\( \mu \text{A} \)) | 14.1815| 14.872| 27.647| 14.705| 10.41 |
| Power(\( \mu \text{W} \)) | 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 \( \mu \text{W/Cm}^2 \) | 0.226 | 8.472% |
| 0.1 M             | 15.3102 \( \mu \text{W/Cm}^2 \) | 0.256 | 14.835% |
| 1 M               | 28.17 \( \mu \text{W/Cm}^2 \)   | 0.242 | 27.305% |
| 1.75 M            | 16.012 \( \mu \text{W/Cm}^2 \) | 0.245 | 15.516% |
| 2 M               | 7.346 \( \mu \text{W/Cm}^2 \)   | 0.224 | 7.118% |

**Table 3** Calculation of max power density, fill factor and power conversion efficiency for each cell (\( \text{ZnCl}_2 \))

| \( \text{ZnCl}_2 \) concentration | Max Power Density | Fill Factor | Power Conversion efficiency |
|-----------------------------------|------------------|-------------|-----------------------------|
| 0.004 M                           | 2.4410 \( \mu \text{W/Cm}^2 \) | 0.2419 | 2.3653% |
| 0.008 M                           | 4.4789 \( \mu \text{W/Cm}^2 \) | 0.2507 | 4.3400% |
| 0.01 M                            | 28.17 \( \mu \text{W/Cm}^2 \)   | 0.242 | 27.305% |
| 0.016 M                           | 3.4600 \( \mu \text{W/Cm}^2 \) | 0.2546 | 3.353% |
| 0.019 M                           | 2.2208 \( \mu \text{W/Cm}^2 \) | 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
Effect of variation of reductant (ZnCl$_2$) 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-ZnCl$_2$ 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 reaction\textsuperscript{16-18} outlined in the introduction section of this document by Girault a reaction mechanism can be postulated.

In the liquid crystal phase

\[ \text{NMP} \xrightarrow{h\nu} \text{NMP}^* \xrightarrow{\text{Fast}} \text{3NMP}^* \]

\[ \text{3NMP}^* + \text{CHCl}_3 \rightarrow \text{Cl}^- + \text{CH}Cl_2 + \text{NMP}^+ \]

Where \(^{1}\text{NMP}^*\) is the excited singlet state and \(^{3}\text{NMP}^*\) is the excited triplet state.

At the light electrode

\[ \text{NMP}^+ + e^- \rightarrow \text{NMP} \]

At dark electrode

\[ \frac{1}{2} \text{Zn} - e^- \rightarrow \frac{1}{2} \text{Zn}^{2+} \]

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 arrangement\textsuperscript{19} of molecules in H$_1$ phase it causes a lot of refraction and less absorbance than L$_\alpha$ 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, \(\approx 27.305\) %. 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 µA and 21.89 µW 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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