

Exploiting Wastewater as a Photoelectrochemical Energy Source in Biphasic Liquid Crystal Batteries

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ABSTRACT

The power conversion was investigated by generating voltage–current plots for each system using N-methyl phenothiazine as the active photoagent, prepared in the L α phase of the liquid crystal. The photogalvanic cell produced measurable photopotential, photocurrent, and power, with a calculated conversion efficiency of 27.305%. A mechanism was proposed for power generation using industrial runoff or other wastewater sources as electrochemical fuel, providing an environmentally friendly and low-cost approach to wastewater management.

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

INTRODUCTION

Photogalvanic Cells and Biphasic Liquid Crystal Systems

Photogalvanic cells work by generating high-energy products when a photon excites the system; these energy-rich products subsequently release their energy electrochemically in the form of electricity. A change in the concentration of the two forms of the redox couple enables the cell to develop a photovoltage. In this study, self-assembled lyotropic liquid crystals were employed to create biphasic photogalvanic cells ('liquid crystal I liquid'). The aim was to design and optimize a

series of photogalvanic cells to achieve maximum power conversion efficiency and to investigate the underlying mechanism of power generation within the cell. While photogalvanic processes and photochemistry are well-established fields, this study seeks to develop a novel system demonstrating how wastewater can be used as a low-cost, environmentally friendly medium for generating electricity.

MATERIALS AND METHODS

Electrochemical Measurements

Electrochemical experiments were

conducted using an Autolab PGSTAT30 potentiostat. A three-electrode setup was employed in all cases, with a nickel wire spiral serving as the counter electrode and a silver/silver chloride electrode as the reference. The working electrode consisted of a 3.0 mm diameter glassy carbon disc (BASI, UK).

Reagents

All chemical reagents were purchased from Sigma-Aldrich.

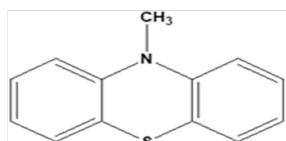
Procedures

Formulation of Lyotropic Liquid Crystals

Surfactant (Brij 35 or Triton X-100) and aqueous electrolyte (KCl) mixtures were prepared according to the mass ratios specified in published phase diagrams. The mixtures were homogenized with the required redox dopant and photosensitizer, N-methylphenothiazine (NMP), by heating to approximately 320 K with stirring for about one hour to form a micellar isotropic phase. 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 connected to a tube and half-filled with the NMP-containing liquid crystal, followed by the addition of aqueous ZnCl solution on top, creating a biphasic system. A two-phase (liquid crystal | liquid) photogalvanic cell was thus constructed and tested. NMP was selected as the photoactive agent due to its structural similarity to thionine and because it had not previously been explored in photocells. Chloroform was used as a mediator, simulating an artificial pollutant for the study.



N-methylphenothiazine

RESULTS AND DISCUSSION

UV-Vis spectra of NMP in $L\alpha$ phase and H_1 phase

The experimentally observed absorption for NMP maxima is π to π^* peak at 352 nm (3.52 eV) in $L\alpha$ phase and in H_1 phase the absorbance is

2.2190 Fig. 1. So it can be seen that the $L\alpha$ phase observed higher absorbance than H_1 . However, the energy band was calculated from the wavelength by using this formula¹²⁻¹⁴: Energy (E) = , 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 $1\text{eV} = 1.6 \times 10^{-19}$ Joules (conversion factor).

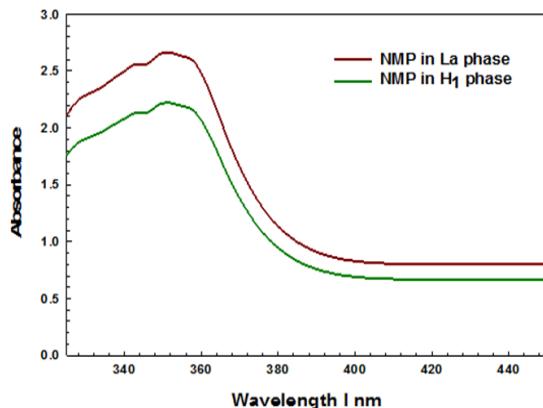


Fig. 1. UV-Vis spectra of 0.1 M NMP in $L\alpha$ phase and H_1 phase

Determination of NMP by differential pulse voltammetry

The DPV15 exhibited anodic peak in about 0.523 V to the oxidation of NMP in $L\alpha$ phase Fig. 2, also exhibited anodic peak in about 0.5532 V to the oxidation of NMP in H_1 phase. Fig. 3. Surfactant changes the potential peak NMP and therefore the charging current. The peak potential at $L\alpha$ phase has lower than at H_1 phase. The height of the current wave of NMP in $L\alpha$ phase was found to be higher than in H_1 phase. Therefore, the $L\alpha$ phase was chosen for use in design of photogalvanic cell.

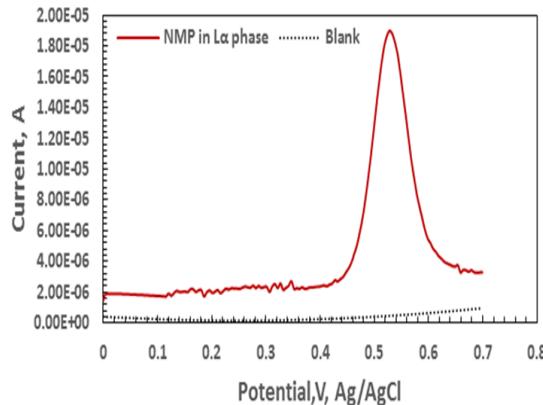


Fig. 2. Differential pulse voltammograms of 0.1 M of NMP, in $L\alpha$ phase, with scan rate 0.05 V/s

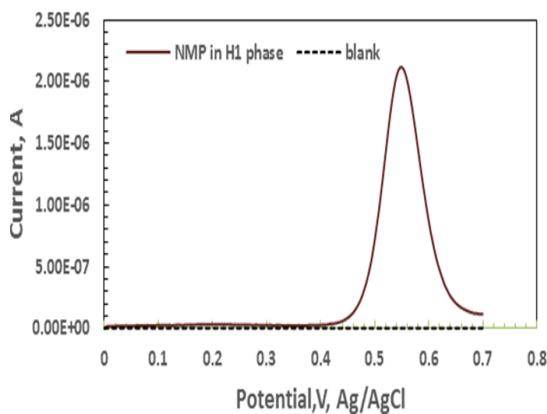


Fig. 3. Differential pulse voltammograms of 0.1M of NMP, in H₁ phase, with scan rate 0.05 V/s

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

All cells measured in the same conditions (light intensity = 103.2 μW/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.

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

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 show the calculation of max power density, fill factor and power conversion efficiency for each cell.

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/cm ²	0.242	27.305%
1.75 M	16.012 μW/cm ²	0.245	15.516%
2 M	7.346 μW/cm ²	0.224	7.118%

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 Fig. 4, however, Table 3 shows the calculation of max power density, fill factor and power conversion efficiency for each cell.

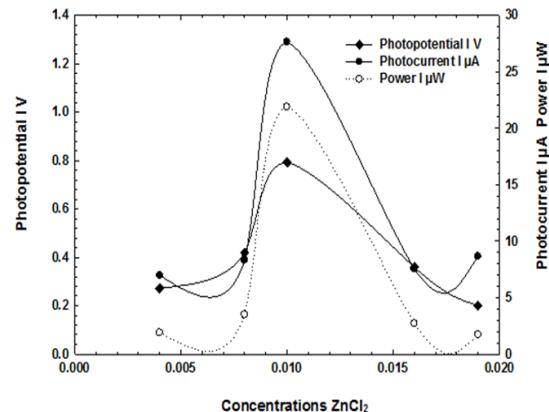


Fig. 4. Effect of variation of ZnCl₂ concentrations on electrical output

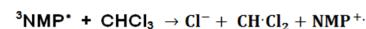
Table 3: Calculation of max power density, fill factor and power conversion efficiency for each cell (ZnCl₂)

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/cm ²	0.242	27.305%
0.016 M	3.4600 μW/cm ²	0.2546	3.353%
0.019 M	2.2208 μW/cm ²	0.2428	2.15203%

Possible reaction mechanism

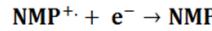
Using the analogues reaction¹⁶⁻¹⁸ outlined in the introduction section of this document by Girault a reaction mechanism can be postulated.

In the liquid crystal phase

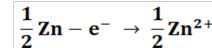


Where 1 NMP* is the excited singlet state and 3NMP* is the excited triplet state.

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 H_1 phase it causes a lot of refraction and less absorbance than $L\alpha$ phase of light. It can be seen Fig. 5 is not an ideal situation as a lamellar phase with 8.864 % PC.

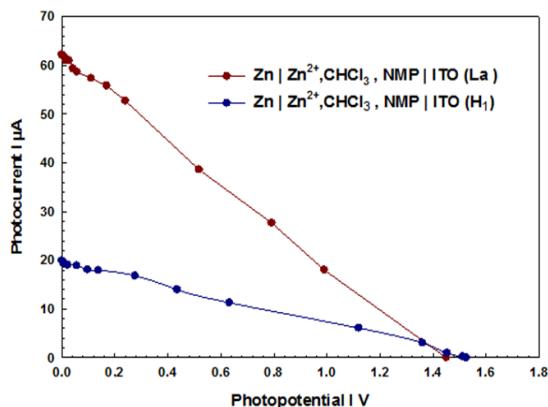


Fig. 5. Current-voltage (i-v) curve of the cell (La, H₁)

CONCLUSION

This study demonstrates that a photogalvanic cell can be constructed with a high conversion efficiency of approximately 27.305%. While the proposed reaction mechanisms cannot be fully confirmed, they appear to align with the empirical observations, particularly showing that the stepwise reaction is significantly less efficient than the faster, concerted reaction. Notably, the cell is capable of producing power even with minimal chloroform present, highlighting a key feature of interest.

A novel approach to power generation was explored through the construction and optimization of a photogalvanic cell system. The study focused on developing a cell that could utilize industrial run-off or other wastewater sources. Multiple cells were fabricated with varying concentrations of NMP solutions, and their power conversion was analyzed using voltage-current plots. The photogalvanic cell exhibited a photopotential of 0.792 V, a photocurrent of 27.647 μ A, and a power output of 21.89 μ W. The conversion efficiency was determined to be 27.305%, with a fill factor of 0.242. Additionally, a mechanism for the power generation process was proposed.

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