

Original Research Article

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Toward Green Battery Cells: Optimization and Characterization of Photo-biphasic Batteries using Liquid Crystals

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ABSTRACT

Keywords

Chlorophyll, Algae, Hexagonal phase, Indium tin oxide, Lamellar phase, Open circuit voltage, Short circuit current

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Photogalvanic cells 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, Liquid crystals (LCs) are matter in a state which has properties between those of conventional liquids and those of solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way, these properties make LCs are promising material to use in photo-biphasic batteries.

Introduction

Koli studied a photogalvanic cell consisting of Fast Green FCF as photosensitizer, fructose as reductant and NaOH as alkaline medium has been studied with 1.33%, the observed results are higher and encouraging enough for ultimate aim of development of applicable and affordable photogalvanic cells in future (Koli, 2014). However, Chlorophyll (Vredenberg, 2011) from fresh spinach leaves and algae were studied to produce a novel system and show how cells can be created with very little cost to operate and environmentally friendly. In this

work it was prepared self-assembles lyotropic liquid crystals (Andrienko, 2006) in the lamellar (L_a) phase by using Brij-35 and in the hexagonal (H_1) phase by using TritonX-100 and use it to produce biphasic photogalvanic cells 'liquid crystal liquid', 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 and photochemistry in general are well studied; however there is still room for huge improvements and investigations within the subject.

Materials and Methods

Instrumentation

Thin films of ITO are used in organic light-emitting diodes, solar cell, antistatic coatings and EMI shieldings. In organic light-emitting diodes, ITO is used as the anode (hole injection layer).

UV-Visible spectrometry

UV- visible spectrometry was undertaken using a Geneys 10S VIS UV-visible spectrometry system (Thermo Fisher Scientific, USA), with a clear quartz cuvette of path length 1 cm.

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 reagents were prepared using analytical grade chemicals, and all aqueous solutions were made up using deionized water. Any solvents used were of HPLC grade, and used without further purification, all chemical reagents were purchased from Sigma-Aldrich or Scharlab S.L.

Procedures

Extraction chlorophyll from spinach leaves

Plant pigment (a mixture of chlorophylls a and b) (Lehmann, 2011) was obtained using

fresh spinach leaves 5g were cut into strips and stirred at room temperature in an aqueous acetone solution (4:1 vol./vol. acetone/ water) for ca.120min (Ermakov, 2016), following with filtration, the solvent was removed using a rotary evaporator, and the resulting solid examined via UV/Visible spectroscopy in 5ml methanol. Percent of chlorophyll (1.7543 μ g/ml total chlorophyll, presented as 1.3904 μ g/ml of chlorophyll a and 0.3637 μ g/ml of chlorophyll b. Chlorophyll was calculated by using the Arnon equation (Rosen, 2012)

$$\text{Total Chlorophyll } (\mu\text{g/ml}): 20.2(A_{645}) + 8.02(A_{663})$$

$$\text{Chlorophyll a } (\mu\text{g/ml}): 12.7(A_{663}) - 2.69(A_{645})$$

$$\text{Chlorophyll b } (\mu\text{g/ml}): 22.9(A_{645}) - 4.68(A_{663})$$

Where: A_{645} = absorbance at a wavelength of 645 nm (0.04nm) and A_{663} = absorbance at a wavelength of 663 nm (0.118nm). The plant pigment was stored in the dark at 277 K when not in use.

Extraction chlorophyll from algae

Approximately 5 g of algae was weighed out. about 5 ml of acetone was added and grind the algae with a pestle until the acetone turns a bright, deep green.20 ml of hexane and 20 ml of distilled water were added to the extract in the tube, then cork it and shake gently. Clearly, there is a cloudy, light green lower water layer and a clear, bright green top hexane layer. Following by filtration then the extract was examined via UV/Visible spectroscopy by using Arnon equation: % chlorophyll (1.664 μ g/ml total chlorophyll, present as 1.505 μ g/ml of chlorophyll a and 0.15866 μ g/ml of chlorophyll b Where: A_{645} = 0.0326nm and A_{663} =0.1255nm

Formulation of normal lyotropic liquid crystals

Lyotropic liquid crystals in the lamellar (L_{α}) or hexagonal (H_1) phases (Toamhane, 2009) were prepared in flat-bottomed sample containers, employing Brij 35 or Triton X 100 surfactants, respectively (Gaikwad, 2013). Briefly, surfactant (Brij35 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 chlorophyll, 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.

Table.1 Current-Voltage (i-V) characteristics of the cell Zn | Zn²⁺, CHCl₃, chlorophyll (spinach)| ITO

V	I μ A	P μ W
0	24.417	0
0.003	23.906	0.071718
0.008	22.9544	0.183635
0.014	22.5324	0.315454
0.02	22.0104	0.440208
0.047	21.1114	0.992236
0.075	19.1422	1.435665
0.103	17.1729	1.768809
0.191	9.9838	1.906906
0.245	7.1859	1.760546
0.273	5.2166	1.424132
0.34	0	0

Table.2 Current-Voltage (i-V) characteristics of the cell Zn | Zn²⁺, CHCl₃, chlorophyll (algae)| ITO

V	I μ A	P μ W
0	34.08	0
0.004	33.9792	0.135917
0.013	32.1024	0.417331
0.022	31.4255	0.691361
0.033	30.9983	1.022944
0.031	30.7487	0.95321
0.071	28.7406	2.040583
0.114	26.5069	3.021787
0.152	23.6491	3.594663
0.24	16.0313	3.847512
0.325	8.639	2.807675
0.446	1.5395	0.686617
0.626	0	0

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

Photogalvanic cells	Max power density	Fill factor	Power conversion efficiency
Zn /Zn ⁺² , CHCl ₃ , Chlorophyll algae / ITO	4.932 μW/Cm ²	0.1803	4.779%
Zn / Zn ⁺² , CHCl ₃ , Chlorophyll spinach/ ITO	2.444μW/Cm ²	0.229	2.368%

Fig.1 UV-Vis spectra of 0.1 M chlorophyll from algae, red line in L_α phase and green line in H₁ phase

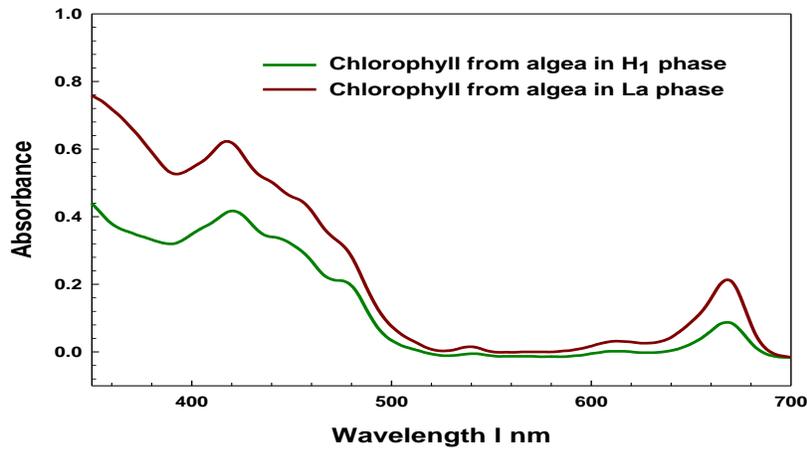


Fig.2 UV-Vis spectra of 0.1 M chlorophyll from spinach, red line in L_α phase and green line in H₁ phase

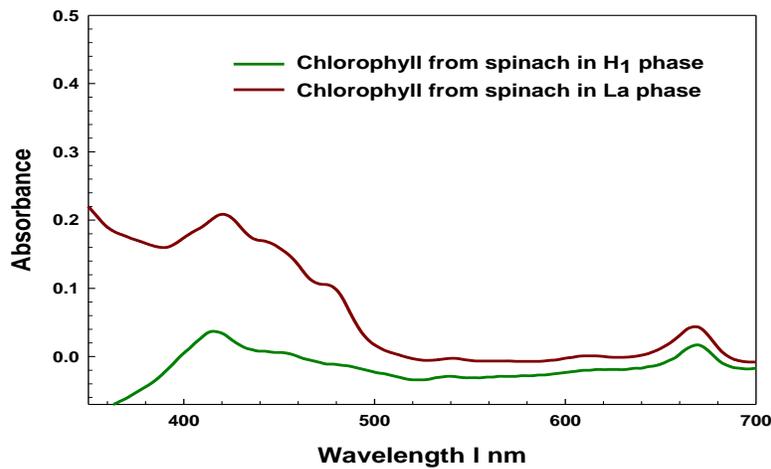


Fig.3 Differential pulse voltammograms of (a) 0.1M chlorophyll from algae ,(b) 0.1M chlorophyll from spinach in L α phase , initial potential 0.0 V, final potential 0.9 V, with scan rate 0.05 V/s

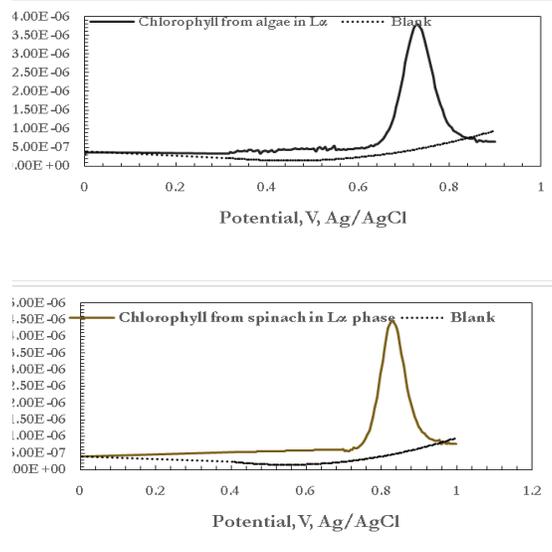


Fig.4 Differential pulse voltammograms of (a) 0.1M chlorophyll from algae, (b) 0.1M chlorophyll from spinach in H $_1$ phase, initial potential 0.0 V, final potential 1.1 V, with scan rate 0.05 V/s

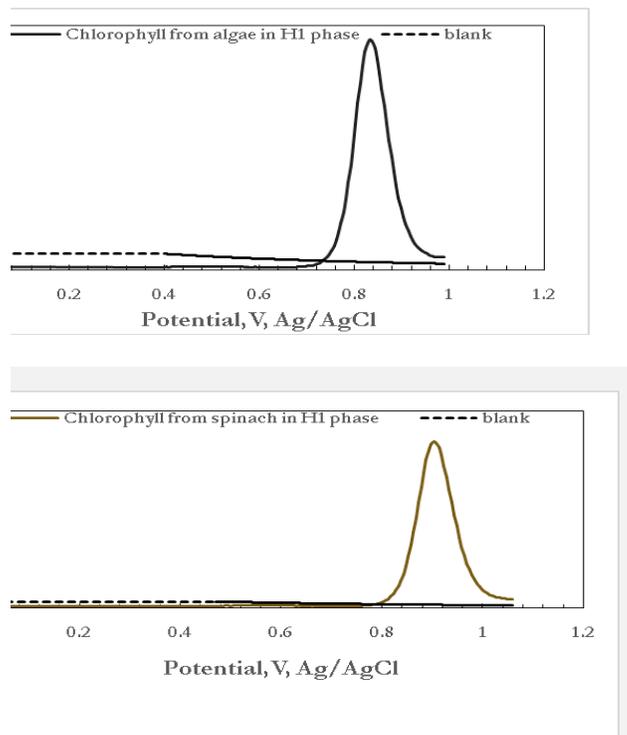


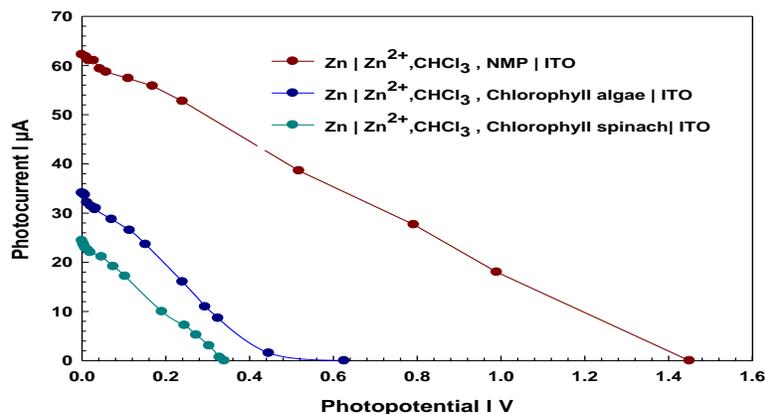
Fig.5 Current-voltage (i-v) curve of the cell (NMP²³, chlorophyll)

Photo-biphasic batteries

For this experiment weighted out 3 g of chlorophyll, 2.5g chloroform were add in 5g of Brij-35, where 5 g of 0.1M potassium chloride was added, this mixture was stirred and heated to $\approx 353\text{K}$ for 1 hour (Amos, 2005). An indium tin oxide (ITO) cell was attached with tube then half filled it with then half filled with the chlorophyll liquid crystal and the aqueous ZnCl_2 solution was then added on top of it. A long wave UV lamp was then focused on the cell. The cell was irradiated with 350nm light. A zinc rod was then placed into the aqueous phase and connected to a voltmeter, ammeter and resistor array. The cell was then tested using a series of fixed resistors as well as a variable resistor. The voltage and current were then recorded after the readings become steady.

UV-Vis spectra of dyes in L_α and H_1 phases

The experimentally observed absorption for chlorophyll from algae observed absorption maxima is π to π^* peak at 418 nm (2.97 eV) in L_α 0.6230 and in H_1 phase the absorbance is 0.4140 and n to π^* peak at 667 nm (1.86 eV) in L_α 0.2120 and in H_1 phase the absorbance is 0.0870 Figure 1. Also we have spectrum for chlorophyll from spinach leave show less

absorption in π to π^* peak at 418 nm (2.97 eV) in L_α 0.2070 and in H_1 phase the absorbance is 0.0360 and n to π^* peak at 667 nm (1.86 eV) in L_α 0.0435 and in H_1 phase the absorbance is 0.0160 Figure 2. So it can be seen that the L_α phase observed higher absorbance than H_1 . Note, the calculation of the energy band from the wavelength was used this formula (Patzelt, 1974): 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) = 2.99×10^8 meter/sec and wavelength (λ) = absorption peak value. Also $1\text{eV} = 1.6 \times 10^{-19}$ Joules (conversion factor) (Mahmoud, 2015).

Determination of dyes by differential pulse voltammetry (DPV)

The DPV (Liang, 2017) exhibited anodic peak at about 0.7179 V and 0.8431 V corresponding to the oxidation of chlorophyll from algae and chlorophyll from spinach in L_α phase respectively Figure 3. Also exhibited anodic peak at about 0.8382 V and 0.9132V corresponding to the oxidation of chlorophyll from algae and chlorophyll from spinach in H_1 phase respectively Figure 4. Surfactant changes the potential peak for each dye and therefore the charging current. The peak potential at L_α phase has lower than at

H₁ phase. The height of the current wave of each dyes in L_α phase was found to be higher than in H₁ phase. Therefore, the L_α phase was chosen for use in design of photogalvanic cell.

The effect of light harvesting agent on PC: Zn | Zn²⁺, CHCl₃, Chlorophyll | ITO

The active, light harvesting, agent of the cell was then changed to see if further deviations on the system could be produced. The use of Chlorophyll, a large and conjugated species, was hoped to invoke much larger power efficiencies and absorb more of the UV light thus driving power production. As you can see from Figure 5 chlorophyll from spinach and algae none of the cells produced a large enough max power or a significantly large power conversation to warrant further study, the reason of lower conversion of chlorophyll (spinach) is the molecular weight of chlorophyll is big and it was concentrated more than chlorophyll (algae) so the excitation and the movement of electron and photon is low and we can see that clearly from UV-vis spectroscopy despite the energy band is lower than NMP but it can be noticed the peaks of chlorophyll accrue in the vis region not in the UV wavelength. Table 1 show current-voltage (i-V) characteristics of the cell (chlorophyll spinach) and Table 2 show Current-Voltage (i-V) characteristics of the cell (chlorophyll algae) (Table 3).

In conclusion the poor efficiency of chlorophyll still requires some explanation. This may be due to the size of the molecule and so the ability to move around the system that limits its efficiency (Yano, 2017). The back reaction may also prove to be prolific. It may be advantages to try this cell with a surfactant molecule present and above the critical micelle concentration (CMC). This would reduce the rate of the back reaction if it is under diffusion control. Further cell

containing different metal ions were discarded due to poor efficacy. Although these devise may prove efficient after further work the time constraints of this project impeded further study.

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