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APPLICATION OF ACIDIFIED CHLOROPHYLLIN COMPLEXED WITH FERROCENE DERIVATIVE IN DYE-SENSITIZED SOLAR CELL

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Abstract— In this work, the application of ferrocene and acetylferrocene in dye-sensitized solar cells (DSSC) was explored. Acidified chlorophyllin was used as the base dye to form a complex with ferrocene and acetylferrocene. It was found that when only acidified chlorophyllin was used, the highest power conversion efficiency (PCE), which was at 0.07%, was obtained at the concentration of 0.075 mmol/L. Different complexes were tested at different initial mole fractions of ferrocene and acetylferrocene. The amount of ferrocene being adsorbed increased as the initial mole fraction of ferrocene increased. On the other hand, the amount of acetylferrocene being adsorbed increased and started to decline slightly at the initial mole fraction of 0.50. Due to weak interaction between ferrocene and acetylferrocene with acidified chlorophyllin, both metallocene were dissolved in the electrolyte solvent when the electrolyte was added to the devices. Redox reaction took place between iodine present in the electrolyte and ferrocene, and resulted in the formation of precipitate, which led to lower concentration of electrolyte. Lower concentration of electrolyte resulted in drastic decline in short-circuit current (J_{SC}), PCE and slight decline in open-circuit voltage (V_{OC}) of acidified chlorophyllin-ferrocene device. On the other hand, acidified chlorophyllin-acetylferrocene device exhibited similar trend to acidified chlorophyllin-ferrocene device with its J_{SC} to be lower than J_{SC} of acidified chlorophyllin-ferrocene device, which might be caused by higher charge recombination due to the presence of acetyl ferrocenium ion in the electrolyte. Therefore, it was discovered that the formation of the complexes between acidified chlorophyllin with ferrocene and acetylferrocene did not help in improving the performance of DSSC

Keywords— Acetylferrocene, Acidified Chlorophyllin, Complex, Dye-Sensitized Solar Cell, Ferrocene

I. INTRODUCTION

Our world heavily relies on fossil fuel to meet our energy demand due to our increasing population. Unfortunately, our fossil fuel reserves are limited. Therefore, it is imperative to find alternatives to support our increasing energy demand and one of the possible alternatives is solar cells. Solar cell converts light into electrical energy and the one that is currently commercialized is crystalline silicon-based solar cell with the power conversion efficiency (PCE) of 26.7% [1]. Despite its material being abundant and achieving high efficiency, it still exhibits some drawbacks, such as high fabrication cost [2]. In the past decades, dye-sensitized solar cells

(DSSC) have been developed as an alternative to silicon-based solar cells due to their ease of fabrication and low production cost.

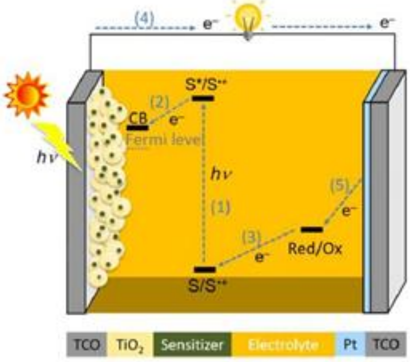


Fig. 1Schematic diagram of DSSC [4]

Fig. 1 illustrates the components and the working mechanisms of DSSC. The device consists of photoanode, dye/sensitizer, electrolyte (I_3^-/I^-electrolyte is commonly used) and counter electrode. The photoanode is prepared by depositing a mesoporous titanium dioxide layer on a transparent conductive oxide (TCO) glass and the sensitizer (dye) is adsorbed on the mesoporous titanium dioxide layer. The way this device operates is through the injection of electrons from the sensitizer into the conduction band of titanium dioxide (TiO_2) layer as it absorbs photon. The electrons travel to the counter electrode through the external circuit and reduces I_3^- ion to I^- ion. The regeneration of the ground state of the sensitizer takes place as it accepts electron from I^- ions and the ions are oxidized back to I_3^- ions [3, 4].

Natural sensitizers have been extensively studied as an alternative to synthetic sensitizers. Despite synthetic sensitizer exhibiting high efficiency, which is currently about 13%, its preparation involves complicated and expensive work. Moreover, as the synthetic dye is toxic and carcinogenic, it could lead to water pollution [5]. By using natural sensitizer, it could help in reducing the cost of the device [6]. From other perspectives, natural dye shows narrow light absorption spectrum, thus performs poorly when only a single natural dye is used. Moreover, natural dye exhibits low electron transfer and less stable [7, 8]. Most of the natural sensitizers can be divided into four groups: chlorophylls, anthocyanins, carotenoids, and betalains. Among those groups, chlorophylls and anthocyanins are the focus of most works.

Chlorophyll a was used by Kay and Griitzel in 1993 as a sensitizer but it was poorly adsorbed onto the TiO_2 layer when dissolved in certain solvents such as ethanol due to weak interaction of its ester and keto carbonyl group with the layer [9, 10]. Due to the poor adsorption of chlorophyll *a* onto TiO_2 layer, some simple modifications were made on chlorophyll *a*. As reported by Calogero et al., copper chlorin e6 (chlorophyllin), which is one of the chlorophyll *a* derivatives was used as a sensitizer. Copper chlorin e6 is obtained through alkaline hydrolysis, where the phytyl ester is saponified, cyclopentanone ring is opened to produce two carboxyl groups and the magnesium ion is replaced with copper ion [11]. The sensitizer exhibited PCE of 0.88% with open-circuit voltage (V_{OC}) of 0.4 V, short-circuit current density (J_{SC}) of 3.36 mA/cm2, and fill factor (FF) of 0.65. On the other hand, another chlorophyll a derivatives sensitizer, which is chlorin e6 (metal-free chlorophyllin) where it is similar to copper chlorin e6, except it does not have any metal ion in its porphyrin core was also used in DSSC. The sensitizer exhibited PCE of 0.45% with V_{OC} of 0.36 V, J_{SC} of 1.88 mA/cm2, and fill factor of 0.67. Both devices used platinum as its counter electrode with I_3^-/I^- redox mediator.

Other than exploring new natural sensitizers and chemically modifying the sensitizer to overcome narrow light absorption spectrum, another approach to improve the performance of natural sensitizers in DSSC is by employing a second sensitizer that acts as co-sensitizer. Co-sensitization could help to achieve panchromatic light harvesting with each of the spectrum of the sensitizer compliments each other, thus boosting the performance of the device [5], [12]. As reported by [7], co-sensitization was applied in developing DSSC by employing chlorophyll *b* (green dye) and anthocyanins (red dye) extracted from Malabar spinach and red spinach, respectively. The authors used I_3^-/I^- redox mediator with carbon electrode as their counter electrode. Green and red dye were mixed at different ratio, and it was found that by mixing 20% green dye with 80% red dye, it generated the highest PCE of the device, which was 0.847% with short-circuit current (I_{SC}) of 4.273 mA, V_{OC} of 0.385 V, and fill factor of 0.515. On the other hand, 100% green dye produced PCE of 0.466%, I_{SC} of 2.875 mA, V_{OC} of 0.347 V, and fill factor of 0.468, and 100% red dye produced PCE of 0.531%, I_{SC} of 2.810 mA, V_{OC} of 0.383 V, and fill factor of 0.494.

Another study was also published by Ossai and his team [8] on a study of the usage of chlorophyll and anthocyanins extracted from Carica papaya leaf and black cherry fruit, respectively. The authors used graphite as their counter electrode. By co-sensitizing the zinc oxide (ZnO) photoanode with both dyes at 3:1 ratio of anthocyanins to chlorophyll, it was observed that the device produced PCE of 0.56%, J_{SC} of 2.15 mA/cm2, V_{OC} of 0.49 V, and fill factor of 0.54. Apart from combining chlorophyll dye with anthocyanins dye, [13] reported the usage of 80% chlorophyll dye, extracted from ivy gourd leaves together with 20% curcumin, extracted from turmeric in co-sensitized DSSC with the application of platinum as its counter electrode. The co-sensitized DSSC device produced PCE of 0.30%, I_{SC} of 1.45 mA, V_{OC} of 0.55 V, and fill factor of 0.38. The author mentioned that 80%/20% ratio is the best ratio based on the spectrometry data.

In this study, a new approach of dye co-sensitization with the application of ferrocene and acetylferrocene paired with acidified chlorophyllin was explored. The idea is to attach acidified chlorophyllin with ferrocene and acetylferrocene without forming any covalent linkage to form a complex. Acidified chlorophyllin, as one of the derivatives of chlorophyll, was chosen due to the presence of strong anchoring group (carboxylic acid group) at the peripheral of porphyrin core and it is known to be more stable than chlorophyll. Ferrocene and acetylferrocene, a metallocene, were chosen as both can undergo simple reversible redox reaction.

II. METHODOLOGY

A. Page Layout Synthesis of Acidified Chlorophyllin

Acidified chlorophyllin was prepared from the reaction of trisodium copper chlorophyllin salt with 1.0 mol/L of sulphuric acid. This involved the conversion of carboxylate groups of the salt to carboxylic groups from the reaction between the carboxylate groups with hydrogen ions (H^+ ion) [14]. Trisodium copper chlorophyllin (Alfa Aesar) was purchased from Fisher Scientific.

About 400 mg of trisodium copper chlorophyllin had been dissolved in 200 mL of distilled water before 1.25 mL of 1.0 mol/L sulphuric acid was added. The reaction produced dark green solid precipitate. The reaction product was filtered to collect the solid precipitate and rinsed with distilled water a few times. It was then dried in a desiccator for three days in a dark and cold environment.

After the drying period, the solid product was dissolved in about 50 mL diethyl ether and filtered. The solid collected on the filter was then dissolved in 50 mL methanol and filtered. After that, the methanol of the collected solution was removed in rotary evaporator to obtain dark green powder.

B. Synthesis of Acetylferrocene

The acylation of ferrocene reaction was performed by reacting ferrocene with acetic anhydride and catalyzed by concentrated phosphoric acid to produce acetyl ferrocene [15]. Ferrocene (Alfa Aesar) was purchased from Fisher Scientific and 85% phosphoric acid (R&M) was purchased from BT Science Sdn Bhd.

The reaction was performed by adding 5 mL of acetic anhydride to 1.5 g of ferrocene with the addition of 1 mL of 85% phosphoric acid dropwise, set at 80ºC in water bath for 40 minutes. The reaction was stopped by pouring the mixture onto ice and neutralized with sodium bicarbonate powder. The crude product (filtrate) of the reaction was obtained by filtering the mixture and rinsing with cold distilled water. Then, the crude product was dried in a desiccator for three days.

Toobtain purified acetyl ferrocene, column chromatography technique was employed, where the column was packed with silica gel (60 Å, 70-230 mesh) and the solvents used were hexane (first eluent) and diethyl ether (second eluent). The second fraction was collected and dried by using a rotary evaporator.

C. Preparation of Titanium Dioxide (TiO_2) Photoanode, DSSC Device Fabrication, and Electrical Testing

Before TiO_2 photoanode was prepared, TiO_2 paste was prepared by mixing 6 g of TiO_2 powder with 9 mL of 0.057 M of acetic acid solution, 1 mL of distilled water and one drop of Triton X-100 until a smooth thin paste was obtained.

The preparation of TiO_2 photoanode was done by applying Doctor's Blade technique to spread TiO_2 paste on Indium Tin Oxide (ITO) coated glass. Three pieces of Scotch Tape were placed at three sides of the ITO coated glass to form an area of 1 cm x 1.5 cm. The Scotch Tape also played a role in levelling the TiO_2 layer at fixed thickness. Then, the Scotch Tape pieces were removed and the photoanode was sintered at 450ºC for 30 minutes.

Fabrication of DSSC device was done by immersing the sintered photoanode in a dye solution. Then, the dye-coated photoanode and a carbon-coated glass (counter electrode) were clamped together with paper clip blinders and a few drops of I_3^-/I^- electrolyte was dropped in between the electrodes. The carbon-coated glass was prepared by placing the ITO coated glass over the flame to collect the soot. To prepare the electrolyte, 4.6844 g of Lithium Iodide (LiI) and 0.6345 g of Iodine (I_2) were dissolved in 50 mL of 3-methoxypropionitrile (MPN) to form an electrolyte with a concentration of iodide (I^-) ion of 0.7 M and a concentration of I_2 of 0.05 mol/L [10].

The electrical testing was done to measure the open-circuit voltage (V_{OC}), short-circuit current (I_{SC}), fill factor (FF), and power conversion efficiency (PCE) that depicted the performance of the fabricated devices. The measurement was done by putting the fabricated device under a solar simulator with the light intensity of 1000 W/m^2. The anode terminal of the source measurement unit (Keithley SMU 2450 Source Measurement System) was connected to the photoanode of the device and the cathode terminal was connected to the carbon-coated glass (counter electrode).

D. Optimization of Acidified Chlorophyllin Adsorption on TiO_2 Photoanode

Acidified chlorophyllin solutions with the volume of 19.5 mL were prepared at the concentration from 0.01 mmol/L to 0.60 mmol/L and at each concentration, one TiO2 photoanode was immersed for 20 hours at room temperature. After that, the photoanodes were used to fabricate the DSSC device to measure its electrical performance. UV-Vis analysis was also performed by using UV-Vis spectrophotometer (Perkin Elmer Lambda 365+) to measure the absorbance value of the solution after the immersion process to calculate the amount of acidified chlorophyllin being adsorbed by the photoanode.

E. Formation and Adsorption of Acidified Chlorophyllin-Ferrocene and Acidified Chlorophyllin-Acetylferrocene Complex

To form the complex, acidified chlorophyllin-ferrocene and acidified chlorophyllin-acetylferrocene mixture solutions (dissolved in ethanol) of 20 mL were prepared where the concentration of acidified chlorophyllin was fixed at 0.075 mmol/L and the concentration of ferrocene and acetylferrocene were varied from 0 mmol/L to 0.375 mmol/L. From the prepared mixture solution, 0.5 mL of each of the solutions was diluted to 5 mL in ethanol and the solutions were analyzed by using UV-Vis spectrophotometer to study the behavior of the light absorption of the solution. The solutions were analyzed at wavelengths of 200 nm to 700 nm.

The remaining solutions were evaporated in a rotary evaporator to form solid powder. The solid powder was analyzed by using Fourier Transform Infrared (FT-IR) equipment (Perkin Elmer Spectrum 65) to observe peak shifts. The sampling technique used to analyze the complex was attenuated total reflectance (ATR). The scanning of the sample was done from a wavenumber of 650 cm^{-1} to 4000 cm^{-1}.

To study the adsorption of the complex in the solution, one photoanode was immersed in each of the solutions with the volume of 19.5 mL for 20 hours at room temperature. The DSSC devices were fabricated with the dye-coated photoanode before measuring the performance of the device. The absorbance value of the solution after the immersion process was measured to determine the amount of the dyes being adsorbed by the photoanode.

III. RESULTS AND DISCUSSION

F. Optimization of Acidified Chlorophyllin Adsorption on TiO2 Photoanode

Optimization of acidified chlorophyllin adsorption on TiO_2 photoanode was performed with the aim of determining the concentration of acidified chlorophyllin to be used during immersion process that could produce the best performance of the device. The concentration of acidified chlorophyllin was varied and the time taken for the immersion process to complete was 20 hours. The concentration of acidified chlorophyllin solution before and after the immersion process was also determined to calculate the amount of acidified chlorophyllin being adsorbed by the photoanode. It was observed that there existed an optimum initial concentration of acidified chlorophyllin that produced the best performance of the device

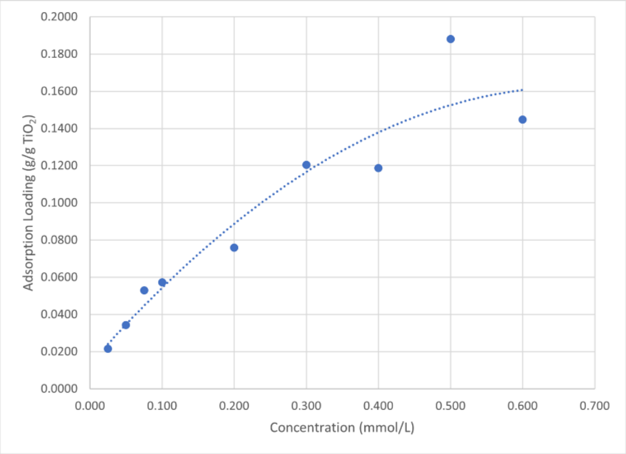


Fig. 2Adsorption loading of acidified chlorophyllin on TiO_2 photoanode for 20 hours at room temperature

The adsorption loading of acidified chlorophyllin on TiO_2 photoanode for 20 hours immersion process at different initial concentration of acidified chlorophyllin was shown in Fig. 2. A correlation can be drawn where the adsorption loading of acidified chlorophyllin increased as the initial concentration of acidified chlorophyllin solution increased. The adsorption loading of acidified chlorophyllin increased linearly up to the concentration of 0.3 mmol/L and started to slow down as the concentration further increased.

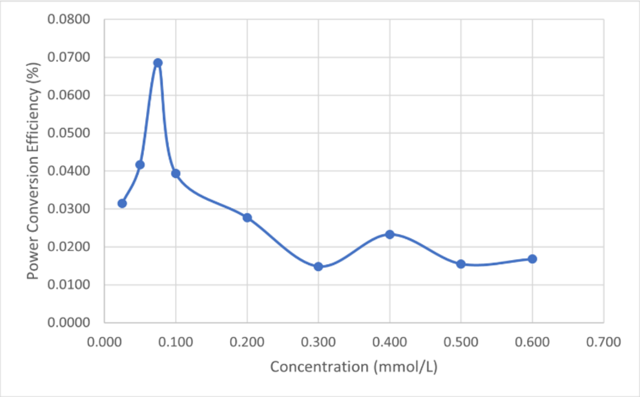


Fig. 3Power conversion efficiency of DSSC at different initial concentration of acidified chlorophyllin

Meanwhile, Fig. 3 showed the correlation between the initial concentration of acidified chlorophyllin and the PCE of DSSC sensitized with acidified chlorophyllin. At low concentration, the PCE and the short-circuit current density (J_{SC}) of the device increased and reached maximum PCE of 0.0686% with J_{SC} of 6.09 A/m^2 and open-circuit voltage (V_{OC}) of 0.26 V at concentration of 0.075 mmol/L. Further increment of the concentration reduced the PCE and J_{SC} of the device. Table 1 summarized the performance of DSSC device sensitized with acidified chlorophyllin at different initial concentrations.

TABLE I

SUMMARY OF THE PERFORMANCE OF ACIDIFIED CHLOROPHYLLIN SENSITIZED DSSC AT DIFFERENT INITIAL CONCENTRATIONS

Concentration (mmol/L)	**Voc (V)**	**JSC (A/m2)**	**FF**	**PCE (%)**
0.010	0.24	1.54	0.52	0.0190
0.025	0.23	2.97	0.47	0.0314
0.050	0.24	4.31	0.41	0.0416
0.075	0.26	6.09	0.43	0.0686
0.100	0.23	4.58	0.37	0.0393
0.200	0.23	3.30	0.37	0.0277
0.300	0.24	2.36	0.26	0.0148
0.400	0.24	3.44	0.29	0.0233
0.500	0.25	2.22	0.28	0.0155
0.600	0.24	2.92	0.24	0.0168

Reduction of the PCE and electrical current generated by the single dye DSSC can be related to the dye aggregation on the photoanode. Even though the amount of acidified chlorophyllin being adsorbed by the photoanode increased as the concentration increased, the result suggested that as the concentration increased higher than 0.075 mmol/L, acidified chlorophyllin molecules had a tendency to form aggregation on the photoanode, thus reducing the PCE of the device. Finally, from the obtained result, the initial concentration of acidified chlorophyllin at 0.075 mmol/L was chosen as a baseline to perform further experiments.

G. Chemical Compatibility of Acidified Chlorophyllin with Ferrocene and Acetylferrocene

In this section, the compatibility of acidified chlorophyllin with ferrocene and acetylferrocene was studied. In Fig. 4 and Fig. 5, it was observed that acidified chlorophyllin does not react with ferrocene and acetylferrocene as the FTIR spectra of acidified chlorophyllin-ferrocene and acidified chlorophyllin-acetylferrocene mixture at different mole ratio did not show any appearance of new peak or disappearance of any peak.

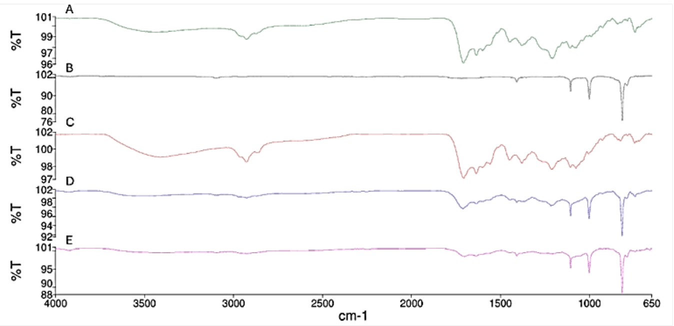


Fig. 4FTIR spectrum of acidified chlorophyllin (A), ferrocene (B), 1:1 mole ratio of acidified chlorophyllin-ferrocene mixture (C), 1:3 mole ratio of acidified chlorophyllin-ferrocene mixture (D), and 1:5 mole ratio of acidified chlorophyllin-ferrocene mixture (E)

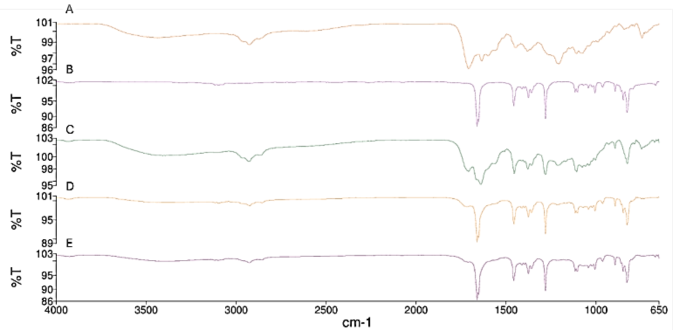


Fig. 5FTIR spectrum of acidified chlorophyllin (A), acetylferrocene (B), 1:1 mole ratio of acidified chlorophyllin-acetylferrocene mixture (C), 1:3 mole ratio of acidified chlorophyllin-acetylferrocene mixture (D), and 1:5 mole ratio of acidified chlorophyllin-acetylferrocene mixture (E)

Both FTIR spectra only show small peak shifts, indicating there were minor changes to the chemical environment between the molecules, which might suggest that acidified chlorophyllin interacted with ferrocene and acetylferrocene through weak intermolecular force. Table 2 and Table 3 summarized some of the selected peaks from FTIR spectra of acidified chlorophyllin, ferrocene, acetylferrocene, and the mixture of acidified chlorophyllin with ferrocene and acetylferrocene.

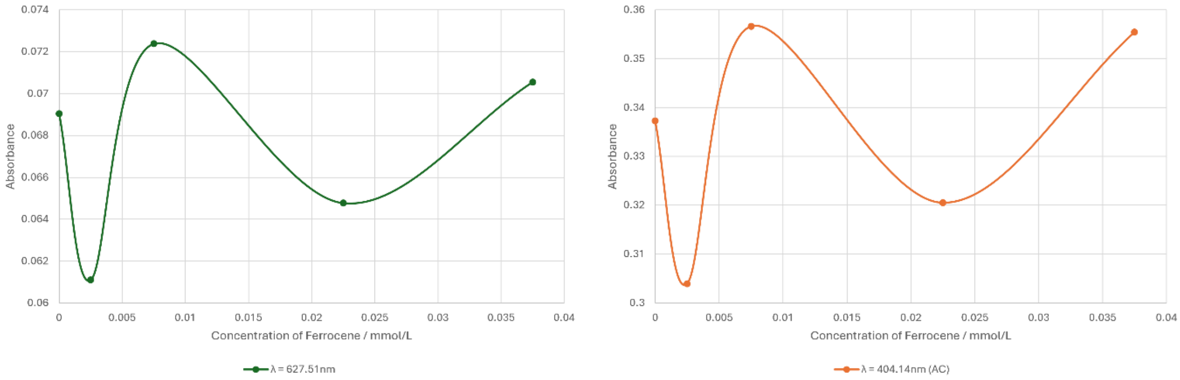
TABLE II
SUMMARY OF SOME SELECTED PEAKS FROM FTIR SPECTRA OF ACIDIFIED CHLOROPHYLLIN, FERROCENE, AND ACIDIFIED CHLOROPHYLLIN-FERROCENE MIXTURE [20], [21]

Sample	Peak Wavenumber (cm-1)			
	C=O (carboxylic acid)	C-O (carboxylic acid)	C-H (out-of-plane bending)	C-H (in-plane bending)
Acidified Chlorophyllin	1708.32	1207.32	-	-
Ferrocene	-	-	815.46	1001.39
Acidified Chlorophyllin-Ferrocene Mixture (1:1 mole ratio)	1706.73	1214.96	-	-
Acidified Chlorophyllin-Ferrocene Mixture (1:3 mole ratio)	1711.40	-	816.84	1002.12
Acidified Chlorophyllin-Ferrocene Mixture (1:5 mole ratio)	1701.40	-	816.34	1001.75

TABLE III
SUMMARY OF SOME SELECTED PEAKS FROM FTIR SPECTRA OF ACIDIFIED CHLOROPHYLLIN, ACETYLFERROCENE, AND ACIDIFIED CHLOROPHYLLIN-ACETYLFERROCENE MIXTURE [20], [21]

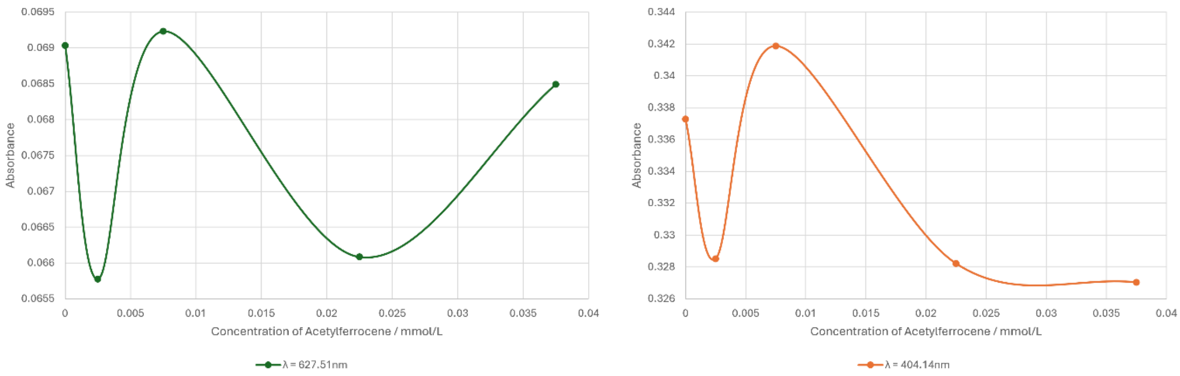
Sample	**Peak Wavenumber (cm^{-1})**		
	C=O (carboxylic acid)	**C=O (acetyl)**	**C-H (out-of-plane bending)**
Acidified Chlorophyllin	1708.32	-	-
Acetylferrocene	-	1661.45	827.41
Acidified Chlorophyllin-Acetylferrocene Mixture (1:1 mole ratio)	1712.60	1661.45	826.55
Acidified Chlorophyllin-Acetylferrocene Mixture (1:3 mole ratio)	1712.60	1661.52	827.91
Acidified Chlorophyllin-Acetylferrocene Mixture (1:5 mole ratio)	1712.60	1661.64	828.27

In Table 2, the carbonyl peak (carboxylic acid), originating from acidified chlorophyllin, showed small deviations in acidified chlorophyllin-ferrocene mixture from pure acidified chlorophyllin. Since ferrocene molecules did not contain any functional group that could interact with the carboxylic acid group of acidified chlorophyllin, the peak shift of the carbonyl peak of carboxylic acid group suggested that the carboxylic acid group might surround the iron atom in ferrocene molecule. Meanwhile, in Table 3, the similar deduction could be made, where the carboxylic acid group of acidified chlorophyllin surrounded iron atom instead of interacting with acetyl group in acetylferrocene molecule as the carbonyl group of carboxylic acid group shifted more than carbonyl group of acetyl group.



(a) (b)

Fig. 6Correlation between the absorbance and theconcentration of ferrocene while the concentration of acidified chlorophyllin remained constant at wavelength of 627.51 nm (a), and 404.14 nm (b)



(a) (b)

Fig. 7Correlation between the absorbance and the concentration of acetylferrocene while the concentration of acidified chlorophyllin remained constant at wavelength of 627.51 nm (a), and 404.14 nm (b)

In solution, the initial concentration of ferrocene and acetylferrocene increased from 0 mmol/L to 0.0375 mmol/L, while the initial concentration of acidified chlorophyllin remained constant at 0.0075 mmol/L. The solutions were analysed by UV-Vis instrument at wavelength of 627.51 nm and 404.14 nm, and the molar extinction coefficient of acidified chlorophyllin, ferrocene, and acetylferrocene at those two wavelengths are shown in Table 4. The increment of the concentration of the metallocene did not cause the absorbance value to increase linearly at wavelength 404.14 nm, which indicated that Beer’s Law failed, as shown in Fig. 6and Fig. 7. Moreover, at wavelength 627.51 nm, the absorbance value of the solution should be constant as ferrocene and acetylferrocene did not absorb light at that wavelength, yet the result showed the deviation of the absorbance value of the solutions.

TABLE IV
MOLAR EXTINCTION COEFFICIENT OF ACIDIFIED CHLOROPHYLLIN, FERROCENE AND ACETYLFERROCENE AT DIFFERENT WAVELENGTHS

Wavelength, λ_{max} (nm)	**Molar Extinction Coefficient (L.mol^{-1}.cm^{-1})**		
	Acidified Chlorophyllin	**Ferrocene**	**Acetylferrocene**
627.51	9647.1	No peak	No peak
404.14	44475	65.80	404.53

If Beer’s Law is obeyed, a linear correlation can be drawn. On the other hand, there is a condition where Beer’s Law fails but, in that condition, the concentration of the solute is high, causing the solute molecules to influence one another as a result of their proximity thus, altering their absorptivity [16]. But, in this experiment, the concentration of the solutes used was low and the deviation from Beer’s Law might suggest that the deviation was caused by the interaction between acidified chlorophyllin with ferrocene and acetylferrocene, forming a complex, which affected the molar extinction coefficient of each of the constituents of the complex.

H. Effect of Concentration of Ferrocene and Acetylferrocene on the Performance of DSSC Device

In this section, the effect of the presence of ferrocene and acetylferrocene in acidified chlorophyllin solution used during immersion process on the performance of its DSSC device was studied. It can be observed that when ferrocene and acetylferrocene present during the immersion process, it produced a device that exhibited lower performance as compared to the performance of the device immersed in only acidified chlorophyllin solution, as shown in Fig. 8.

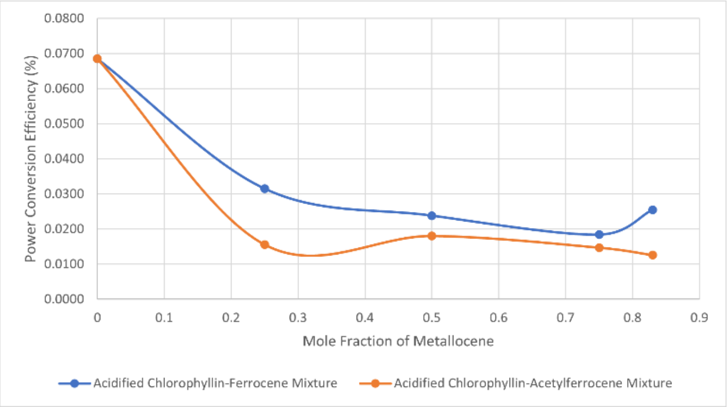


Fig. 8Correlation of PCE of the device with varied initial mole fraction of ferrocene and acetylferrocene while the concentration of acidified chlorophyllin remained constant (0.075 mmol/L)

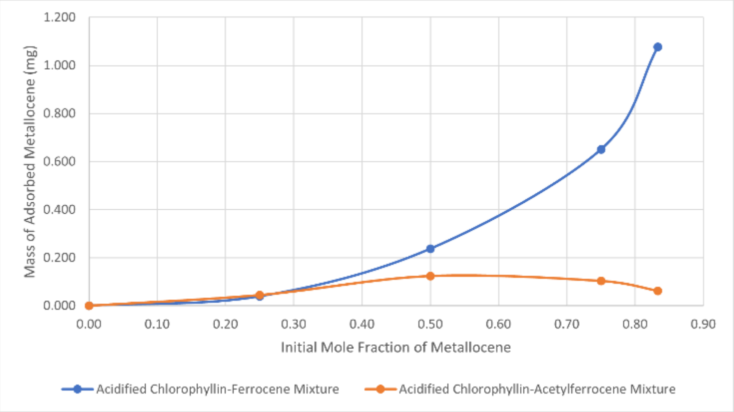


Fig. 9The amount of ferrocene and acetylferrocene being adsorbed at different initial mole fraction at constant amount of adsorbed acidified chlorophyllin (0.053 g/g TiO_2)

The absorbance of the mixture solution was measured before and after immersing TiO_2photoanode. As the initial mole fraction (concentration) of ferrocene and acetylferrocene increased, the amount of ferrocene being adsorbed also increased and for acetylferrocene, it increased and started to decline slightly at initial mole fraction of 0.50, as shown in Fig. 9. Meanwhile, it was also observed that the amount of acidified chlorophyllin being adsorbed was approximately at 0.053 g/g TiO_2 and the loading of acidified chlorophyllin was also not affected by the presence of ferrocene and acetylferrocene in the solution.

When a blank TiO_2photoanode was immersed in 1 mmol/L of ferrocene and acetylferrocene solution, and the absorbance of the solutions before and after 20 hours immersion was measured, it was found that there was no change occurred in the absorbance value of the solution. This indicates that ferrocene and acetylferrocene were not adsorbed by TiO_2 photoanode. Thus, the TiO2 layer in the photoanode did not contribute to the increment trend of the amount of adsorbed metallocene.

Referring to Table 5, in acidified chlorophyllin-ferrocene and acidified chlorophyllin-acetylferrocene device, J_{SC} and PCE of the device showed a trend where it decreased exponentially with V_{OC}slightly decreased as the initial mole fraction of ferrocene and acetylferrocene increased. It was also observed that the PCE of acidified chlorophyllin-acetylferrocene device was lower than the PCE of acidified chlorophyllin-ferrocene device and that was contributed by lower J_{SC} in acidified chlorophyllin-acetylferrocene with V_{OC} and FF for both devices to be about the same. The observed downtrend of both devices involved theinteraction of the metallocene with the solvent used in the electrolyte.

TABLE V
SUMMARY OF THE PERFORMANCE OF DSSC DEVICE THAT WAS SENSITIZED WITH ACIDIFIED CHLOROPHYLLIN-FERROCENE AND ACIDIFIED CHLOROPHYLLIN-ACETYLFERROCENE MIXTURE

Initial Mole Fraction	**Acidified Chlorophyllin-Ferrocene Mixture**				**Acidified Chlorophyllin-Acetylferrocene Mixture**			
	V_{OC} (V)	**J_{SC} (A/m^2)**	**FF**	**PCE (%)**	**V_{OC} (V)**	**J_{SC} (A/m^2)**	**FF**	**PCE (%)**
0.00	0.26	6.09	0.43	0.069	0.26	6.09	0.43	0.069
0.25	0.26	3.67	0.33	0.032	0.27	1.85	0.32	0.016
0.50	0.23	3.09	0.33	0.024	0.21	2.46	0.36	0.018
0.75	0.24	2.84	0.28	0.018	0.21	2.07	0.34	0.015
0.83	0.23	3.18	0.35	0.026	0.18	2.21	0.32	0.013

It was observed that ferrocene and acetylferrocene were soluble in MPN (electrolyte solvent). As both metallocene being soluble in MPN, this caused the dissolution of ferrocene and acetylferrocene in the solvent once the electrolyte was dropped into the device. Even though ferrocene and acetylferrocene were held by acidified chlorophyllin, the interaction between the metallocene and acidified chlorophyllin involved weak intermolecular forces and the result obtained was aligned with FTIR analysis which suggested that ferrocene and acetylferrocene interacted weakly with acidified chlorophyllin, thus resulting in dissolution of ferrocene and acetylferrocene in the electrolyte solvent.

There was a study reporting on the value of reduction potential of ferrocene and acetylferrocene with lithium/lithium ion as the reference. It was reported that ferrocene exhibited a reduction potential of 3.44 V and acetylferrocene exhibited 3.65 V [17]. From the reported reduction potential, the reduction potential with standard hydrogen electrode (SHE) as its reference for both metallocene can be calculated where ferrocene exhibited reduction potential of 0.4 V and 0.61 V for acetylferrocene. Meanwhile, the reduction potential of iodine was 0.54 V [18]. Based on the value of the standard reduction potential of the three chemical species, iodine acts as an oxidizing agent when it is mixed with ferrocene. On the other hand, acetylferrocene is the strongest oxidizing agent among the three chemical species.

Fig. 10Redox reaction between ferrocene and iodine led to the formation of precipitate (at the bottom of the centrifuge tube)

The redox reaction occurred between ferrocene and iodine in the electrolyte contributed to the lower performance of the acidified chlorophyllin-ferrocene device. With the presence of iodine in the electrolyte, ferrocene was oxidized by iodine to form ferrocenium ion and iodide ion, thus forming insoluble ionic compound in MPN. This resulted in lower concentration of iodine and iodide ion presence in the electrolyte, which might lead to lower rate of dye regeneration process that affected the generated electrical current.This can clearly be seen that the J_{SC} value for acidified chlorophyllin-ferrocene device exhibited drastic decrease.

One test was conducted to confirm the reaction between ferrocene and iodine by dissolving ferrocene and iodine in MPN solvent, and both solutions were mixed and centrifuged at 4000 rpm for 20 minutes. It was observed that there was precipitation collected at the bottom of the centrifuge tube, as shown in Fig. 10.

Similar testing was conducted for acetylferrocene, but there was no change observed. This aligned with the prediction based on the standard reduction potential of acetylferrocene and iodine. For acidified chlorophyllin-acetylferrocene device, lower J_{SC} with almost similar V_{OC} and FF as compared to acidified chlorophyllin-ferrocene was observed and it might be caused by higher charge recombination rate through back electron transfer from TiO_2 to redox mediator.

Acetylferrocene might reduce the oxidized acidified chlorophyllin, thus forming acetyl ferrocenium ion. This acetyl ferrocenium ion co-existed with iodine and iodide ion in the electrolyte. The rate of electron transfer from TiO_2 to triiodide ion is remarkably slow due to a complicated multielectron transfer mechanism [19]. Thus, due to its strong oxidizing ability, the presence of acetyl ferrocenium ion might increase the rate of back electron transfer where the electron that had been injected into the conduction band of TiO_2were attracted by some acetyl ferrocenium ions, thus reducing the electron flow in the external circuit. Therefore, it can be concluded that the presence of metallocene did not help in improving the performance of the device and it declined even further as the amount of metallocene increased.

IV. CONCLUSION

In conclusion, acidified chlorophyllin did not form a covalent bond with ferrocene and acetylferrocene, instead, it formed a complex where acidified chlorophyllin interacted weakly with ferrocene and acetylferrocene through intermolecular forces. As the mole fraction of ferrocene and acetylferrocene increased, a different complex was formed, as can be observed from the changes of its absorbance value that failed to obey Beer's Law. As the initial mole fraction of the ferrocene and acetylferrocene increased, the amount of the ferroceneand acetylferrocene being adsorbed also increased, whilefor acetylferrocene, it started to decline slightly after initial mole fraction of 0.50. The presence of ferrocene and acetylferrocene on the photoanode worsens the performance of the device as both metallocene were solvated in the electrolyte solvent. The redox reaction between the ferrocene and iodine in the electrolyte might have taken place and formed an insoluble ionic compound, thus lowering the concentration of iodine and iodide ion in the electrolyte, leading to lower V_{OC} and J_{SC} of acidified chlorophyllin-ferrocene device. On the other hand, charge recombination might lead to lower J_{SC} in acidified chlorophyllin-acetylferrocene device due to the presence of acetyl ferrocenium ion in the electrolyte. Therefore, it can be concluded that the formation of complex between acidified chlorophyllin with ferrocene and acetylferrocene did not help in improving the performance of DSSC device.

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