Synthesis and Electrochemical Characterization of Redox-Based Conductive Gel for Low-Grade Heat Harvesting Applications

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Abstract-Thermoelectric generators (TEG) are one of the sources for renewable energy. They utilize heat waste and produce electrical energy. Aniline is an aromatic compound with benzene ring while Ammonium peroxy disulfate (APS) is an oxidant. The chemical interaction between Aniline and APS was carried out under stirring at 30^0C and then allowed to cool it after drop casting at room temperature. Another sample was prepared by addition of Gum Arabic (GA) and the iodide/triiodide redox couple in the base film. Result analyses indicate the incremental change in Open circuit voltage (Voc) due to the presence of redox couple from 0.0014 mV to 0.76 mV. Furthermore, the Seebeck coefficient of the gel has been increased 100% as compared to the film without Redox couple. This confirms the formation of TEG conductive gel. Moreover, the role of GA is pivotal for the formation of flexible gel i.e. without GA the gel is not formed.

Keywords-Aniline, Ammonium Peroxydisulfate (APS), Iodide/Triiodide Redox Couple, Conductive Gel, Thermo-Electric Generator (TEG), Wearable Electronics.

I. INTRODUCTION

The thermoelectric generators (TEG) are one of the significant sources of green energy because it transmutes absorbed heat energy into electric voltages.[i] The uses of TEG devices are well observed in automotive industries [ii-iii], house utensils [iv] and technical textile [v]to transform heat waste for practical applications. The curiosity in the research of TEG tends to produce more TEG devices and improves the quality of pre-existing once.[vi] This will allow us to fabricate exciting ideas into reality.

In the field of technical textile, the source for TEG is body generated heat waste. Micro-voltages produced from heat harvesting devices qualify to use in micro-electric devices. They provide a continuous supply of energy which will eliminate the use of batteries up to some extent. This phenomenon is generating low weight, long lasting, body sustainable, environment-friendly and wearable electronics. [vii]

To contribute our part in this field, herein we synthesized low-grade heat harvesting conductive gel by using Aniline, Gum Arabic (GA) and electron transferring redox couple.

Aniline is an aromatic compound having benzene ring attached to an amino group. It is used in dyes [viii] and in the synthesis of polyaniline [ix]. The APS is an inorganic compound that is highly soluble in water and works as a strong oxidizing agent. [x]

Gum Arabic (GA) is a natural gum extract from the acacia tree. It is composed of glycoprotein and polysaccharides. It is an excellent hydrophilic stabilizer, emulsifier and has excellent adhesion. All of these distinguished properties promote it as a promising candidate as stabilizing agent in the food industry [xi], the surfactant in chemical polymerization [xii], emulsifier and an adhesive agent in conductive/ non-conductive paints and gel formation. [xiii] It can also be used as green corrosion inhibitor [xiv] and electrochemical applications as composite. [xv]

The Iodide/Triiodide is polyiodide ions. Tri-iodide exhibit three Iodine ions while Iodide has two. Collaboratively they form a very exceptional redox couple which is a very useful mediator in dye-sensitized solar cells [xvi] and other charge storing devices. [xvii]

Synthesization procedure and electrochemical characterization of our product are discussed in this paper.

II. MATERIALS AND METHODS

Aniline (monomer) is purchased from MERCK and double distilled before use. Ammonium peroxy disulfate (APS, Sigma Aldrich) worked as an initiator. The Gum Arabic was purchased from Sigma Aldrich and use without any further processing. The (I_3^-/I^{-2}) redox couple was prepared by mixing Potassium Iodide (KI, Sigma Aldrich) and Iodine (I_2, Sigma Aldrich) in ionic liquid media in 2:1 ratio. All the reagents used are of analytical grade.

Two samples A and B were synthesized to study the qualitative analysis of reaction methodology. Film was formed by stirring 4ml of Aniline with 0.5g of APS at 30°C for 12 hours. Gel was prepared by stirring 4ml of Aniline with 0.5g of APS at 30°C for 12 hours. Additionally, solution B also possess 0.1ml of Redox couple (I_3^-/I^{-2}) and 0.25g of GA. Later both the samples were drop cast and then allowed to cool at room temperature. Both the reactions were performed in a dry condition such that no use of water.

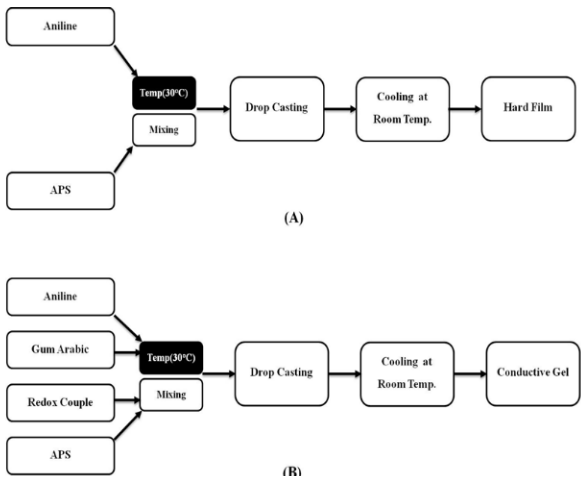


Fig. 1. Schematic diagram of Synthetic methodology for both samples. (A) Steps for Synthesization of Film. (B) Steps for Synthesization of Gel.

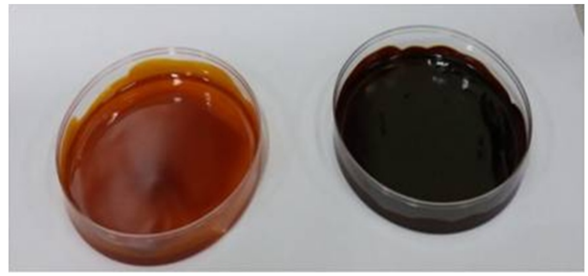
III. Results and Discussion

The reaction A, as shown in fig. 1a results in a film of burnt orange color which indicates that the oxidative polymerization of Aniline, in presence of APS, has not been accomplished. This incomplete polymerization may be due to environmental conditions i.e. exposure to light and air. Furthermore, we also have heated the samples at 30°C which may also contribute to the abrupt polymerization. This is a common attribute of Aniline which requires aqueous or inert environment. Aniline monomers are very sensitive in nature and have low durability.

The presence of GA in the chemical recipe, as shown in fig. 1b works simultaneously as a green emulsifier and stabilizer. The presence of GA in the compound is also essential for the gel formation i.e. if GA is added the resultant is a gel as shown in fig. 2 otherwise a flexible film. Therefore, the overall presence of GA substitutes the need for aqueous solvent and also provides additional features to the reaction system. The Aniline monomer consists of a phenyl group attached to an amino group. There are three idealized oxidation states of polyaniline

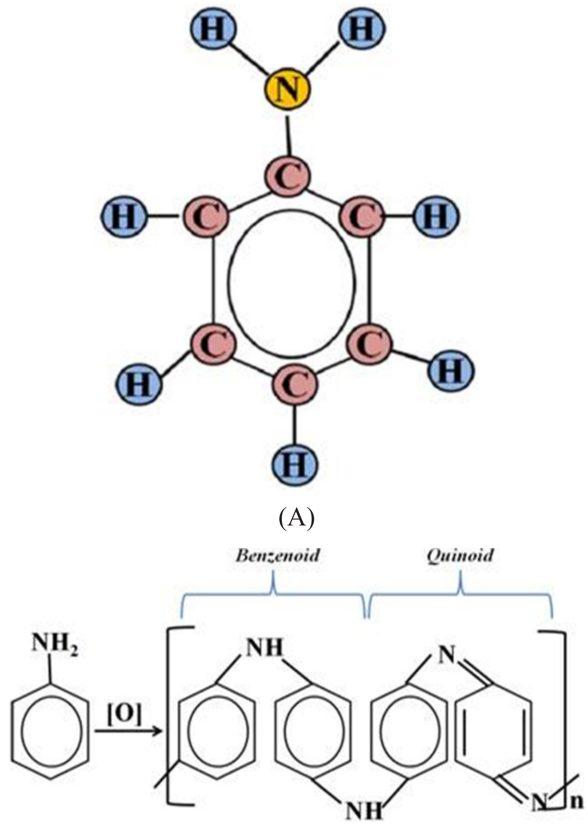
(a) Leuco-emeraldine fully reduced form.
(b) pernigraniline fully oxidized from.
(c) emeraldine base which has both oxidized and reduced part.

The reduced part of the polymer chain is called Benzenoid while it oxidizes part is called Quinoid. The Benzenoid has amine links while Quinoid has imine linkages [xviii] as shown in Fig. 3.



(A) (B)

Fig. 2. Resultant product of both samples. (A) Aniline-APS sample. (B) Aniline-APS-GA-Redox Couple sample.



(B)

Fig. 3. Chemical Structures (a) Structure Aniline (monomer). (B) Structure of Polymerization of Aniline.

The electro-active nature of the film and the gel has also been characterized by current-voltage (I-V) measurements as shown in figure 4. In order to see the conductive nature of the samples, external resistances were applied to drive the sample from short-circuiting to open circuit voltage (Voc) conditions. The Voc of the film is extremely minute i.e. 0.0014mV which has increased to 0.76 mV in case of the gel as shown in figure 4. This improvement in electro-active nature is owing to the added iodide/triiodide (I_3^-/I^{-2}) redox couple which induces a free electron in the sample. The chemical reaction happening during the redox reaction is shown in equation 1.

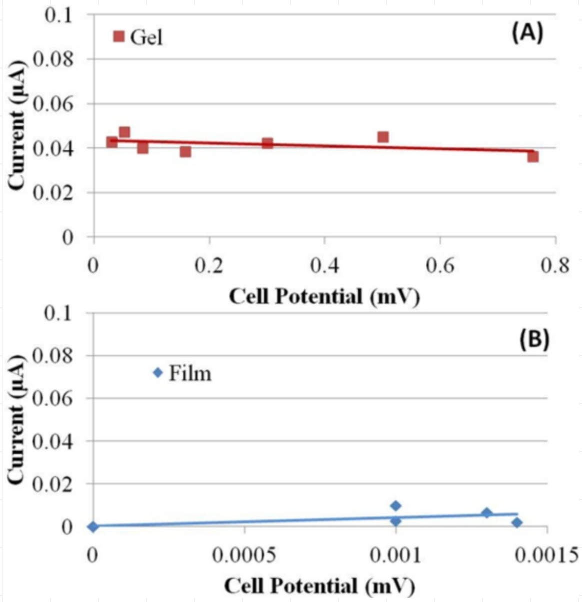
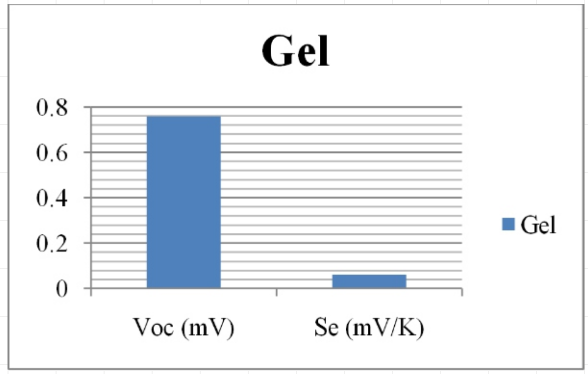


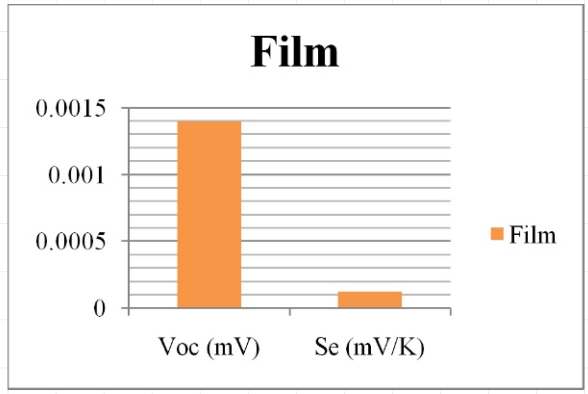
Fig. 4. Current-Voltage (I-V) curves of (A) Gel and (B) Film.

The iodide/triiodide redox couple has multiple applications in Solar cells, [xix] thermocells and electrochemical batteries [xx]. Our gel can be another application of the redox couple in the field of flexible textile.

There has been intensive interest to harvest body heat to generate electricity in the field of wearable thermoelectric. Although the generated voltages are significantly small, however, it suffices the microelectronic device requirements. Therefore, we also studied the thermoelectric behaviour of our film and gel at the temperature gradient of 12 K. We realized that the Seebeck coefficient of the film is 0.00012 mV/K which illustrate that the film is inappropriate for thermal to electrical energy conversion. However, the Seebeck coefficient of the gel is 0.063 mV/k, thus it is still a minute value but shows improved thermoelectric performance. The thermoelectric coefficients and Voc of the film and gel are shown in Fig. 5.



(A)



(B)

Fig. 5. Results of Open-Circuit Voltage and Seebeck Coefficient (A) Gel (B) Film.

IV. Conclusion

In conclusion, we have prepared an electro-active gel based on Aniline monomers. We have used Gum Arabic which emulsifies and stabilizes the sample resulting in a gel. Furthermore, the open-circuit voltage of gel is significantly higher as compared to the film owing to the free electrons induced by iodide/triiodide redox couple. Finally, we show the thermoelectric behaviour of the gel paving the way of our gel for the wearable thermoelectric textile materials.

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