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14. ABSTRACT Konarka Technologies and University of Massachusetts Lowell have developed quasi-solid electrolytes based on two classes of bioderived polymeric materials. In first class, highly grafted ethylene oxide copolymers were prepared using novozyyme-435 catalyzed esterification reactions. A bienzymatic process was employed to prepare second class of materials based on polyphenol derivatives with tethered oligo(ethylene oxide) segments. The highly irregular tethering groups on the bioderived polymers will avoid crystallization of the polymers and overcome consequent failure of the gel electrolyte incorporated solar cells that are exposed to extreme temperature variations during use. Solar conversion efficiencies of respective 4.3 and 4.6 % were achieved from bioderived gel electrolyte incorporated flexible solar cell at corresponding 1 and 0.55 Sun equivalent of solar irradiation conditions.					
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## Final Technical Report

GRANT #: N00014-02-M-0227

PRINCIPAL INVESTIGATOR: Kethinni G. Chittibabu, Ph.D. (email: kchittibabu@konarkatech.com)

INSTITUTION OR FIRMS: Konarka Technologies, Inc and  
University of Massachusetts Lowell

GRANT TITLE: Flexible Solar Cells Using Biotech Materials Processing

AWARD DATE: July 2002-May 2003

TECHNICAL OBJECTIVE: The primary objective of STTR Phase I research program is the development of high performance, low cost raw materials that could be incorporated into roll-to-roll manufacturable dye sensitized solar cells on flexible substrates. Development of sensitizing macrodyes and quasi-solid state redox electrolytes were proposed to be developed during this research grant employing biocatalytic processes. Technical objectives included identification of appropriate sensitizing dyes, desired complexable macromolecules for gel electrolyte preparation, synthesis of these macromolecules using horseradish peroxidase (HRP) or other biomimetic catalyzed polymerization techniques, characterization of polymers, formulation and testing of quasi-solid electrolytes and incorporation of bioderived materials in dye sensitized solar cells.

APPROACH: Biocatalytic and biomimetic processes were employed to synthesize complex polymeric materials for applications in dye sensitized solar cells.

ACCOMPLISHMENTS: Konarka Technologies and University of Massachusetts Lowell have developed many macrodyes for sensitizing titanium dioxide nanoporous membrane as well as non-crystallizable polymeric materials for quasi-solid electrolytes employing biocatalytic route during Phase I research. The developed macrodyes and quasi-solid electrolytes were incorporated into dye sensitized solar cells to evaluate their photophysical properties. Photovoltaic characteristics of some of the bioderived polymer based quasi-solid electrolyte incorporated dye sensitized solar cells on plastic substrates matched to that made with best viscous liquid electrolyte. Solar conversion efficiency of ca.

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4.6 % was achieved using bioderived, polymeric electrolyte incorporated flexible solar cell during this grant period.

The quasi-solid electrolytes prepared are expected to show enhanced long-term stability, due to nonvolatile components used and non-crystalline behavior of bioderived polymeric materials. Highly grafted ethylene oxide copolymers were prepared using Novozyme-435 catalyzed esterification reactions. A bi-enzymatic process was employed to prepare polyphenol derivatives with tethered oligo(ethylene oxide) segments. The macromer of oligo(ethylene oxide) functionalized phenol derivative was synthesized using Novozyme-435 and was subsequently polymerized using horseradish peroxidase to a polyphenol derivative with tethered oligomeric ethylene oxide segments of defined chain length. The polymers prepared by both the biocatalytic routes are glassy materials and do not undergo crystallization due to their irregular structure. A detailed study on polymer structure-physical property (photovoltaic, thermal and rheological) relationship was proposed to be conducted during Phase II research to identify efficient, and stable quasi-solid electrolyte. Few polymer derivatives with a variety of ethylene oxide segment lengths were synthesized employing biocatalytic route during Phase I option period. The search will be continued during Phase II to identify best polymer based gel electrolyte composition with high efficiency and exceptional stability at elevated temperatures, which is essential for deploying solar cells for outdoor applications. Macrodyes were made by complexing the polyligands prepared via hematin catalyzed polymerization technique, with ruthenium compounds. The macrodyes synthesized using biocatalytic route were used to sensitize nanoporous titanium oxide film and the macrodye-sensitized solar cells were characterized for photovoltaic performance. The solar conversion efficiency values measured from macrodye-sensitized solar cells were compared with *cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) (N3 dye)*, which is a commonly used sensitizing dye. For the first time, biomimetic hematin was used to convert aminophenanthroline to tetrapyrrodo[3,2- a:2', 3'- c:3'', 2''- h:2'''-3'''- j] phenazine bridging ligand (TPPHZ). Bridging ligands are potential candidates for making bi- and poly-nuclear metal complexes, where long distance electron transfer could be achieved with interesting photovoltaic characteristics.

**CONCLUSIONS:** Konarka Technologies and University of Massachusetts Lowell have been developing quasi-solid electrolytes based on two classes of bioderived polymeric materials. Highly grafted ethylene oxide copolymers were prepared using novozyme-435 catalyzed esterification reactions. A bienzymatic process was employed to prepare polyphenol derivatives with tethered oligo(ethylene oxide) segments. The highly irregular tethering groups on the bioderived polymers will

avoid crystallization of the polymers and consequent failure of the gel electrolyte incorporated solar cells that are exposed to extreme temperature variations during use. Solar conversion efficiencies of respective 4.3 and 4.6 % were achieved from bioderived gel electrolyte incorporated flexible solar cell at corresponding 1 and 0.55 Sun equivalent of solar irradiation conditions.

SIGNIFICANCE: KTI's technology and product development program will ultimately provide the Navy with a lightweight alternative power source, which is consistent with broader Navy research objectives as well, such as the ONR's Science & Technology "Expeditionary Energy Program." The payoff to the Navy will be improved mobility of operational forces, and extended hours of independent operation through the integrated use of lightweight solar technology. We envision a broad set of products that are suited for commercial and military applications, ranging from enhanced performance for handheld electronics, e.g., GPS, to portable (wearable) PV generators for communications, powering lightweight displays, bio-sensors, etc

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PUBLICATIONS AND ABSTRACTS (for total period of grant):

1. Ionic Liquid Based Gel Electrolyte Compositions for Dye Sensitized Solar Cells, K. G. Chittibabu, S. Hadjikyriacou, and L. Li; Mat. Res. Soc. Symp. Proc. Vol. 736, 245-250, 2003.
2. Biocatalytic Route for the Synthesis of PEGylated Polyphenolics: Application in Photonics and Electronics; R. Kumar, F. Bruno, K.G. Chittibabu, V. S. Parmar, L. A. Samuelson, A. C Watterson, and J. Kumar; submitted to Organic Letters.
3. Biocatalytic Synthesis and Ion Transport Properties of PEGylated Polyelectrolytes; R. Kumar, V. S. Parmar, L. A. Samuelson, A. C Watterson, K.G. Chittibabu and J. Kumar; submitted to ACS Preprints, 2004.
4. Biocatalytic Synthesis of Ion-Transporting and Complexable Macromolecules, R. Kumar, A. K. Sharma, V. S. Parmar, J. Kumar, A. C. Watterson, K. G. Chittibabu and L. A. Samuelson, presented at Sukant Tripathy Memorial Symposium 2003, Lowell, MA and will be published in J. Macromol Sci. A. Macromol. Chem.