

Final Scientific Report

Project title: Advanced Electrolytes and Electrodes for Improved Dye-Based Solar Cells

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Introduction

The main factor that restricts the widespread application of conventional solar cells is their high cost. One of the most promising low-cost solar cell technologies is the dye sensitized solar cell (DSSC). The key components of DSSC are a photoanode, which is a layer of nano-scale semiconductor particles stained with light absorbing dyes to inject electrons into the electrode when the dye is excited by light, and an electrolyte which is a redox couple dissolved in solvents to provide an electron-replenishing medium.¹ The most important factor in limiting the stability of dye-sensitized solar cells is the use of volatile liquid solvents in the electrolytes, which causes leakage during extended operation especially at elevated temperatures. This, together with the necessary complex sealing of the cells, seriously hampers the industrial-scale manufacturing and commercialization feasibilities of DSSCs.

Accomplishments versus goals

This program is part of the Department of Energy, Golden Office, program on Future Generation Photovoltaic Devices and Processes. The objective of this program was to bring about a significant improvement in the longevity and performance of DSSCs leading to commercialization, which involved three closely coupled tasks:

1. Synthesis and characterization of polymeric and oligomeric solvents for the formulation of low-volatility and highly ion-conductive electrolytes based on organophosphazene and organophosphate platforms
2. Fabrication of titanium dioxide nanostructured electrode surfaces to present a high surface area for contact with the dye molecules and high-viscosity electrolytes
3. Evaluation of various combinations of electrolytes and titanium dioxide surface structures from the viewpoint of the electrochemistry and working solar cell assemblies

Program accomplishments for task 1

To explore for the first time the feasibility of employing organophosphazenes as solvents for electrolytes of DSSCs, a series of nonvolatile liquid electrolytes based on hexakis(2-(2-methoxyethoxy)ethoxy)cyclotriphosphazene (MEET), compound **1** in **Figure 1**, with different iodide salts were examined. We found that 1-methyl-3-propylimidazolium iodide (PMII) is a better iodide source for MEET electrolytes than LiI, NaI, or NH₄I. Solid-state gel electrolytes based on propylene carbonate plasticized [bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP), polymer **2** in **Figure 1**, showed better performance relative to polyethylene oxide (PEO) based gel electrolytes of equivalent formulation. Although the power conversion efficiency is currently low (1.88%), the amorphous nature of the MEEP and the improved photovoltaic performance relative to PEO with similar molecular weight are encouraging.

10 organophosphates, compounds **3** through **12** in **Figure 1**, with etheric side groups were synthesized and tested as solvents for liquid electrolytes. The

selected properties of MEET, 3-methoxypropionitrile (MPN) and representative organophosphates bis(2-methoxyethyl) methyl phosphate (BMEMPh) **9** are summarized in Table 1. The higher boiling points compared to commonly used low-vapor-pressure organic solvent MPN, and higher conductivities compared to MEET suggest that these organophosphates are promising candidates to replace low-boiling-point solvents in the electrolytes of DSSCs.

Table 1 Comparison of low-volatility solvents for DSSC.

Solvent	bp. (°C)	bp. (°C) at 760 torr	Conductivity (S/cm) ^b
MEET	– ^a	–	1.33*10 ⁻⁴
MPN	72 (15 torr)	166	1.11*10 ⁻²
BMEMPh	>185(35 torr)	>357 ^c	2.33*10 ⁻³

a. Boiling point is too high to be measured. b. Electrolytes consist of 1.0 M PMMI, 0.15 M I₂ and 0.5 M N-methylbenzimidazole and 0.1 M guanidinium thiocyanate in corresponding solvents. c. Calculated.

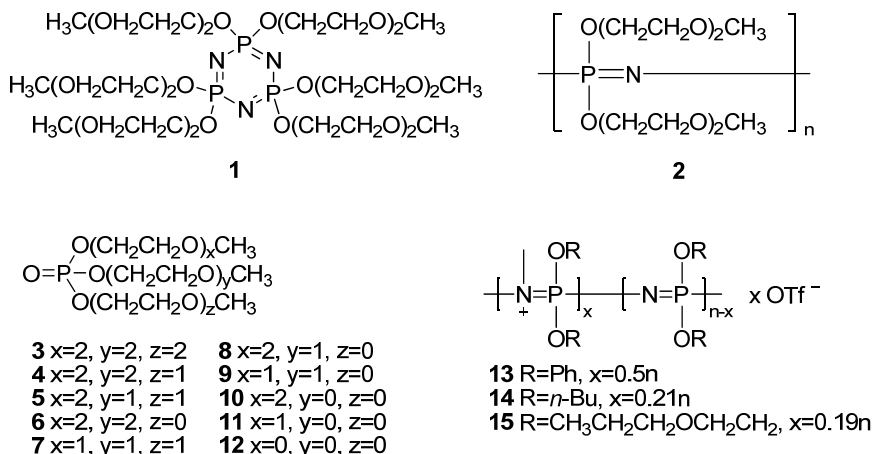


Figure 1 Structure of phosphazenes and organophosphates

Novel single-ion-conducting polymers, polymers **13** through **15** in **Figure 1**, were synthesized by quaternization of the backbone nitrogen atoms of polyphosphazenes with strong alkylation reagents. The quaternized polyalkylphosphazenes showed high ionic conductivities of $2.58 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 25 °C and $2.09 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 80 °C, which are among the highest conductivities of known solvent-free ion-conducting polymers. These result also demonstrated that the new concept of immobilizing ions onto or near to polymer backbones may have several advantages over conventional polymer/salt complexes or side chain functionalized polyelectrolytes.

Program accomplishments for task 2

The growth mechanisms of sculptured thin films (STFs) allow for unique opportunities to engineer the spacing between nanowires during deposition.² In an attempt to obtain full infiltration of high viscosity MEEP electrolyte, the larger spacing using templated growth was studied as a control before using STFs with nanometer spacing. **Figure 2** shows the uncoated and TiO₂ coated silicon template architecture. MEEP infiltration was then tested using heat and vacuum

combinations and was qualitatively analyzed using scanning electron microscopy. MEEP electrolyte fully infiltrated the larger 500 nm to 2 μm pores under all tested conditions. These results demonstrated how engineered morphologies can be used to overcome the infiltration limitations of standard colloidal TiO_2 electrodes.

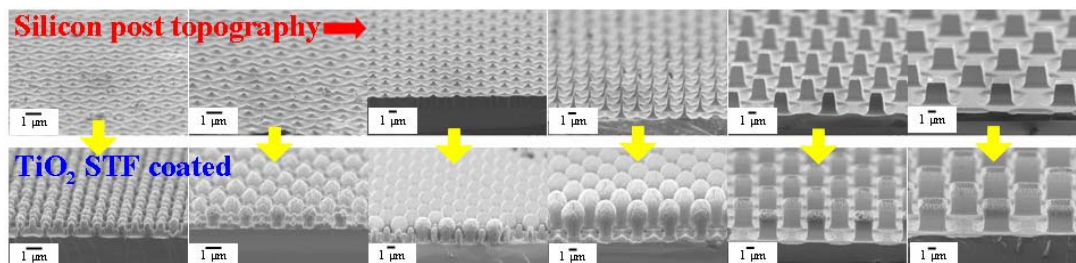


Figure 2 Topography of Si Substrates templated using photolithography that was used to investigate TiO_2 STF growth and MEEP infiltration.

Higher dye absorption per volume allows electrodes to be thinner and still maintain sufficient light collection, thus shortening the required electron diffusion length and reducing recombination sites. Dye desorption measurements showed that various morphologies of nanowire STF electrodes grown on bare glass contained more dye per volume, up to three times more, than the standard colloidal electrode. High dye absorption values may be due to increased surface area or improved dye packing on the oriented nanowire surfaces when compared to the standard colloidal electrodes.

Program accomplishments for task 3

DSSCs utilizing low-volatility organophosphate based electrolytes were first tested on colloidal electrodes to evaluate various compositions of electrolyte. Photovoltaic parameters of cells using exactly the same architectures with 3-methoxypropionitrile (MPN), and BMEMPh based electrolytes, are shown in **Table 2**. Significantly, the V_{oc} of BMEMPh-based cell is higher than that of MPN-based cells. This can be attributed to co-absorption of BMEMPh with the photosensitizer to form a monolayer on the surface of the electrode to retard interfacial recombination of photo-generated charge carriers.³ The standout performance and higher boiling point of BMEMPh over MPN suggest that these new organophosphates are attractive as low-volatility solvents and plasticizers for DSSC applications.

Table 2 Comparison of performances of MPN and organophosphate based electrolytes.

Solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor	Efficiency %
MPN	0.750	8.759	0.66	4.3
7	0.770	7.790	0.67	4.0

Electrodes consist of 6–7 μm colloidal films with an active area of 0.8 cm². Photosensitizer is N719 dye. Electrolytes consist of 1.0 M PMII, 0.15 M I₂ and 0.5 M *N*-methylbenzimidazole and 0.1 M guanidinium thiocyanate in corresponding solvents.

Progress was made to construct large area (~10 cm²) strip cells utilizing both colloidal and STF photoanodes filled with phosphate-based electrolytes for the

assessment of massive productivity. More than 20 cells were constructed while optimizing the fabrication process. Some of them are shown in **Figure 3**. The best cell, consisted of a 4-5 μm thick colloidal photoanode with a Nb_2O_5 blocking layer and an organophosphate-based electrolyte, has an efficiency of 2.8%. Large-area cells suffer from lower fill factors (around 50%) than those of smaller test cells, which hamper higher efficiencies. We believe that this is due to contact issues, and could be overcome in further optimization.

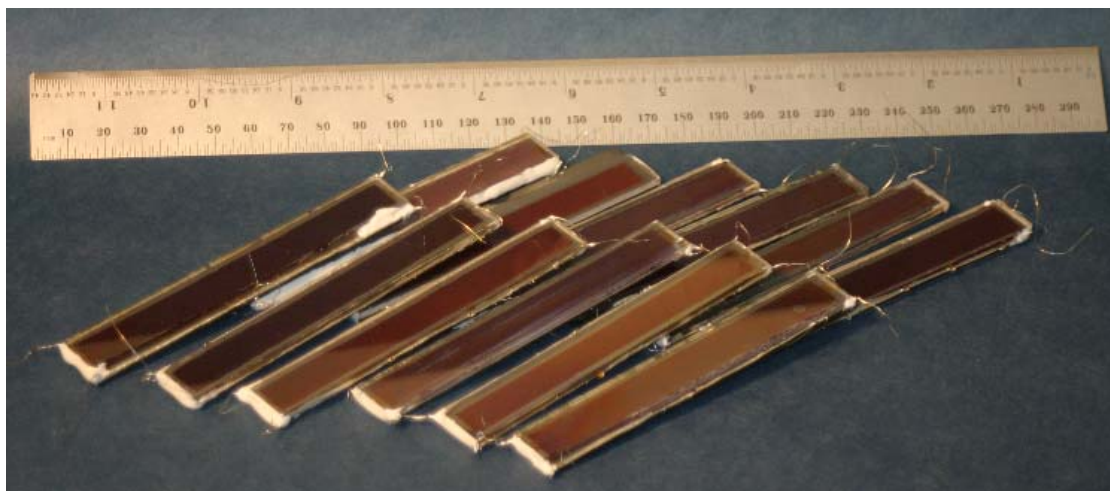


Figure 3 Strip cells made at Penn State.

Summary of Project Activities

Novel polymeric and oligomeric electrolytes and TiO_2 sculptured thin films have been produced and applied to improve the stability and performance of DSSCs. Systematic fundamental studies of electrolyte infiltration and the electrochemical performance of DSSCs employing high-viscosity electrolytes and finely tuned nanostructured electrodes were performed. On the application side, promising cell performances have been accomplished with organophosphates in prototype cells, which still possess great potential of improvement in the future. The valuable data accumulated during these studies are great assets toward the commercialization of DSSCs and could be significant in improving the safety and performance of other electrochemical devices, such as rechargeable lithium ion batteries.

Publications

4. Chen, C.; Hess, A. R.; Jones, A. R.; Liu, X.; Barber, G. D.; Mallouk, T. E.; Pursel, S. M.; Horn, M. W.; Allcock, H. R. Syntheses of Novel Polyelectrolytes via Backbone Quaternization of Polyaryloxy- and Polyalkoxyphosphazenes, *Macromolecules* **2012**, *45*, 1182
3. Hess, A. R.; Chen, C.; Barber, G. D.; Mallouk, T. E.; Pursel, S. M.; Horn, M. W.; Allcock, H. R. Synthesis of Non-Volatile, Fire-Retardant Organophosphates for Use in Dye-Sensitized Solar Cells and Lithium Batteries, to be submitted
2. Fei, S.-T.; Lee, S.-H. A.; Pursel, S. M.; Basham, J.; Grimes, C. A.; Horn, M. W.;

Mallouk, T. E.; Allcock, H. R. *J. Power Sources* **2011**, *196*, 5223.

1. Lee, S.-H. A.; Jackson, A.-M. S.; Hess, A.; Fei, S.-T.; Pursel, S. M.; Basham, J.; Grimes, C. A.; Horn, M. W.; Allcock, H. R.; Mallouk, T. E. *J. Phys. Chem. C* **2010**, *114*, 15234.

References

¹ O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

² Zhang, X.; Whitney, A. V.; Zhao, J.; Hicks, E. M.; Van Duyne, R. P.; J. *Nanosci. Nanotechnol.* **2006**, *6*, 1.

³ Wang, M.; Li, X.; Lin, H.; Pechy, P.; Zakeeruddin, S. M.; Grätzel, M. *Dalton Trans.* **2009**, 10015.