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Report Title

Novel Nanocomposite Materials for Solar Cell Fabrication

ABSTRACT

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In parallel with carrying out the tasks of materials engineering, we have developed a relatively novel electro-analytical technique to facilitate quantitative testing of laboratory scale photovoltaic cells. These device-testing methods have been standardized in our present work by using crystalline silicon solar cells. Voltage bias dependent behaviors of dark as well as illuminated DSSCs have also been investigated. The IL electrolytes designed during this project should also be usable for certain energy-storage as well as sensor devices that could potentially be integrated with solar cells. For this reason, we have investigated supporting active materials for energy storage, focusing specifically on LiMn_2O_4 cathodes for Li ion (solar) batteries. We have also explored the adsorption characteristics of ILs on Au thin films for sensor-type applications. The results obtained from these studies have been reported in a number of peer-reviewed publications, and presented at various conferences and meetings.

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Sincerely,

Dipankar Roy

Co-PIs: Sitaraman Krishnan and John McLaughlin

Technical Report: Project 2

“Novel Nanocomposite Materials for Solar Cell Fabrication”

PIs: Sitaraman Krishnan, John McLaughlin and Dipankar Roy

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Project personnel for the reporting period:

Two faculty co-PIs (Krishnan and Roy) are involved with the experimental aspects of synthesis and characterization for this project, and one faculty co-PI (McLaughlin) is undertaking the computational tasks necessary for material characterization. One Postdoctoral Associate (Xinli Jia) also is involved in these computational studies.

Several graduate and undergraduate students, supported mostly by Clarkson University, have participated in this project during the current reporting period. Chemical & Biomolecular Eng. graduate students Lalitha Ganapatibhotla and Lin Wu have worked on this project. Lalitha was supported through a Teaching Assistantship from Clarkson (1 year), and Lin Wu was supported by a research assistantship funded by the ARO grant (1 year). Two other graduate students from the physics department (Daniel Crain and Jianping Zheng) have spent approximately 0.5 FTE (each student) on this project, and have been supported through Teaching Assistantships (TAs) from Clarkson University. A third physics graduate student, John Garland, has participated full time in the project, and has been funded mostly by a TA from the physics department, with partial support (17.4% of an academic year) obtained through the present project.

Theodore Glave, an undergraduate student in the department of Chemical and Biomolecular Engineering, assisted McLaughlin in self-consistent mean field simulations of ionic-liquid/carbon-nanotube blends. Undergraduate students Sydney Laramie and Joshua Franclemont assisted Krishnan in quantitative structure-property correlation studies for ionic liquid properties. Physics undergraduate student Tyler Mosher has recently joined this project (as a student enrolled in a credit-carrying directed study research course) to help with the measurements of IL conductivities and to assist with data analysis.

Summary of most important results:

We have synthesized and characterized an imidazolium iodide ionic liquid containing an ω -perfluoroalkyl poly(ethylene glycol) (PEG) tail [1]. The solid phase of this material was accomplished through the generation of ionic clusters by electrostatic interactions, as well as through microphase separation of the immiscible perfluoroalkyl and PEG segments of the cation used. We have performed self-consistent mean field calculations to probe the formation of nanostructures in the ionogel. The high conductivity, and the nonvolatile, gel-like properties of this electrolyte should be useful to support the function of high-performance, leakage-proof DSSCs. We have also synthesized and characterized certain PEGylated ILs [2]. These latter ILs exhibit satisfactory conductivities ($\sim 0.13 \text{ mS cm}^{-1}$ at room temperature) despite their relatively high viscosities, and support a temperature-independent electrochemical window of $\sim 2 \text{ V}$.

We have developed an electro-analytical approach to quantitative characterization of solar cells. Crystalline Si cells have been used to establish the essential analytical protocols of this method [3-6]. We have demonstrated how this method can evaluate the temperature and voltage sensitive features of the minority carrier lifetimes, series and shunt resistances and back surface field (BSF) parameters of a solar cell. Apart from displaying their characteristic temperature dependencies, the parameters measured in this way have responded to variations of the cell voltage, and exhibited mutually interacting features of the observed effects [3-5]. These results have shown how the characteristic features of charge recombination in the quasi-neutral and space charge regions of the solar cell could be resolved with D.C. voltage dependent A.C. impedance measurements.

The diode-like electrical behavior of a DSSC has been studied to evaluate the detailed charge recombination characteristics of the cell [6]. A forward biased dark DSSC has been used to preferentially activate the recombination reactions, and the kinetics of these reactions have been probed by using electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV). The ohmic and non-ohmic series resistances of the DSSC have been separated, and their origins have been investigated. The characteristic impedance parameters of the different active interfaces of the multi-component solar cell have been obtained from complex nonlinear least square (CNLS) analysis of the EIS data. Among these parameters, the electron lifetime and the resistance of charge transfer at the TiO_2 -electrolyte interface have followed the same diode-like voltage dependence of the D.C. current. We have shown that, this diode feature of the DSSC played a critical role in determining the overall performance of the cell, and that the diode ideality factor was governed by the Butler-Volmer kinetic of charge recombination.

Figure 1A schematically shows the main components of a typical DSSC used in the present work. The mesoporous TiO_2 photoanode contains differently sized nanoparticles (white circles). Fig. 1B shows the corresponding cell-equivalent circuit model obtained from CNLS analysis of EIS results. I_3^- from the electrolyte is reduced by an electron from the conduction band of TiO_2 , and Γ^- is oxidized at the Pt counter electrode (CE). The space between the mesoporous anode film of dye-covered TiO_2 and the CE is filled with an electrolyte containing an electron mediator redox couple of I_3^-/Γ^- . The TiO_2 film contains particles (10-400 nm diameters) of progressively increasing sizes in going from the fluorinated tin oxide (FTO) substrate to the electrolyte boundary. The largest particles (~400 nm) of this film, placed immediately next to the electrolyte, form the light scattering layer (LSL), while the transparent smaller particles introduced between the anode FTO and the LSL serve as the main active material of the cell. Sample results of DSSC characterization experiments performed in the present work are shown in Figs. 2-4.

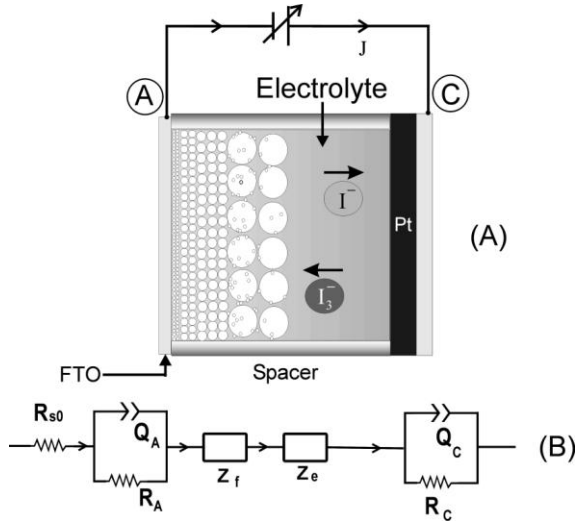


Figure 1. (A) Schematic of an un-illuminated DSSC under forward bias (FB). The FTO substrates on the anode and the CE sides are labeled as A and C, respectively. The sensitizer dye is not shown. (B) Experimentally determined equivalent circuit model of the DSSC. The FTO- TiO_2 and the Pt-FTO interfaces are represented by the (Q_A-R_A) and (Q_C-R_C) units, respectively. Q_A (or Q_C) and R_A (or R_C) are the constant phase element (CPE) and the resistance of the anode (or the CE), respectively. R_{s0} is the external series resistance, Z_f is the impedance of the TiO_2 film, and Z_e is the impedance of I_3^- (Γ^-) transport in the electrolyte.

Figure 2A shows current density (J) vs. voltage (V) plots of the DSSC recorded at (a) 25 and (b) 30 °C under FB. The currents show their expected diode-like characteristics. Fig. 2B displays the diode circuit that corresponds to the data in Fig. 2A. The internal shunt resistance R_{sh}^f develops across the TiO_2 film due to some uncovered sites of the anode-side FTO, where charge recombination is supported by the electrons from the conduction band of FTO.

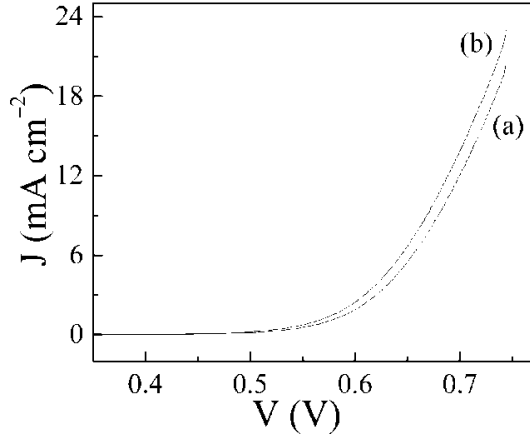
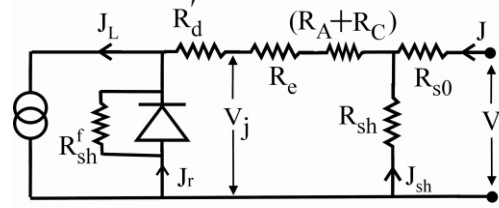


Figure 2A. J - V plots of the DSSC recorded at (a) 25 and (b) 30 °C.



B. Single-diode D.C. circuit model of a DSSC under illumination. The cell current (J) in this includes both the photo-current (J_L) and the dark recombination current, J_r . The lower and the upper horizontal lines in this Figure correspond to the “C” and “A” sides of the cell, respectively.

The main shunt resistance R_{sh} of the DSSC accounts for the recombination paths supported by the CE substrate. J_{sh} is the external shunt current, and V is the terminal voltage of the DSSC.

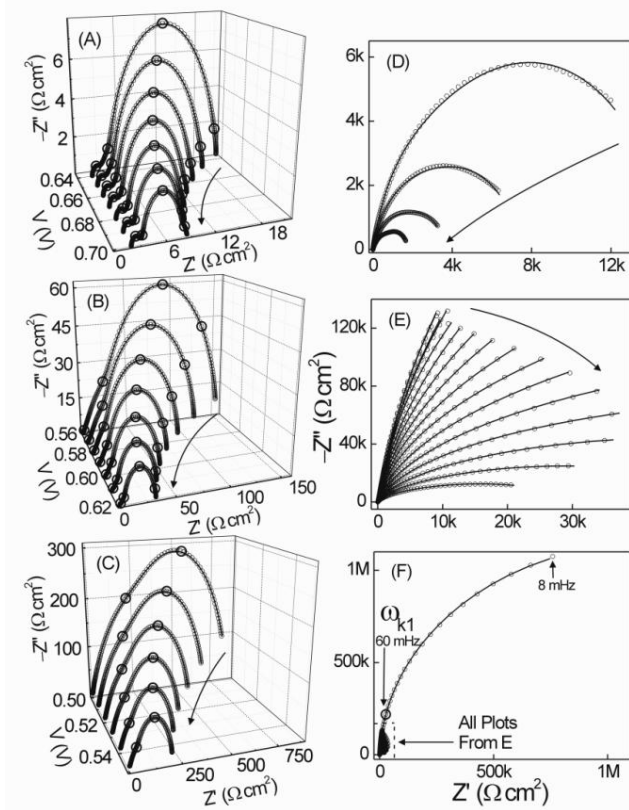


Figure 3. D.C. voltage induced evolution of the Nyquist plots for a dark DSSC maintained at strong (panels A-C) and moderate/weak (panels D-F) FB voltages. The progressively shrinking plots in (A) were collected at 10 mV intervals between 640 and 700 mV going in the direction of the arrow placed on the V - Z' plane. The plots in (B) and (C), arranged in the same order as in (A), were also recorded in 10 mV intervals exploring the ranges 560-620 mV and 500-550 mV, respectively. The data in (D)-(F) correspond to lower FB voltages, where the signature features of the TiO_2 photo-anode disappear and the overall impedance of the DSSC increases with decreasing voltages. V increases in the directions of the arrows, from 400 to 475 V in steps of 25 mV in (D), and from 50 to 375 mV in steps of 25 mV in (E). The large plot in (F) is for $V = 0$ V. The symbols on all these plots denote data points and the lines represent CNLS fits to the data.

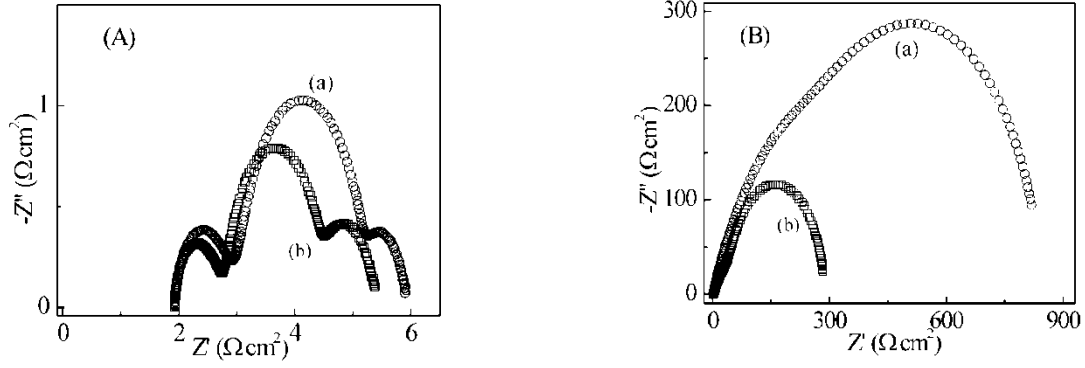


Figure 4. Nyquist plots for a DSSC recorded at (a) 25 and (b) 30 °C, with the bias voltage set at (A) 0.75 V and (B) 0.5 V. Z' and Z'' denote the real and imaginary parts of the complex impedance of the DSSC, respectively. In (A) the middle impedance arc (for the larger particles of the anode) drops most noticeably with the increase of cell temperature from 25 to 30 °C. In (B) the larger anode particles dominate the data trend and the overall impedance of the spectra drops by a factor of three, unlike the much smaller percentile drop seen in (A).

Fig. 4 shows Nyquist plots for a DSSC recorded at (a) 25 and (b) 30 °C, with the bias voltage set at three different values selected from the moderate-high forward bias region. At $V = 0.75$ V, the middle impedance arc Nyquist spectrum (impedance Z_{f2} of the LSL region) drops most noticeably with the increase of T from 25 to 30 °C. In Figure 3B, Z_{f2} (impedance of the LSL containing region of the photo-anode) dominates the Nyquist spectra and becomes even more sensitive to temperature variations, as the rate of charge recombination is decreased at $V = 0.5$ V. This effect is further enhanced at $V = 0.4$ V, where the D.C. dark current is forced down near its onset value, restricting the active zone of the recombination reaction mostly outside the LSL film. These rather drastic temperature induced variations of Z_{f2} , observed in response to the corresponding modest changes in the reaction currents, indicate restricted surface density of active electrochemical sites in the LSL.

The electro-analytical studies of DSSCs carried out through our project show that, strategically selected experimental control variables, coupled with CNLS analysis of experimental data can enable the component-specific resolution of EIS. This in turn helps to resolve the individual impedance parameters of the FTO-TiO₂ and Pt-FTO interfaces from those of the TiO₂ anode film in the DSSC [6]. EIS also detects the different electrical characteristics of the morphologically different TiO₂ layers included in the photo-anode of the cell. Furthermore, the power-consuming series resistance (R_s) of the DSSC is determined directly from CNLS-analyzed EIS results; the ohmic and non-ohmic components of this resistance also are resolved in this approach [6]. These R_s data facilitate an accurate evaluation of the internal voltage of the DSSC, and allow for a rigorous examination of the cell's electrical attributes. A specific electrical feature of the DSSC studied in our present work is the diode-like behavior of the cell. It is shown that the diode nature of a DSSC is closely linked to the charge recombination characteristics and hence the overall performance of the device [6].

We have tested a cathode of lithium manganese oxide using a mixture of nanometric and micrometric active particles [7,8]. The goal of this specific study was to explore selected

materials for energy storage components (such as Li ion solar batteries) that could be integrated with solar powered devices. To conduct these experiments, commercially available particles were mechano-chemically modified by ball-milling. Ragone plots, recorded using galvanostatic measurements indicated enhanced power delivery characteristics of the ball-milled material compared to its unprocessed counterpart [8]. The processed material also exhibits improved resistance against electrolyte reactions and surface film formation. Due to these advantageous electrochemical attributes, the ball-milled cathode material also has served as an adequately suited system for exploring various fundamental aspects of Li intercalation [8]. Scan rate dependent slow scan cyclic voltammetry has helped to identify the kinetic and diffusion controlled features of Li transport in the processed active particles. The observations have been substantiated further by using EIS and by measuring the voltage dependent charge transfer resistance and diffusion coefficient of Li transport.

We have combined SPR and electrochemical measurements to study the interactions of a gold film electrode with concentration dependent electrolytes of an IL [9]. The purpose of this particular study was to understand the adsorption characteristics of an IL on a typical sensing electrode, and to further explore IL based device applications. Voltage- and/or electrolyte-induced variations were detected in the critical angles and SPR angles measured in the attenuated total reflection geometry. The optical response of the bulk electrolyte strongly affected the SPR angles; the critical angle data helped to separate these effects from those arising strictly from the electrode surface. The optical parameters of the Au-electrolyte system were determined by fitting the SPR angle-spectra to calculated results of a multi-layer reflectivity model. Both in the absence and in the presence of externally applied voltages, the SPR signal of the experimental interface was dominated by the dielectric behavior of the bulk electrolyte, with no significant effects detected for IL chemisorptions. The results demonstrated how angle resolved SPR measurements could be used to determine the surface adsorption characteristics of ILs.

References

1. L. V. N. R. Ganapatibhotla, L. Wu, J. P. Zheng, X. Jia, D. Roy, J. B. McLaughlin and S. Krishnan, "Ionic liquids with fluorinated block-oligomer tails: Influence of self-assembly on transport properties", *J. Mater. Chem.* 21 (2011) 19275-19285.
2. L. V. N. R. Ganapatibhotla, J.P. Zheng, D. Roy and S. Krishnan, "PEGylated Imidazolium Ionic Liquid Electrolytes: Thermophysical and Electrochemical Properties", *Chem. Mater.* 22 (2010) 6347–6360.
3. D. J. Crain, J. E. Garland, S. E. Rock and D. Roy "Quantitative characterization of silicon solar cells in the electro-analytical approach: Combined measurements of temperature and voltage dependent electrical parameters", *Analytical Methods* 4 (2012) 106-117.
4. J.E. Garland, D.J. Crain and D. Roy, "Impedance spectroscopy coupled with voltammetry for quantitative evaluation of temperature and voltage dependent parameters of a silicon solar cell", *Solar Ener.* 85 (2011) 2912-2923.
5. J.E. Garland, D.J. Crain, J.P. Zheng, C.M. Sulyma and D. Roy, "Electro-analytical Characterization of Photovoltaic Cells by Combining Voltammetry and Impedance Spectroscopy: Voltage Dependent Parameters of a Silicon Solar Cell under Controlled Illumination and Temperature", *Energy Env. Sci.* 4 (2011) 485-498.
6. J.E. Garland, Ph.D. Thesis, Clarkson University (2011).

7. D. J. Crain, J.P. Zheng, C.M. Sulyma, C. Goia, D.Goia, D. Roy, Electrochemical features of ball-milled lithium manganate spinel for rapid-charge cathodes of lithium ion batteries, *J. Solid State Electrochem.* (2012) DOI 10.1007/s10008-012-1677-8.
8. J.P. Zheng, D.J. Crain and D. Roy, "Kinetic aspects of Li intercalation in mechano-chemically processed cathode materials for lithium ion batteries: Electrochemical characterization of ball-milled LiMn_2O_4 ", *Solid State Ionics* 196 (2011) 48-58.
9. C. M. Sulyma, C. M. Pettit, J. E. Garland, D. Roy, "Surface plasmon resonance as a probe of interactions between a thin-film gold electrode and an aqueous supporting electrolyte containing 1-ethyl-3-methyl-imidazolium ethyl sulfate ionic liquid", *Surf. Interface Anal.* (2012), DOI: 10.1002/sia.4808.