

Enabling Methods and Materials for Stackable Tandem Solar Cells with Polymer Electrolyte Interconnect

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3 ABSTRACT

This interdisciplinary project studies the use of liquid and solid state electrolyte interconnects to create Schottky and tandem junction solar cells. This approach avoids the complex fabrication processes required to make tunnel junctions typically required for multijunction photovoltaics. Instead it relies on low temperature, easy to fabricate polymer layers which can be optimized independently of the semiconductor junctions.

In the 2015 funding year we have initiated 3 core studies: the first is to reproduce and surpass previous performance benchmarks using a liquid electrolyte Schottky junction with crystalline silicon; the second is to use the liquid electrolyte junction in a tandem architecture with amorphous silicon p-i-n junctions, and the third, is to develop and optimize a solid state polymer electrolyte layer to eventually replace the liquid electrolyte in Schottky and multijunction (tandem) architectures.

In our first study we have designed and fabricated Schottky junctions using crystalline silicon and non-aqueous liquid electrolytes. Owing to its relatively simple architecture the Schottky design offers a great proving ground to optimize many of the components that will be needed later on in the tandem architectures. Such early experiments allow us to examine the quality of our redox couples and identify loss mechanisms such as light absorption and series resistance. Using this initial structure we have already achieved short-circuit photocurrents as high as 20 mA cm^{-2} and open-circuit voltages of 0.6 V. Still much work is necessary to improve light absorption and reduce series resistance.

In our second study we replace the transparent counter electrode with an amorphous silicon p-i-n junction front cell to evaluate the liquid junction design in a multijunction architecture. We find that

although high series resistance is a significant issue, we can achieve very good photovoltage addition and photocurrent matching between the front and back cells. Overall we have been able to achieve open-circuit voltages as high as 1.46 V with further improvements still possible from better light management.

Finally we have started to design a solid state polymer interconnect by incorporating our redox couple into an ion gel thin film matrix. When used to replace the liquid electrolyte in the Schottky architecture described above, we were able to achieve a rectifying junction in the dark. Performance appeared to be limited by diffusion transport of the ionic species resulting in what we believe to be high recombination rates that prevent the realization of photocurrent and photovoltage when tested under light. Further work on the composition and structure of the conductive matrix is required to improve transport and cell performance.

4 INTRODUCTION

Photovoltaic cells employing liquid-semiconductor junctions may have advantages over solid-state devices. Controlling band bending in the junction can be achieved by tuning the redox couple of the electrolyte. This offers a flexible method for device junction design that may be significantly cheaper than in solid state device fabrication using ion implantation and diffusion. This may be especially true in tandem architectures where design of tunnel/recombination junctions can be especially challenging as they often rely on advanced semiconductor fabrication techniques such as epitaxial growth¹.

The goal of this project is to build off of existing work on liquid-junction devices that has been developed and optimized mostly for single junction solar cells to create an electrochemically coupled tandem solar cell which can be manufactured at low temperature using relatively easy fabrication techniques. Amorphous silicon has been selected as a suitable top junction to be used in combination with crystalline silicon. Previous studies have already shown the compatibility of these materials in micromorph tandem photovoltaics². In parallel we hope to design and optimize a solid state polymer system which may offer a more stable, more reliable replacement for the liquid electrolyte system we are presenting working on.

5 BACKGROUND

Some of the early research on liquid-semiconductor junctions using GaAs^{3,4}, CdSe⁴, and CdTe⁴ materials used aqueous electrolytes and achieved efficiencies approaching 12%. However for some semiconductor materials, like crystalline silicon, the presence of water may eventually be detrimental due to photocorrosion and oxidation of the interface⁵. It is for this reason why electrolytes composed of non-aqueous solvents have also been considered for liquid-semiconductor systems. Work by Gibbons et al.⁶ determined that methanol can serve as a suitable solvent for silicon electrochemical cells as the methoxylated silicon interface is well passivated offering relatively low surface recombination. When used with a dimethylferrocene (dmFc)/dimethylferrocenium (dmFc⁺) redox couple a Schottky junction solar cell was created providing open-circuit voltages >0.6 V which is comparable to some of the best MIS Schottky solar cells⁷. The dmFc/dmFc⁺ has an absolute reduction potential⁸ of 4.935 V (in 1,2-dichloroethene) relative to vacuum which provides the work function difference to create the Schottky

junction with n-type Silicon. When tested under AM1.5 conditions open circuit voltages >0.6 V were achieved, which is comparable to some of the best MIS Schottky junctions.

Polymeric ion gels are among the most conductive solid electrolytes. Recent advances⁹ have demonstrated that ion gels using 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) ionic liquid (IL) and poly(styrene-*b*-methyl methacrylate-*b*-styrene) (SMS) can achieve dc conductivity of 5-10 mS/cm at room temperature. [EMIM][TFSI] has high ionic conductivity and a wide electrochemical window¹⁰, while weight percentage as low as 5-10% of SMS can provide good mechanical integrity, thus the high conductivity of IL is largely preserved. These ion gels can be made into thin films down to tens of nanometer scale, creating an opportunity for our study of ion gel connected tandem solar cells.

6 RESULTS

6.1 LIQUID-JUNCTION SOLAR CELLS

6.1.1 Schottky Junction Architecture

We have fabricated Schottky junction regenerative solar cells (**Figure 1**) using n-type silicon in contact with an indium tin oxide (ITO) conductive contact through a thin electrolyte layer. The electrolyte volume is created with a thin Surlyn gasket, a Dupont ionomer film, which also serves to bond the ITO coated glass and n-silicon wafer together when heat and pressure is applied. Surlyn was chosen due to its previous use as an encapsulant material in dye sensitized solar cells for its ability to provide an adequate sealant for the electrolyte material. Various types of Surlyn of 7.5 μm , 10 μm , and 25 μm thickness have been obtained which allows us to vary the interelectrode distance and electrolyte volume¹¹. Previous work on photoelectrochemical cells have shown that series resistance and fill factor losses can be minimized if the interelectrode separation (Surlyn thickness) can be held as low as 10-20 μm ⁶.

To create a properly methoxylated silicon surface n-type silicon wafers were etched in 10:1 HF dip (5%) for 45 s. Under these conditions etch rates are more than adequate to completely remove the ~2nm native oxide layer. The result is a hydrogen passivated silicon surface which is then rinsed and placed in dry methanol containers which are then stored inside a nitrogen filled glovebox with <1 ppm O₂ content. Storage inside methanol immediately after HF etching leads to a methoxylated silicon surface needed for this architecture¹².

The electrolyte solution was prepared by dissolving dimethylferrocene and dimethylferrocenium tetrafluoroborate in dry methanol in quantities necessary to achieve 0.2M concentration. Lithium perchlorate to improve ionic conductivity, in quantities necessary to yield 1.0M concentration

A precut Surlyn gasket was placed between the ITO substrate and the silicon sample and then placed on a hot plate and heated to 150°C with a small weight used to provide some pressure. After bonding of the components electrolyte solution was injected with a pipette through two 0.75 mm holes drilled through the ITO coated glass substrates. These holes were then covered with UV Epoxy (Epotek) and cured with 5 minutes exposure to a UV lamp to prevent electrolyte evaporation.

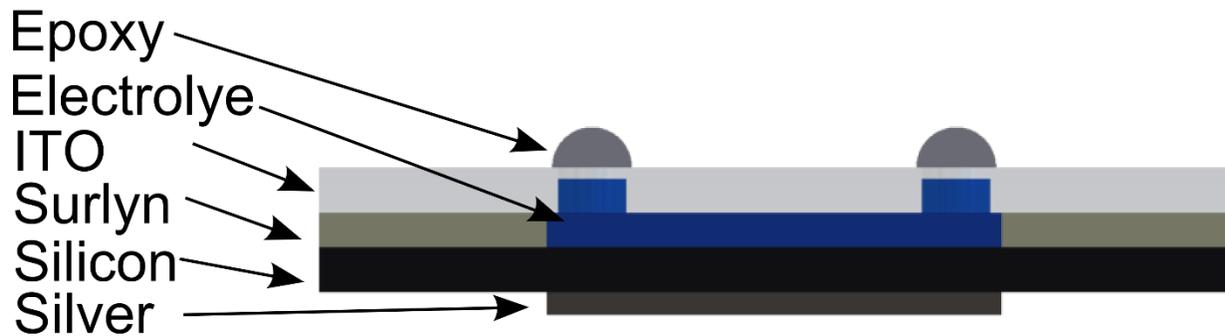


Figure 1: Schematic of a liquid-junction Schottky solar cell based on ITO and Silicon separated by a thin electrolyte layer.

We have tested these devices under simulated AM1.5 conditions (**Figure 2**). We have found initial performance efficiencies of 5% with open-circuit voltages of 0.6 V and short-circuit current densities as high as 21 mA cm^{-2} . Performance was found to be limited by both the low short-circuit current density relative to the maximum for silicon¹³ under 1 sun AM1.5 conditions of 44 mA cm^{-2} and the relatively low fill factor of 40%. As bias voltages approach 0 V the current-voltage (I-V) curve appears relatively flat suggesting that photocurrent may be limited more by reflection and parasitic absorption losses than through charge carrier transport. It should also be noted that due to leakage of the electrolyte over time there is significant uncertainty in the active area of the device and therefore the overall photocurrent densities. The low fill factor appears to be the result of high series resistance as evidenced by the slope of the I-V curve near open circuit conditions. Analysis of I-V curve shows a series resistance of 35Ω with contributions from the ITO resistance, back contact resistance to the silicon substrate, and transport resistance within the electrolyte solution layer.

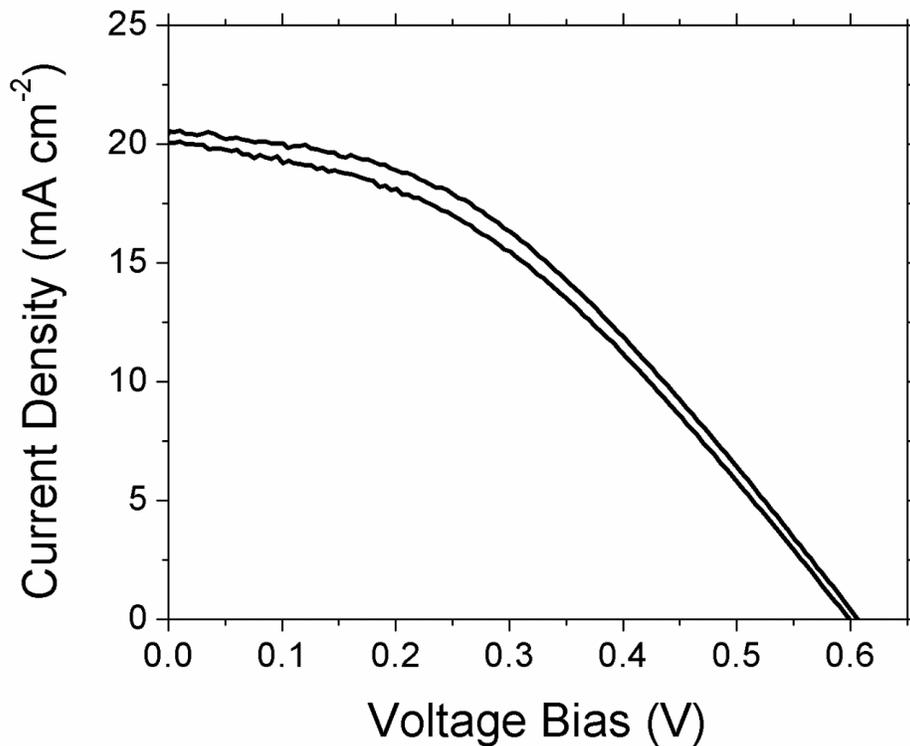


Figure 2: Photovoltaic response of a Schottky ITO/n-type silicon solar cell using dimethylferrocene/dimethylferrocenium tetrafluoroborate redox couple in dry methanol.

6.1.2 Tandem Junction Architecture

We hoped to showcase the usefulness of this approach by implementing it in a tandem architecture. We were able to procure amorphous silicon (a-Si) p-i-n devices from Oerlikon, a former Swiss materials processing company. The amorphous silicon devices consist of a p-i-n junction grown on boron doped ZnO coated glass. An ohmic contact to the top, n-type a-Si layer, with additional boron doped ZnO. We were able to mask the top ZnO:B TCO and use HCl etching to pattern the top contact to match the area of the electrolyte spacer. The a-Si devices are bonded to the Surlyn in place of the ITO in the Schottky device architecture and can be drilled similar to ITO coated glass. Instead of n-type silicon we have elected to use p+n junctions obtained from collaborators at the Tyndall National Institute in Ireland which should lead to higher open-circuit voltages when used in a tandem architecture. The p+ regions are created by boron ion implantation in n-type silicon wafers and annealing to create a junction that is 450 nm thick and has $5 \times 10^{19} \text{ cm}^{-3}$ p type doping.

These devices were tested under AM1.5 conditions (**Figure 3**). In our initial trials we were able to realize open circuit voltages of 1.46 V. As the a-Si devices typically yield open circuit voltages of 0.86 V this implies an additional photovoltage of 0.6 V from the back p+n junction. Using the p+n junction we

appear to matching the open-circuit voltage obtained from Schottky architectures even at the lower light absorption.

The a-Si device has a bandgap of ~ 1.7 eV which absorbs most of the visible light. The overall short-circuit current density of 9 mA cm^{-2} is slightly less than half that achieved in the Schottky cell which suggests close to ideal current matching between the two cells. Nevertheless further improvement to the overall photocurrent density may still be necessary. Previous external quantum efficiencies measurements (EQE) show that photocurrent densities of 12 mA cm^{-2} are achievable with the front a-Si cell which would require 24 mA cm^{-2} light total absorption in an unfiltered silicon back cell.

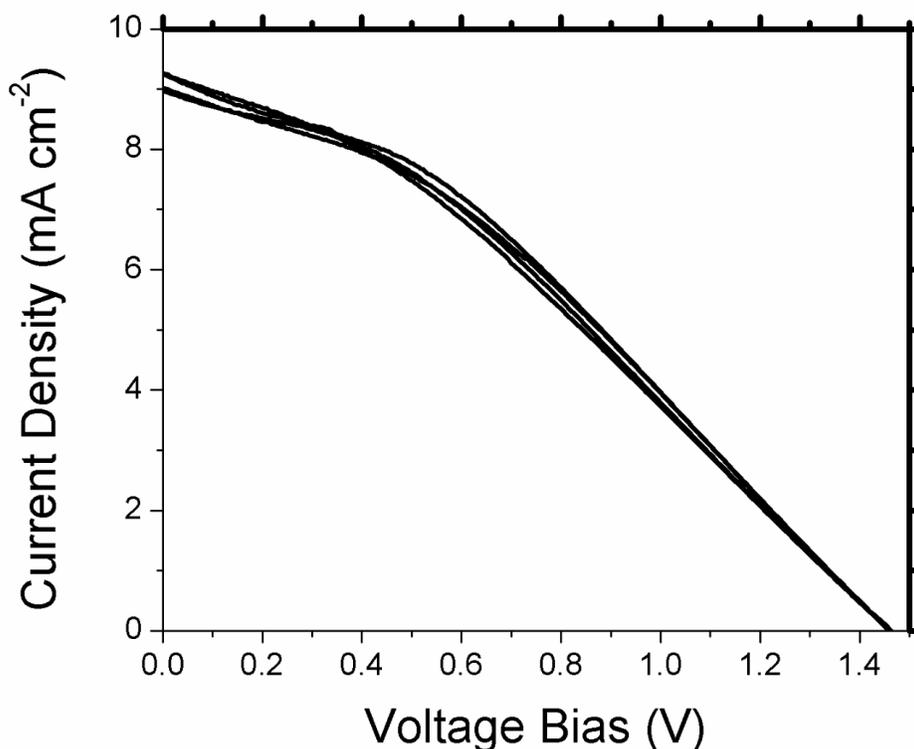


Figure 3: Photovoltaic response of an a-Si/p+n silicon tandem solar cell using dimethylferrocene/dimethylferrocenium tetrafluoroborate redox couple in dry methanol.

From the I-V response photovoltaic efficiencies of 4.6% were achieved. It is found that performance was limited primarily by low fill factor of 34% with a series resistance of 170Ω . In addition there appears to be a relatively low shunt resistance of 430Ω which also plays a role in limiting fill factor. The lower shunt resistance may be due to pin holes in the a-Si thin film where electrolyte may penetrate and reach down to the back transparent conductive oxide.

6.1.3 Solid State Electrolyte Junction

As mentioned previously we desire to create a conductive solid electrolyte system to take the place of the liquid electrolyte. To create this solid electrolyte dimethylferrocene and dimethylferrocenium

tetrafluoroborate were dissolved in dichloromethane (DCM) to form a 0.2M solution. Separately we created a 95 mg/mL solution of triblock-copolymer SMS and the ionic liquid [EMIM][TFSI] (1:3.5 by weight) in DCM. The two solutions are mixed in a 1:1 ratio by volume. Thin films were created through spin-coating on ITO coated glass substrates at 1000 rpm which gives gel films about 500 nm thick. Finally the n-type silicon substrates were etched in HF and stored in dry methanol to create a methoxylated silicon surface, similar to our liquid-junction cells. The silicon substrates were then pressed into the polymer gel and sealed with UV epoxy around the edges.

The initial dark I-V curve of the Schottky junction with polymer interconnect shows rectifying behavior between 0 and -1 V with minimal hysteresis (**Figure 4**). In the forward bias regime ($>0V$) the current appears to saturate at forward bias above 0.4 V indicating that diffusion limited ion transport through the polymer film may be present. Under simulated AM1.5G conditions we again see signs of diffusion limited current in both the reverse and forward bias regimes (**Figure 5**). The shape of the IV characteristics is that of a classical cyclic-voltammogram for a redox couple which shows clear cathodic and anodic peaks due to diffusion limited transport. From the IV characteristics no open-circuit voltage and no short-circuit current density are developed under illumination. This suggests that heavy recombination may be present within the polymer interconnect film. Tuning of the redox couple, ionic liquid, and polymer ratios may be necessary to increase concentration and mobility of ions to improve carrier transport and reduce recombination in order to achieve a photovoltaic response.

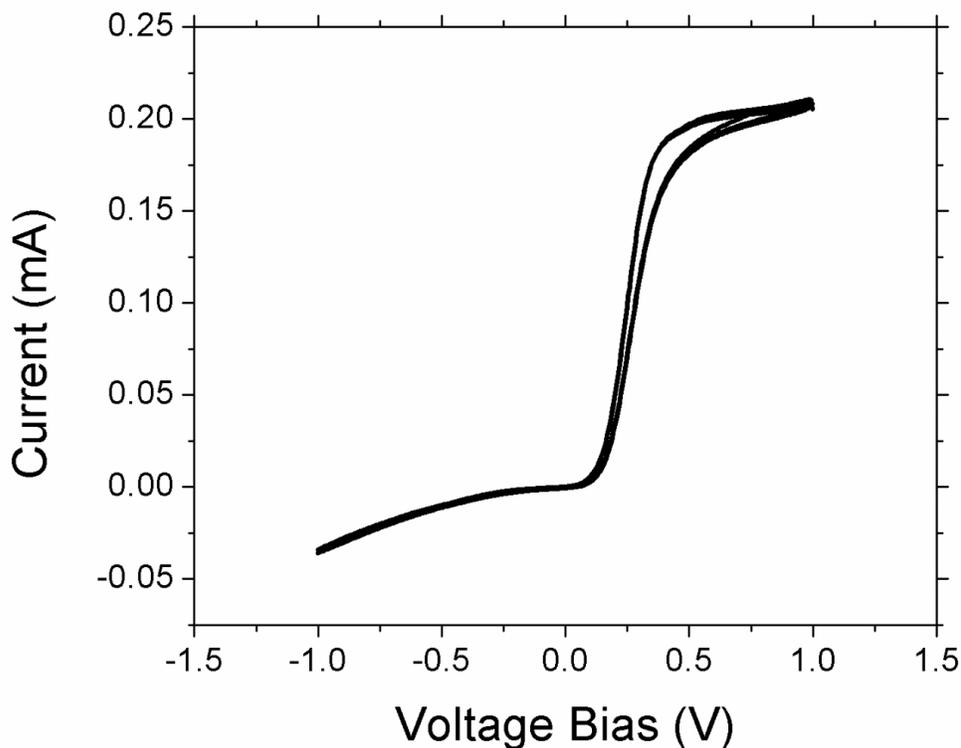


Figure 4: Current-voltage data for a Schottky solar cell ITO-silicon solar cell with a solid state electrolyte interconnect in the dark.

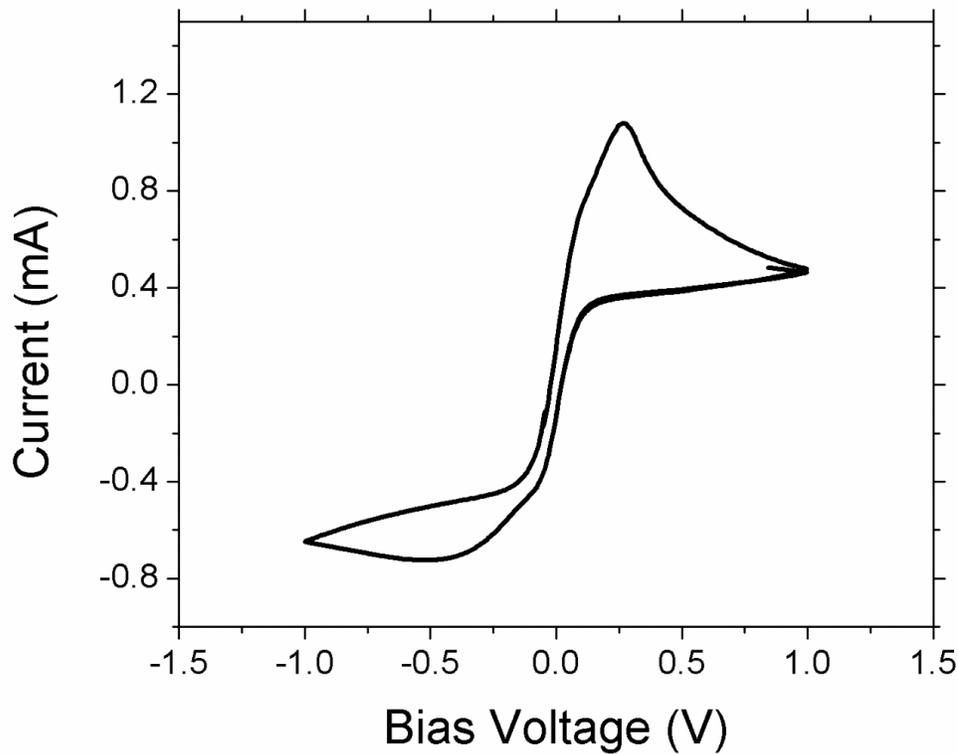


Figure 5: Current-voltage data for a Schottky solar cell ITO-silicon solar cell with a solid state electrolyte interconnect under AM1.5 conditions.

7 PROGRESS

The main advancements of the three core studies are summarized below:

1. *Liquid Junction Schottky Solar Cells*

We have created crystalline silicon Schottky solar cells using non-aqueous liquid electrolytes. Our initial work has yielded high open-circuit voltages of 0.6 V and reasonable photocurrents of 20 mA cm^{-2} .

2. *Liquid Junction Tandem Solar Cells*

The architecture developed for silicon Schottky solar cells has been restructured to include an amorphous silicon p-i-n top cell to form a tandem photovoltaic device. Although fill factor and series resistance still require much optimization we have been able to achieve good photocurrent matching which is only slightly less than half that achieved for the single junction crystalline silicon cell. An open-circuit photovoltage of 1.46 V was realized indicating close to ideal photovoltage addition between the front and back cells.

3. *Solid State Electrolyte Solar Cells*

Initial work on solid state polymer electrolyte thin films has been carried out for use in Schottky devices. Preliminary results indicate that rectifying junctions can be fabricated but more work is

needed on the composition and structure of these films to improve transport and reduce charge recombination to achieve photovoltaic devices using these materials

8 FUTURE WORK

Some leakage of the electrolyte appears to take place over time. This presents a problem not only for the long term stability of the device but also for the practical determination of the device area to determine the full photocurrent density. Small pores in the Surlyn may still be present where electrolyte can leach into overtime. Finding more robust ways of applying heat and pressure bonding of the Surlyn may help remove the leakage loss. Addition of epoxy around the edges of the device may also help prevent methanol leakage over time. So far attempts to use epoxy have proven to be unreliable as the UV epoxy we have been using has been found to leach into the device over time. A more viscous epoxy may be more reliable and may avoid this leaching issue. We will also explore the use of photolithography to create an oxide gasket similar to the work conducted by Gibbons et al.⁶. An oxide gasket may serve to be more robust against electrolyte leakage and offer more fine control of the interelectrode distance.

So far the performance of these liquid-junction cells (both Schottky and tandem architectures) have been limited primarily by a lower than ideal short-circuit current density and a fill factor dominated by a high series resistance. Fortunately both of these factors may be improved by decreasing the interelectrode separation to reduce electrochemical series resistance and parasitic absorption in the electrolyte solution. Electrolyte resistance will be characterized through electrochemical impedance spectroscopy. Impedance spectroscopy will also allow us to determine the relative contribution from contact series resistance. Improvements to the electrical connection to the silicon back cell and to the top ITO/aSi cell should also lead to significant improvements in the overall series resistance of the cell. This could be achieved by introduction of metallized bus bars which may help provide better contact to the top transparent conductive oxide used in these cells. Finally by switching to a more conductive silver paste we can achieve a more conductive ohmic contact to the n-type silicon back cell.

One of the more interesting studies we wish to undertake is whether we can create a more stable silicon electrolyte interface by introduction of atomic layer deposited TiO_2 . Previous studies by the McIntyre group have shown that thin TiO_2 layers on silicon can provide suitable protection from photocorrosion and oxidation^{5,14}.

We will explore different concentrations and ratios of dmFc+/dmFc, [EMIM][TFSI] IL, and SMS polymer, and measure gel thickness and conductivity, aiming to achieve better stability and higher conductivity. By achieving more efficient charge transport through the solid electrolyte we will hope to decrease recombination improving both the photocurrent and photovoltage. These optimized gel electrolytes will be tested in both the Schottky and tandem photovoltaic architectures.

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10 CONTACTS

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