Dissecting an Important Phenomenon in a Rapidly Growing Solar Technology

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Summary for RSS Feeds: Progress is made in characterizing what could be an important contribution to hysterical behavior in current-voltage curves obtained from hybrid perovskite solar cells.

In 2014, Professor Aron Walsh, of the University of Bath, along with group members Dr. Keith Butler and Dr. Jarvist Frost, wrote a computer simulation to explore a potential contributing factor to difficulties that are encountered in measuring the efficiency of hybrid perovskite solar cells. Perovskite solar cells are the fastest growing solar cell technology, but their detailed operation is not yet well understood. Interest in this technology began in 2009 when Akihiro Kojima, Kenjiro Teshima, Yasuo Shirai and Tsutomu Miyasaka of the University of Tokyo showed that it was possible to use organolead halide perovskite nanocrystals as absorbers in solar cells, with a solar conversion efficiency of 3.8%. Since then, the measured efficiencies of perovskite solar cells have risen to over 20% as of 2014. However, measurements of perovskite solar cell efficiencies are considered unreliable because the current-voltage curves that are used to characterize the performance of the solar cell are sensitive to initial conditions, history of the cell and exactly how the curves are measured. Factors that influence the measurements include scan direction, speed, light conditions, forward biasing as well as how the films themselves are produced. A paper written by Dr. Walsh and his group members explores the ferroelectric contributions to this hysteretic effect through simulations of the ordering of dipoles in methyl-ammonium lead iodide solar cells, chosen because this perovskite material had the most widely reported hysteresis.

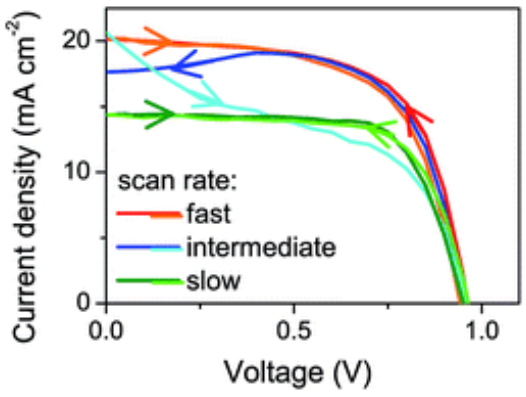

Figure 1: Hysteresis in I-V Curves

On how it occurred to Walsh and his coauthors to look for ferroelectric contributions, Walsh stated:

"Initially I would say chemical intuition in a way… methyl-ammonium had quite a large electric dipole, and from our simulations we could see those dipoles were quite mobile in that they could rotate relatively freely… it was our idea that different orderings of the molecules could give rise to an electric field that would directly influence the photovoltaic performance."

The two dimensional simulations that are the subject of the paper begin with methyl-ammonium dipoles randomly orientated, and after picoseconds of evolution the dipoles would arrange themselves in an ordered way that depended both on temperature and the electric field present in the cell.

In a video published by the American Chemical Society, Dr. Henry Snaith of Oxford University, who in 2012 contributed to the advancements in solar cell technology that made it possible to achieve perovskite solar cell efficiencies of greater than 10%, explained why perovskite materials will play a key role in the future of solar cells:

"We can really class photovoltaics into two classes. One, based on very pure but expensive materials that are extremely efficient, and one that is based on more amorphous materials that are less efficient but fundamentally cheaper. Historically there has been this divide in that materials that are cheap and easy to process have really had fundamental efficiency limits that made them uncompetitive in performance with the best materials. Very recently over the last year or two, the emergence of organometal halide perovskites has occurred and this has really been a paradigm shift because these materials are extremely inexpensive, they are processed by many means through low cost processing and they promise to reach the highest efficiencies. This really is going to enable a new era in photovoltaics research and eventually deployment of extremely inexpensive solar cells."

Most solar cells are silicon based, making them expensive and troublesome to work with. A cheaper alternative is a dye sensitized cell, but that technology has not seen large increases in efficiencies for decades and still remains at around 12%. Understanding the behavior of perovskite cells so that these cheaper materials, which may soon come to match the efficiencies of the expensive silicon based cells, can have their efficiencies accurately characterized is an important goal considering the technology's promise for high efficiency and the brisk pace of its development.

Previously TiO_2 was used as a conducting electrode in perovskite cells, and one of the reasons for the progress that occurred in 2012 was the realization that the TiO_2 surface was the limiting factor for perovskite cell efficiency. The surface itself would be a combination of titanium cations and hydroxide groups that could trap charge carriers, reducing the efficiency. However, after the realization that perovskite materials did not actually require the TiO_2 electrode, because methyl-ammonium lead iodide is a good conductor of charge carriers in its own right, the electrode could be removed and this improved the efficiency of perovskite cells. With this development came the discovery that the current-voltage behavior was hysterical and multiple causes were proposed including the movement of ions and polarization effects.

Walsh had this to say about their simulation:

"The problem… is you can't go to beyond about 50 picoseconds of time because it gets too computationally expensive to do these calculations. The two dimensional simulation that was in that paper was a Monte Carlo simulator, and so there, rather than trying to explicitly follow the kinetics, you take a step back and actually just construct the Lagrangian of the entire system and it's well defined to move around in the configuration space to find the equilibrium configuration. What you have in terms of simulation time isn't really linkable back to the real time. It's a different way of sampling the statistical mechanics ensemble, formally."

In their simulations, they allowed each dipole to rotate without frustration. Each dipole would interact with their neighbors up to 3 units away, and each dipole would interact with the applied field. What they found was that at finite temperature the dipoles would not be completely ordered nor completely disordered, but still a domain structure would appear that became more disordered as temperature increased and very ordered at the lowest temperatures. During the interview with Dr. Walsh and Dr. Frost, Frost spoke of the interaction of the dipoles with the electric field:

"When you apply an electric field across a material essentially what you're getting is the dielectric response, so the material polarizes in a way that's trying to counter the electric field. If you applied an extremely strong field what you would get is all of the dipoles pointing in a way that would oppose the field. But what's interesting in this case is the actual field present in a solar cell is quite small so it's not strong enough to fully align all the dipoles so to the eye it still looks quite disordered… but when you apply a more sophisticated analysis you see that there has been a change. And we think that change is significant enough to effect the solar cell performance."

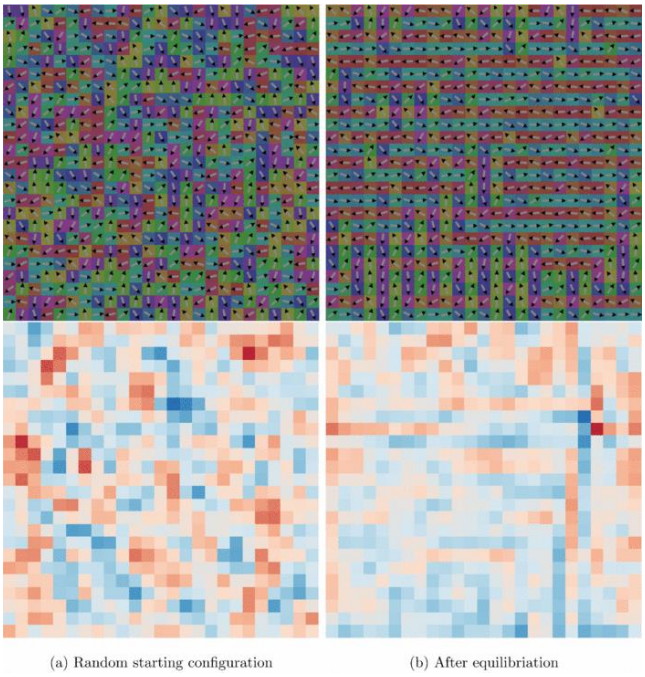

Figure 2: (Top) Orientation of dipoles. Left is initial random orientation of dipoles and the right side depicts the equilibrium configuration at 300K. (Bottom) Electrostatic potential.

Since their publication, they have made their simulation fully three dimensional, including a strain term that introduces complicated phase behavior as the strain fights the dipoles as they try to align themselves against the field. So far, their simulations have modelled the morphology of the material, but they hope that in the future they can simulate charge carriers interacting with the perovskite material to see how the charge carriers interact with the dipoles. Though Dr. Walsh believes it will be difficult to verify experimentally all the sources of the observed hysteresis, Walsh and other scientists are continuing to pursue an accurate model of hybrid perovskite solar cells so that one day we may understand the current-voltage behavior and general inner workings of this rapidly developing renewable energy technology.