

composite) as determined by the Brunauer-Emmett-Teller (BET) method. The Hall measurement indicated a slight decrease in carrier concentration from $1.91 \times 10^{19} \text{ cm}^{-3}$ (bare MoS_2) to $1.86 \times 10^{19} \text{ cm}^{-3}$ ($\text{MoS}_2/\text{NiCo-LDH}$ composite). The slight decrease in carrier concentration (or electrical conductivity) here does not compromise the contribution from the increased specific surface area. Finally, the composite electrocatalyst showed significantly enhanced electrocatalytic activity for HER in alkaline solutions compared to that for each of the simple components alone. Using the standard three-electrode method, the authors reported an overpotential as low as 78 mV versus RHE for achieving a catalytic current density of $j = -10 \text{ mAcm}^{-2}$, which was 126 mV and 322 mV lower than that of bare MoS_2 and NiCo-LDH catalysts, respectively. This catalytic performance is among the best seen for the most active HER catalysts in alkaline conditions.⁵

Furthermore, the intrinsic mechanism leading to this significant improvement was investigated. The authors showed that the very small difference in electrochemical surface area (ECSA) of different samples cannot be respon-

sible for the remarkable enhancement of catalytic performance seen in the $\text{MoS}_2/\text{NiCo-LDH}$ composite. The significantly smaller Tafel slope of $\text{MoS}_2/\text{NiCo-LDH}$ composite (76.6 mV/dec) than that of MoS_2 (95.7 mV/dec) indicated superior HER kinetics. Using electrochemical impedance spectroscopy (EIS), the authors showed that the $\text{MoS}_2/\text{NiCo-LDH}$ composite exhibited a much lower charge transfer resistance (R_{ct}) than that of the bare MoS_2 , confirming a faster charge transfer process in HER. Further, the authors found that the turnover frequencies (TOF) calculated for $\text{MoS}_2/\text{NiCo-LDH}$ is $\sim 2.4 \text{ H}_2$ molecules/s, which is at least 10 times larger than that of the bare MoS_2 , demonstrating well-optimized catalyst-intermediate energetics via the introduction of the $\text{MoS}_2/\text{NiCo-LDH}$ interface.³ In addition, chronopotentiometric measurement in combination with structural analyses after HER process demonstrated excellent long-term stability. Hu and coworkers have also synthesized other hybrid catalyst systems, including the $\text{MoS}_2/\text{NiFe-LDH}$ and $\text{MoS}_2/\text{CoFe-LDH}$ composites, which also showed much higher activities for HER catalysis than bare MoS_2 and the respective LDH in alkaline solutions. These results not

only provide a highly active, inexpensive, and robust catalyst for HER catalysis in alkaline solutions, but also demonstrate that this strategy for composite electrocatalysts has great potentials for renewable energy conversion systems.

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Preview

Perovskite Precursors Get a pH Tune-Up

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The role of solvent pH has been an unexplored lever in the formation of high-performance metal halide perovskite films. In this issue of *Joule*, Noel and coworkers have demonstrated that systematic control over the pH of perovskite precursor solvents can dissolve large colloids, enabling films with reduced defects. Using this method, a perovskite solar cell with a record low open-circuit voltage deficit of 360 mV has been achieved.

In the field of solution-based materials, it is statistically unlikely that a pure solvent is perfectly optimized for a given precursor system. “Additive engineering” is a long-studied approach to improve the quality of materials by incorporating various acids, bases, catalysts, salts, other solvents entirely, and/or other seemingly magical ingredients into the precursor

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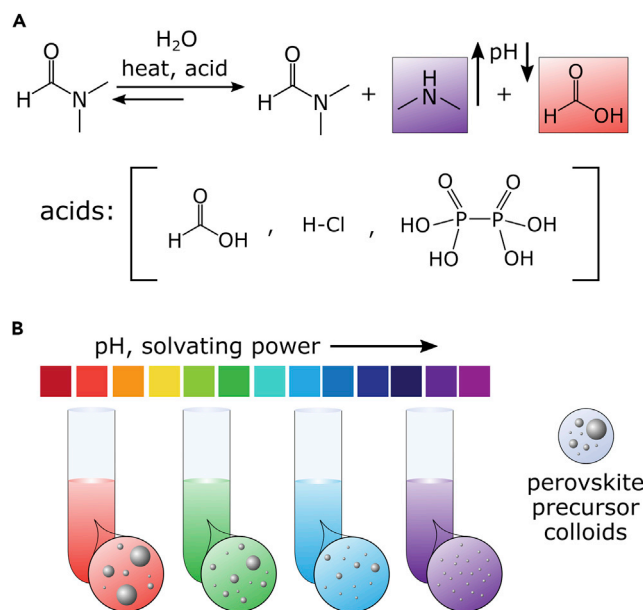


Figure 1. Perovskite Precursor Colloid Dissolution with pH Control

(A) Temperature and acid-catalyzed hydrolysis of DMF leads to increased solvent alkalinity, despite presence of acid additive.

(B) Increased solvent alkalinity increases the solvating power of DMF, enabling the dissolution of large colloids and reduced colloid size distribution.

solution. Metal halide perovskites, a class of high-efficiency solar-harvesting materials,¹ have benefitted greatly from additive engineering, often showing improved material morphology, optoelectronic properties, and efficiency in photovoltaic cells. However, due to the complex nature of the additive-solvent-precursor chemistry space, it is often difficult to gain an understanding of the fundamental role of the additive. Additionally—as perovskite researchers are deeply aware of—blind recipe-following is usually a quick way to make a poor-performance solar cell. Therefore, it is increasingly imperative that new processing methods should not only demonstrate reproducible benefit, but further illuminate an important insight into the fabrication process that can be further adapted, optimized, and replicated in diverse environments. A new study by Noel and coworkers published in the second issue of *Joule* has explained the ostensibly universal role of solvent heating and acid additives in perovskite precursor solutions. Through this new understanding, a systematic method to

form perovskite films with improved optoelectronic properties was demonstrated, leading to a stabilized 19.9% efficient perovskite solar cell with a record-low open-circuit voltage (V_{OC}) deficit of 360 mV.²

Dimethylformamide (DMF) is a strong polar, aprotic solvent and a weak acid (pH of 6.3) used to solvate perovskite precursors. Upon addition of various acids, such as hydroiodic acid, hypophosphoric acid, and others, it has routinely been demonstrated that perovskite thin films with improved properties can be formed.^{3–5} The exact recipes and methods that lead to optimized films and devices vary from report to report, and further, the exact role of the additive remains debatable. The authors of this work aimed to address this by examining the specific role of pH in common perovskite precursor solutions.

It is known that DMF can be hydrolyzed to form dimethylamine (DMA, a weak base) and formic acid (FAH, a weak acid). Upon controlled heating of the

DMF, the hydrolysis is further catalyzed and an increase in the solution pH is observed. This indicates that DMA is a stronger base than FAH is an acid. If an acid additive is introduced to the DMF, as expected, the pH of the solution decreases. However, upon heating the acidified DMF, the pH is shown to increase with higher acid concentrations. While this may seem counterintuitive, it can be explained by the acid-catalyzed dissociation of DMF (Figure 1A). Therefore, by combining acid additives and controlled heating, the pH of DMF can be carefully controlled. The process is irreversible upon cooling of the solution, enabling perovskite film deposition with hydrolyzed DMF at room temperature.

The authors sought to study the effects of solvent pH on perovskite precursor solutions. These solutions are known to contain colloidal suspensions of the precursor salts with large size distributions, up to and greater than 1 micron diameter.⁶ Hydrolyzed DMF is shown to radically reduce the size of these colloids, and this is attributed to increased solvating strength (Figure 1B). This is an interesting discovery—that partially decomposed DMF can have close to the ideal balance of acids and bases for effective perovskite precursor solvation. Much of the benefits seen from solvent heating and additives in perovskite films and devices can thus be attributed to improved solvating strength leading to reduced colloid sizes of the precursor salts. This has a multifaceted effect. It can enable improved thin-film morphology when using slow-crystallization methods. It can further reduce trap state density in fast-crystallization methods, as these large colloids can create undesirable interface defects. Both benefits have been shown to enable improved perovskite solar cell performance in this work.

V_{OC} deficit is an important quantity in solar cells. It is a measure of the

difference in material bandgap (divided by the electronic charge constant) and open-circuit voltage in the cell. Solar cells with carefully engineered contacts and efficient radiative recombination can achieve small V_{OC} deficits, leading to cell output voltages close to the thermodynamic Shockley-Queisser (SQ) limit.⁷ For perovskites with a bandgap of ~ 1.55 eV, the radiative V_{OC} deficit limit is ~ 280 mV.⁸ Careful control over the solvent strength can reduce defect states associated with large precursor colloids, enabling a smoother energy landscape and improved V_{OC} . Through careful pH control, Noel and colleagues show a mixed $FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3$ perovskite solar cell with a stabilized efficiency of 19.9% and a V_{OC} of 1.21 V. For a material with a 1.57 eV bandgap, this leads to a V_{OC} deficit of 360 mV, a full 30 mV lower than the previously best-reported value for perovskite solar cells⁹ and only 80 mV shy of the SQ limit for this bandgap.

This is an important result for perovskite solar cells as it not only pushes V_{OC} closer to the radiative limit, it highlights the importance of precursor solvating power in forming defect-minimized films. With the near-optimal V_{OC} reported in this work, the focus now lies in increasing short-circuit current (SQ limit of ~ 25 mA/cm²)⁸ and fill-factor (SQ limit of ~ 0.90)⁸—and doing so without compromising V_{OC} . This can be achieved through optimized contact and extraction layers, and by employing photonic optimizations to maximize light absorption. Careful and quantitative control over the precursor solution pH should be an important point of consideration as perovskite photovoltaic researchers continue to strive toward the elusive $>25\%$ power conversion efficiencies set by crystalline silicon.¹⁰

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Preview

Pseudo-solid State Batteries See the Light

Rahul Malik^{1,*}

Dunn and colleagues design and synthesize a thin film pseudo-solid state electrolyte for next-generation lithium batteries based on solution-processed ionogels. They first demonstrate 125 mAh/g capacity for 150 cycles with minimal capacity loss in lithium iron phosphate and lithium metal full cell devices at C/2 rate. Next, they demonstrate the ability to photo-pattern the ionogel, and thus enable versatile and scalable fabrication and processing routes, while also retaining similar excellent electrochemical performance.

In the human struggle to address climate change while also meeting anticipated increases in energy demand associated with rising world living standards and population, prominent voices have singled out advances in en-

ergy storage, specifically battery technology, as necessary.^{1,2} Lithium ion (Li-ion) batteries are the current gold standard for energy storage—today they power billions of mobile electronic devices, and in the projected near

future they are expected to replace gasoline in vehicular transport, even without subsidy.³ While the decrease in energy storage cost (evaluated in \$/kWh) associated with Li-ion has actually outpaced expectations following an accelerated learning curve,⁴ we are still fast approaching fundamental electrochemical performance limits in terms of energy density that can be achieved with canonical Li-ion battery chemistries and cell architecture.⁵ In recent years, this has motivated a substantial research push in so-called “post Li-ion” technologies, which look to novel chemistries or cell designs (or both).⁶

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