

## **Perspective**

# Solar Charging Batteries: Advances, Challenges, and Opportunities

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Energy for a sustainable future motivates today's R&D, enabling technologies such as smart consumer electronics, electric vehicles, and smart grids. These technologies demand the use of batteries. Sunlight, an abundant clean source of energy, can alleviate the energy limits of batteries, while batteries can address photovoltaic intermittency. This perspective paper focuses on advancing concepts in PV-battery system design while providing critical discussion, review, and prospect. Reports on discrete and integrated PV-battery designs are discussed. Three key technical challenges, namely energy density, efficiency, and stability, toward further advancement of integrated PV-battery systems are discussed. We present a perspective on opportunities and future directions, highlighting key strategies on developing such PV-battery systems. Key focus should be on the development of innovative designs that incorporates high-capacity, efficient, and stable materials, emphasizing the demonstration of practical viability of such integrated PV-battery systems.

### **Drive for New Technologies for a Sustainable Future**

Today's mass consumers heavily rely on energy technologies and their ongoing development. Three key technologies that encompass the present energy scenario are smart consumer electronics, electric vehicles, and smart grids. Smart electronics depend on capacity-limited batteries, making recharging a necessity. Continuing advancement in consumer electronics demands additional battery power. With the mobility delivered to users by modern technology, frequent recharging of the electronics using a wired connection seems inhibiting. Solar or photovoltaics (PV) provide the convenience for battery charging, owing to the high available power density of 100 mW cm<sup>-2</sup> in sunlight outdoors.

Sustainable, clean energy has driven the development of advanced technologies such as battery-based electric vehicles, renewables, and smart grids. Electric vehicles currently represent a thriving market. Although electric vehicles do not produce carbon emissions, users charge the vehicles using, typically, fossil-fuel-generated grid electricity. Unless the vehicle is charged with electricity generated by renewable resources, electric vehicles for sustainability hold less significance. Additionally, the inflexibility of charging stations challenges the large-scale practical applications of battery-based electric vehicles. Distributed generation such as PV is most suitable among renewables for electric vehicle charging. Using PV will help mass consumers to embrace electric vehicles.

The other prospect is the electric grid. Renewable energy is steadily expanding. Sunlight is arguably the most abundant source to provide clean energy. The biggest concerns in using PV are lack of sunlight at night and intermittent availability during daytime due to cloud cover. This intermittency results in fluctuations in power output, a critical concern for grid applications. Therefore, electric utilities have

#### **Context & Scale**

Today's world is energy driven and batteries have become an integral part as an energy source considering the technological advances in consumer electronics to electric vehicles, renewables. and smart grids. Batteries are energy limited and require recharging. Recharging batteries with solar energy by means of solar cells can offer a convenient option for smart consumer electronics. Meanwhile, batteries can be used to address the intermittency concern of photovoltaics.

This perspective discusses the advances in battery charging using solar energy. Conventional design of solar charging batteries involves the use of batteries and solar modules as two separate units connected by electric wires. Advanced design involves the integration of in situ battery storage in solar modules, thus offering compactness and fewer packaging requirements with the potential to become less costly. This advancement can be advantageous for consumer electronics where space, size, and packaging requirements hold greater value. Three major metrics, namely energy density, efficiency, and stability, have been addressed by presenting relevant challenges and potential opportunities. The integrated





imposed ramp-rate limitations for PV power integration into the grid.<sup>2</sup> This vastly underutilizes the PV power. Batteries can be a solution to these issues. Batteries can be charged during the day and discharged at night, and can also provide support during intermittency and help meet the desired ramp rates of PV power integration into the grid.

#### **Traditional versus Advanced PV-Battery Systems**

The traditional battery-charging method using PV is a discrete or isolated design (Figure 1A) that involves operation of PV and battery as two independent units electrically connected by electric wires. Such systems tend to be expensive, bulky, and inflexible, require more space and packaging requirements, and undergo energy loss through external wires. Combining energy generation and energy storage into a single unit creates an integrated design. The integrated design of PV and battery will serve as an energy-sufficient source that solves the energy storage concern of solar cells and the energy density concern of batteries.

It is evident that the inclination toward volume minimization has been monumental in enabling today's transformative technologies. One approach to achieve the volume minimization is multi-functionalization, which involves executing two or more functions by a single integrated device. This trend drives today's smart consumer electronics. The same notion applies to the integrated PV-battery systems.

The integrated PV-battery design offers a compact and energy-efficient version of the PV-battery systems. The flexibility the design offers with fewer required wirings and packaging requirements, while the smaller footprint is significant especially for small-scale consumer electronics. This design potentially reduces the balance-of-system cost and increases the practicality of PV systems. Despite the merits of the integrated approach, major challenges of low efficiency, capacity, and stability exist, which should be addressed to make this approach a commercial reality. The research is still in early stages and significant advances, which focus on material and device designs, will be required to surmount these challenges.

Integrated PV-battery systems can be realized in two different configurations: (1) three-electrode (Figures 1B and 1C) and (2) two-electrode (Figure 1D). In the three-electrode configuration, one electrode is employed as a common electrode as cathode or anode between the PV device and battery. In the two-electrode configuration, the positive electrode performs function of photoconversion as well as storage. This perspective provides key insights and recent developments in these approaches.

## **Advances in Discrete PV-Battery Design**

The dominant silicon PV technology has been employed for battery charging. In 2010, a single 190-W Sanyo HIP-190BA3 PV module was used to directly charge a lithium-ion battery (LIB) module consisting of series strings of LiFePO<sub>4</sub> cells (2.3 Ah each) from A123 Systems with no intervening electronics. This test was carried out as a proof of concept for the solar charging of battery electric vehicles. A 15-cell LIB module charging obtained an overall efficiency of 14.5% by combining a 15% PV efficiency and a nearly 100% electrical to battery charge efficiency. This high efficiency was attributed to matching the maximum power point of the PV module with the battery's charging voltage. Use of triple-junction solar cell with stacks of thin-film silicon solar cells (a-Si:H/a-Si:H/ $\mu$ c-Si:H) to charge an Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiFePO<sub>4</sub> LIB was investigated by Agbo et al. The triple-junction solar cell had a short-circuit current density ( $J_{SC}$ ) of 2.0 mA cm<sup>-2</sup> and open-circuit voltage ( $V_{OC}$ ) of 2.09 V under

design is still in the early R&D phase. There is a need for innovative designs that explore high-capacity, efficient, and stable materials. Meanwhile, to demonstrate its practical viability, this integrated design should also focus on real-world applications such as wearables that demand specific requirements of energy and power.

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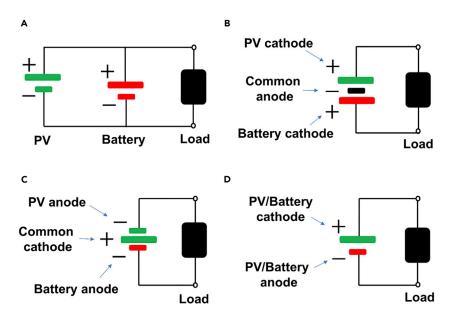


Figure 1. Circuit Representation of PV-Battery Systems

(A) Conventional discrete charging.

(B–D) Integrated charging. (B) Three-electrode configuration with common anode; (C) three-electrode configuration with common cathode; (D) two-electrode configuration.

attenuated illumination of  $37.4 \,\mathrm{mW \, cm^{-2}}$ , which matched the battery characteristics. The solar to battery charging efficiency was 8.5%, which was nearly the same as the solar cell efficiency, leading to potential loss-free energy transfer to the battery.

Emerging perovskite PV technology has also been investigated for battery charging.  $^{5-8}$  In 2015, four series-connected perovskite solar cells (PSCs) were employed to charge an LiFePO<sub>4</sub>/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> LIB (Figure 2A)<sup>9</sup> that provided required charging voltage with  $V_{\rm OC}$  of 3.84 V at an efficiency of 12.65%. Overall system efficiency of 7.36% at 0.5C (Figure 2B) was achieved with storage efficiency of ~60%. Our group performed a similar study using a single PSC with inline low-power DC-DC boost converter and maximum power point tracking (MPPT) to charge an LiCoO<sub>2</sub>/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> LIB<sup>10</sup> (Figure 2C). The DC-DC converter boosted the low voltage of the single junction solar cell to the required charging voltage of the 2.4-V LIB. The MPPT in the converter tracked the maximum power of the PV cell. This approach led to a high overall efficiency of 9.36% (average 8.52%) (Figure 2D) and storage efficiency of ~77.2% at 0.5C discharge. The battery charging occurred within ~6% of the actual MPP. In the same study, single dye-sensitized solar cell (DSSC) charging was demonstrated with an overall efficiency of 5.62% (Figure 2D).

#### **Advances in Integrated PV-Battery Designs**

Most reports on integrated designs focused on use of PV for capacitive energy storage <sup>11–24</sup> rather than battery storage. <sup>23,24</sup> The integrated PV-battery systems have been realized with three types of designs: (1) direct integration, (2) photoassisted integration, and (3) redox flow battery integration. Direct integration involves stacking of the solar cell and battery together (excluding redox flow batteries) that can operate autonomously. Photoassisted integration uses photocharging to partially charge the battery. Redox flow integration involves use of a redox flow battery with photocharging. Reports on these designs are discussed in the following sections.



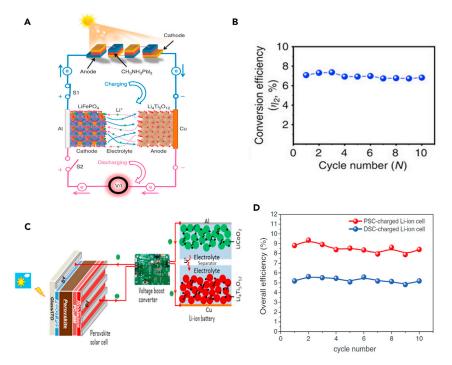


Figure 2. Discrete PV-Battery Systems

(A and B) Four perovskite solar cells charging an  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiFePO}_4$  LiB. (A) Schematic. (B) Overall efficiency versus cycle number. Reproduced from Xu et al., with permission from Springer Nature. (C and D) Single-junction perovskite solar cell charging an  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LiCoO}_2$  LiB using a DC-DC converter. (C) Charging schematic. (D) Overall efficiency versus cycle number. Reproduced from Gurung et al., with permission from John Wiley and Sons.

#### Direct Integration

A monolithically integrated design with crystalline Si cells and LIB (Figure 3A), enabled by use of an aluminum metal electrode of the PV module as current collector for the LIB, was reported by Um et al.<sup>25</sup> The device consisted of 25 units of Si solar cells connected in series and a solid-state LIB with a bipolar cell configuration fabricated using a UV curing-assisted printing process. The device demonstrated a high overall efficiency of 7.61% (Figure 3B) with a 15.8% efficient Si solar module. They demonstrated charging of portables such as smartphones and MP3 players using the integrated device, which displays significant steps toward practicality of the PV-battery integrated systems.

Wang et al. reported a series-connected tandem DSSC on top of titanium foil with LIB on the other side with the use of titanium dioxide nanotubes.  $^{27}$  The integrated power pack was charged from 0.55 to 2.996 V in 440 s. The device showed a capacity of 33.89  $\mu\text{Ah}$  with a low overall efficiency of  $\sim\!0.82\%$  and storage efficiency of 41%. Zhou et al. reported an approach with integration of Pt-modified CdS photocatalyst into a hybrid lithium-sulfur (Li-S) battery.  $^{28}$  A specific capacity of 792 mAh g $^{-1}$  was achieved during the 2-hr photocharging process. The device demonstrated a discharge capacity of 288 mAh g $^{-1}$  upon exposure to sunlight for 2 hr, revealing the practical feasibility of the design. However, one requirement for this type of design is the cathode must be directly oxidized by photoexcited holes in the photoelectrode. This limits the scalability of this design because most of the cathode materials for conventional LIBs are insulating and insoluble in organic/aqueous electrolytes.  $^{29}$ 



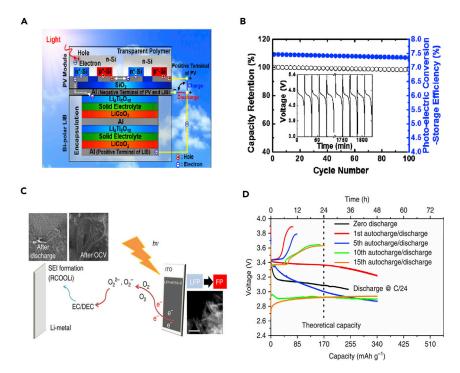


Figure 3. Direct Integration Approach of PV-Battery System

(A and B) Three-electrode design of silicon solar cell charging bipolar Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/LiCoO<sub>2</sub> LIB. (A) Schematic. (B) Photo-charge/galvanostatic discharge cycling performance. Reproduced from Um et al.,<sup>25</sup> with permission from the Royal Society of Chemistry. (C and D) Two-electrode design involving photo-oxidation of lithium iron phosphate (LiFePO<sub>4</sub>) nanocrystals in the presence of dye as hybrid cathode and lithium metal as anode. (C) Photocharging process. Scale bar of TEM image is 200 nm. (D) Charge/discharge voltage profiles. Reproduced from Paolella et al.,<sup>26</sup> with permission from Springer Nature.

Recently, a two-electrode photorechargeable LIB was demonstrated that was enabled by direct photo-oxidation of LiFePO $_4$  nanocrystals in the presence of dye as hybrid cathode and lithium metal as anode (Figure 3C). Dye-generated holes enabled delithiation of LiFePO $_4$  to form FePO $_4$ . Electrons enabled reduction of oxygen-forming peroxide and/or superoxide that react with carbonate-based electrolyte to form a solid electrolyte interphase (SEI) layer as in an Li-O $_2$  battery. The overall efficiency of the system was 0.06%–0.08%. It is interesting to note that the photocharged battery was kept illuminated during discharge, demonstrating a discharge capacity of 340 mAh g $^{-1}$  (Figure 3D), while discharge in the dark resulted in a capacity below 40 mAh g $^{-1}$ . Surface area of LiFePO $_4$  nanocrystals was found to be a dominant factor facilitating the delithiation process. Furthermore, the photo-oxidation only worked in the presence of oxygen. The design requires interfacial engineering of the LiFePO $_4$ /dye photocathode to reduce charge recombination losses and improve the efficiency.

## Photoassisted Integration

In this integration approach, the PV cell is integrated with battery storage to assist the battery-charging process. The primary objective of the photoassisted charging is to reduce high charging voltage of the battery and consequently the overpotential loss.

This photoassisted charging was employed in a lithium-air battery by integrating a dye-sensitized  $TiO_2$  photoelectrode with oxygen electrode via linkage of

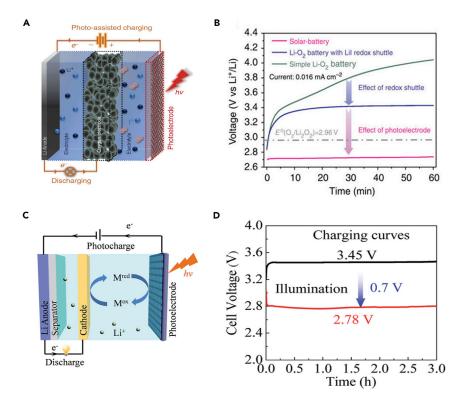


Figure 4. Photoassisted Charging Approaches

(A and B) Integration of dye-sensitized  $TiO_2$  photoelectrode with oxygen electrode of Li-oxygen battery. (A) Schematic. (B) Charging curves. Reproduced from Yu et al., <sup>30</sup> with permission from Springer Nature.

(C and D) Integration of  $TiO_2$  photoelectrode with iodide (I<sup>-</sup>) ion redox shuttle in Li/LiFePO<sub>4</sub> LIB. (C) Schematic. (D) Photo-charging and discharging curves. Reproduced from Li et al.,<sup>29</sup> with permission from the Royal Society of Chemistry.

tri-iodide/iodide redox shuttle <sup>30</sup> (Figure 4A). Under illumination, the photoelectrode generated tri-iodide ions that subsequently diffused to the oxygen electrode to oxidize  $\text{Li}_2\text{O}_2$ . The charging voltage was reduced from 3.6 to 2.7 V (Figure 4B). However, the cell exhibited voltage instability with cycling. Another work on photoassisted charging reported use of a  $\text{TiO}_2$  photoelectrode coupled with an iodide (I<sup>-</sup>) ion redox shuttle in an Li/LiFePO<sub>4</sub> LIB (Figure 4C). <sup>29</sup> The photovoltage reduced cell charging voltage to 2.78 V (Figure 4D), which was lower than the discharge voltage of 3.41 V, leading to an energy saving of ~20%. Similar work was reported with integration of dye-sensitized photoelectrode in an LiI redox flow battery via linkage of an  $\text{I}_3$ <sup>-</sup>/I<sup>-</sup>-based catholyte. <sup>31</sup> The charging voltage was reduced from 3.6 to 2.9 V. This translated to an energy saving of ~20% compared with conventional Li-I batteries typically charged at higher voltage of 3.6 V. However, these photoassisted integrated systems still require an external charging source to fully charge the battery, which does not make them an energy self-sufficient integrated design.

## Redox Flow Battery Integration

Redox flow batteries have gained attention owing to their flexibility, scalability, high lifetime, low operating costs, and potential to store energy in large amounts. 32-34 These attributes make redox flow batteries competitive with lithium-ion technology for large-scale grid storage. A typical redox flow battery consists of two compartments of redox electrolytes separated by a membrane and can be fed by pumping electrolyte through the cathode (catholyte) and anode (anolyte) stored externally.

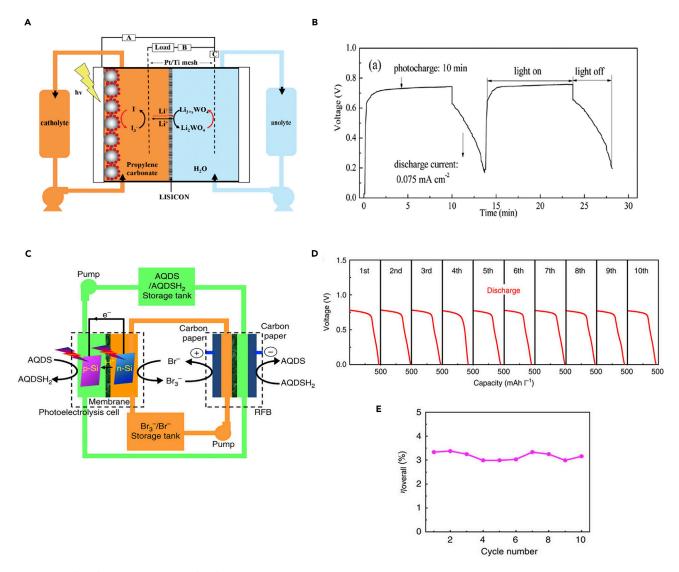


Figure 5. Redox Flow Battery Integrated with PV

(A and B) Solar rechargeable redox flow batteries based on  $\text{Li}_2\text{WO}_4/\text{Lil}$  couples in dual-phase electrolytes. (A) Schematic. (B) Photo-charge and galvanostatic discharge voltage profiles. Reproduced from Yan et al.,  $^{36}$  with permission from the Royal Society of Chemistry. (C–E) Integration of dual-silicon photoelectrochemical cell and quinone/bromine redox flow battery. (C) Schematic. (D) Galvanostatic discharge curves. (E) Overall efficiency as function of cycle number. Reproduced from Liao et al.,  $^{37}$  with permission from Springer Nature.

Energy is stored in the form of Nernst potential shift of redox couples of the catholyte/cathode and anolyte/anode.

The tri-iodide/iodide redox couple is the most commonly studied catholyte in solar redox flow batteries. Liu et al. used  $TiO_2$ -DSSC for charging a redox flow battery with two redox couples ( $I_3^-/I^-$  and DMFc $^+$ /DMFc in organic solvents) and demonstrated an overall efficiency of 0.05% with 0.15% photoconversion efficiency of DSSC. The large DSSC area and thick inorganic separator led to large internal resistance and, thus, low efficiency. Gao et al. investigated a solar rechargeable redox flow battery based on  $Li_2WO_4/Lil$  redox couples in dual-phase electrolyte, dye-sensitized  $TiO_2$  as photoanode, soluble  $Li_2WO_4$  as anode-active species in aqueous electrolyte, Lil as cathode-active species in organic electrolyte, and lithium superionic conductor glass ceramic as separation membrane (Figure 5A). A discharge capacity of

0.0195 mAh mL<sup>-1</sup> at a current density of 0.075 mA cm<sup>-2</sup> was demonstrated (Figure 5B). This use of aqueous-compatible redox couple has an advantage of higher working voltage and low fabrication cost, and is environmentally benign. However, these solar rechargeable iodine-based redox batteries have limitations such as low energy storage capacity, insufficient light absorption, and corrosive iodine-based catholyte. This situation demands further advancements.

As an alternative, solar rechargeable vanadium redox flow batteries were demonstrated by integrating  ${\rm TiO_2}^{38}$  and  ${\rm 1D\text{-}TiO_2}$  nanobelts $^{39}$  as photoelectrode into all-vanadium two redox couples of  ${\rm VO_2}^+/{\rm VO^{2+}}$  and  ${\rm V^{3+}/V^{2+}}$  separated by a Nafion membrane. Use of  ${\rm TiO_2}$  with a large bandgap limited light absorption. This was followed by another study by Liu et al. with WO<sub>3</sub> decorated  ${\rm TiO_2}^{40}$  to enhance the light absorption of the photoelectrode and promote extra energy storage. However, use of acidic media for the vanadium redox couples limits the selection of a wide range of light absorbing materials. Alternatively, a lower-bandgap polyaniline polymer deposited hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) as photoelectrode was studied in combination with redox couple aqueous solution of ferrocyanide/anthraquinone-2,7-disulfonate in NaOH to enhance photovoltage.  $^{41}$ 

Low-bandgap semiconductors such as Si and GaAs are the most suitable candidates for efficient light harvesting. Recently a solar rechargeable flow cell was developed based on a dual-silicon photoelectrochemical cell and a quinone/bromine redox flow battery (Figures 5C and 5D).<sup>37</sup> This device showed an overall efficiency of 3.2% (Figure 5E) that outperforms other reported solar rechargeable flow cells. The use of narrow-bandgap silicon for efficient photon collection and fast redox couples for efficient charge transfer at the interface were responsible for the high efficiency. The device could be photocharged to 0.8 V demonstrating a discharge capacity of 730 mAh  $L^{-1}$ . Another work using silicon solar cells with a tandem design of redox flow battery was demonstrated with a 9,10-anthraquinone-2,7-disulfonic acid (AQDS)/1,2-benzoquinone-3,5-disulfonic acid (BQDS) redox couple.<sup>42</sup> Although the overall efficiency was 1.7%, the design exhibited a high capacity at 3,500 mAh L<sup>-1</sup>. These solar rechargeable redox flow battery systems are restricted by a narrow voltage window, limiting their energy density. Therefore, novel redox couples with a wider voltage window and stable photoelectrodes need to be explored.

#### **Technical Challenges and Opportunities**

Capacity (or energy density), overall efficiency, and stability are three key performance metrics that determine the advancement of integrated PV-battery technology while considering the cost.

#### Capacity or Energy Density

One of the major challenges for the integrated PV-battery system is the capacity or energy density. LIBs are traditionally packed in a "jelly roll" architecture whereby anode and cathode are stacked together, rolled with a polymeric separator, and encapsulated within metal lamination. This architecture provides batteries with a high capacity (mAh) and energy density (Wh L<sup>-1</sup>). The same architecture is not practically feasible with the PV-battery integrated system. The practical design of a directly integrated system would be a planar architecture with layers of battery anode, separator, and cathode stacked together on top of a PV module. This design would be capacity limited by the surface area of the PV. However, a bipolar design of the battery as demonstrated in a silicon PV/LIB system<sup>25</sup> can be used for higher areal energy density. Detailed engineering of such designs that addresses available PV

surface area, possible numbers of stacks of batteries, and power matching is required. This will be application dependent and need to consider different power and energy requirements for each application.

Use of materials with high specific capacity is one of the solutions. Silicon-NMC batteries have the capability to deliver energy density of 400 Wh kg<sup>-1</sup>. <sup>44</sup> Silicon is also the dominant PV material. For the integrated PV-battery cell, the ideal system would be the two-electrode design wherein the same silicon PV electrode can function as the battery electrode. Silicon solar cells require high-quality silicon crystals for efficient PV performance. However, it is evident that lithiation of silicon leads to its amorphousization. Silicon can be tolerant to a certain concentration range of Li<sup>+</sup>, but lithiation with a high Li<sup>+</sup> concentration would be required to obtain high energy density. Therefore, a detailed optimization study would be useful. Nevertheless, this problem can be partially solved by use of silicon in a three-electrode design wherein the silicon battery electrode is deposited on the metal contact of the silicon solar cell. The degradation of PV performance of the silicon solar cell due to lithiation can be prevented by barrier layers (Ti, W, or TiN) that prevent Li<sup>+</sup> diffusing into the silicon solar cell. <sup>45</sup> However, such barrier layers must be conductive in order to avoid resistive losses.

Another potential anode material is lithium metal, which can deliver a higher energy density at 500 Wh kg<sup>-1</sup> with NMC cathode.<sup>44</sup> Lately, research in lithium-metal batteries has been revived with several innovative designs focused on proper use of lithium metal.<sup>46,47</sup> Use of lithium metal as anode can be an efficient way to increase the energy density of the integrated system. Further, photoconversion material such as perovskites has already been demonstrated to have lithium-ion storing capability.<sup>48</sup> In addition, lithium doping of perovskites has been reported to have a positive effect on its PV performance.<sup>49</sup> This makes perovskite a suitable candidate as a high-capacity bifunctional material for the integrated PV-battery system.

For applications demanding higher bulk energy, a PV integrated redox flow battery system would be suitable if the volume and weight are not the issues. However, the redox flow battery has lower energy density in comparison with LIBs. This demands innovation in redox flow batteries that can achieve higher energy density. Such innovations may include a new redox species that has tunable redox potential, excellent redox kinetics, and suitable catholyte-photoelectrode combination with low interface charge recombination.

For smaller energy systems such as wearables, a flexible integrated PV-battery system will be required. <sup>50</sup> PSCs can offer the flexibility required for wearables. Also, a number of innovative designs have been demonstrated for flexible batteries, but with poor areal capacity in the range of 0.1–0.5 mAh cm<sup>-2</sup> due to low thickness of the active layers. <sup>43</sup> Relatively thick active layers and thinner metal current collectors and separators are needed to achieve high areal and volumetric energy densities for the flexible batteries. Another direction might be to explore the use of lithium-ion capacitors in the integrated PV-battery system that implements an anode of LIB and a cathode of supercapacitor. These lithium-ion capacitors are capable of exhibiting higher energy density of LIBs and higher power density of supercapacitors. <sup>51,52</sup>

#### Overall Efficiency

Overall efficiency demonstrated with lab-scale integrated PV-battery devices is only 7.61% for a three-electrode directly integrated system, 0.08% for a two-electrode directly integrated system, and 3.2% for a redox flow integrated system. These

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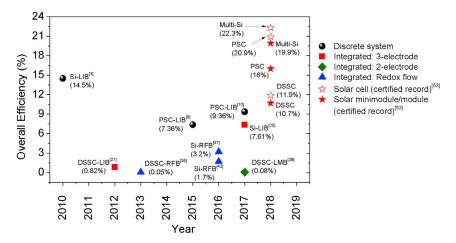


Figure 6. Progress of Solar Charging Batteries over the Years

Multi-Si, multi-crystalline silicon solar cell; DSSC, dye-sensitized solar cell; PSC, perovskite solar

cell; LIB, lithium-ion battery; RFB, redox flow battery; LMB, lithium-metal battery.

efficiencies are not sufficient to justify commercial viability of the integrated PV-battery system.

The overall efficiency of an integrated PV-battery system is a product of photoelectric conversion efficiency of PV and energy storage efficiency of the battery. The maximum overall efficiency is the photoelectric conversion efficiency of PV. As shown in Figure 6, the integrated systems are far from the possible record efficiencies of the solar module or cell.<sup>53</sup> It should be noted that photoconversion and storage components of the integrated systems are similar but not identical to a system with separate solar cell and battery. This modification in the integrated system does not mimic the maximum performance of separate solar cells or batteries. Furthermore, battery chemistries such as lithium ion need more than 3 V or higher to fully charge. This requires series-connected solar cells or a solar module, thus increasing the losses and lowering the PV efficiency to certain extent. This implies that high-efficiency solar cells should be employed. The mature and dominant Si solar cells would be an obvious choice. Alternatively, thin-film PV such as CIGS solar cells are also an option. PSCs that have already demonstrated to be superior to thin-film PV (at lab scale) can also be used. The other option is tandem solar cells, which offer higher efficiency.<sup>53</sup>

The other aspect of the integrated system is MPPT. PV panels are connected to power electronics units with charge controllers and inverters that are incorporated with maximum power tracking. The integrated PV-battery designs might not offer the flexibility of power tracking built into it. The scientific approach would be to properly match voltage and current between PV module and battery. For maximum overall efficiency, the integrated PV-battery cell needs to be operated at maximum power point of the PV cell. For this, the coupling factor between PV module and battery should be considered; that is, the ratio of measured PV power (when connected to the battery) to the maximum PV power. A high coupling factor approaching 1 indicates an efficient maximum power tracking. To achieve a high coupling factor, the PV  $V_{\rm OC}$  must be greater than the maximum battery voltage to ensure full charging and the PV MPP voltage should match the battery plateau voltage. In addition, the charging current should not affect the battery cycling stability.

Alternatively, an external MPPT or charge controller can be used that would offer a better and efficient control of the integrated system by facilitating maximum PV power tracking and battery overcharge/over-discharge protection. Furthermore, the power electronics can incorporate the blocking diode required to prevent battery discharge via the solar cell during non-illumination periods. However, for an integrated system without power electronics, a rectifying barrier layer needs to be incorporated at the PV-battery interface to function as a blocking diode. Besides, the use of power electronics can simplify the integrated PV-battery structure by providing a voltage step-up option. This would enable using a single solar cell rather than series-connected or tandem solar cells to charge a high-voltage battery.

Battery chemistry with energy storage efficiency as high as possible should be employed to achieve high overall efficiency. The storage efficiency depends on battery chemistry and is related to the types of battery electrodes and electrolyte. Storage efficiency is proportional to change taken in the reaction path by the battery between charge and discharge processes.

#### Stability

Stability is a concern for any new energy technology. The stability of an integrated PV-battery system mainly concerns photostability, electrochemical stability, and environmental stability. Selection of materials plays a significant role in determining stability. It should be noted that the integrated PV-battery system will benefit from the advances in stability that take place in PV and battery research individually.

Use of perovskites for integrated PV-battery systems will require significant advances in stability despite their high efficiency. Recently, extensive efforts have been geared toward enhancing stability of PSCs in response to moisture, heat, continuous illumination, and air. Results have been very encouraging. These advances can directly be incorporated into the integrated system. However, perovskites are at their early development stage and with all these efforts dedicated toward their stability, more breakthroughs are expected. For practical feasibility, the cells need to be demonstrated to withstand accelerated aging tests and follow the International Electrotechnical Commission performance PV standards to be competitive with silicon.

On the other hand, the use of volatile liquid electrolyte and corrosion-sensitive electrolytes and electrodes is another concern for the stability of the integrated PV-battery system. This can be eliminated by the incorporation of solid-state electrolytes for the directly integrated PV-battery systems. Solid-state LIBs are now being pursued for electric vehicles because they can mitigate the battery safety issues and provide lightweight design. <sup>57,58</sup> The integrated PV-battery systems based on redox flow are more susceptible to corrosion of photoelectrodes. Therefore, careful selection of materials focused on compatibility between redox couples and photoelectrodes is critical. The commonly used approach is the use of a photoanode to photoelectrochemically oxidize the catholyte where an n-type photoelectrode undergoes oxidative corrosion at the electrolyte interface by photogenerated minority carriers. The use of a photocathode that can photoelectrochemically reduce the anolyte does not undergo photocorrosive reduction and can lead to improved long-term stability. <sup>59</sup>

The other issue related to stability is the thermal response of the storage system concerning the direct heat generated by the solar part. This should be addressed by use of battery chemistries that are more tolerant to higher temperatures, for which solid electrolytes would be a suitable option.

#### **Future Directions and Outlook**

The integrated PV-battery system approach is still in the early research and development stage. Reports to date focus on the feasibility of innovative materials development and new device designs, and should continue in that direction. Novel designs that incorporate high-capacity, efficient, and stable materials should be emphasized. The integrated PV-battery designs can be further improved by focusing on the aforementioned strategies and opportunities such as use of bifunctional materials with energy harvesting as well as storage properties, use of highly specific capacity storage materials, incorporation of power electronics, maximum power tracking, use of lithium-ion capacitors, solid-state electrolytes, electrochemical compatibilities between electrodes and electrolytes, new redox species with tunable redox potential, and excellent redox kinetics.

The integrated PV-battery system could also benefit from simulation or modeling studies that can better predict these systems. Numerical modeling approaches in solar cells<sup>60–62</sup> and LIBs<sup>63–65</sup> can be combined to better identify limiting factors in the integrated system and provide solutions to better designs. Modeling would guide optimal experimental conditions concerning doping concentration of lithium ions lithiated without significantly affecting PV performance of the PV part and electrochemical cycling performance of the battery part. For example, for a silicon-based integrated cell the PV modeling would address effect of amorphousization of the silicon such as introduction of defect densities due to lithiation on PV performance, while the battery modeling would address the effect of the SEI layer and volume change of the silicon due to lithiation.

Besides this, future efforts should demonstrate the integrated system to meet real-world applications such as sensor networks, wearables, and electronics. These applications have specific requirements of average and peak power consumption, which would determine the type and dimensions of the integrated system to power the load efficiently. This would better demonstrate the practical viability of the intrinsically integrated PV-battery systems.

Commercialization of intrinsically integrated PV-battery systems is a long way from the present. However, the integrated system will benefit from and depend significantly on the individual advances in both the PV and battery areas. The initial focus should target low-power applications whereby compactness and minimum packaging requirements have more merit. Success in these low-power applications will open opportunities toward large-scale energy applications. Furthermore, economic aspects surrounding the transition from traditional isolated PV-battery systems to an advanced integrated system need to be addressed. This will be application dependent, with much bigger challenges for larger energy systems concerning energy capacity, system lifetime, and economics to justify the transition.

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#### REFERENCES

- Yang, Z., Zhang, J., Kintner-Meyer, M.C.W., Lu, X., Choi, D., Lemmon, J.P., and Liu, J. (2011). Electrochemical energy storage for Green grid. Chem. Rev. 111, 3577–3613.
- Marcos, J., Storkël, O., Marroyo, L., Garcia, M., and Lorenzo, E. (2014). Storage requirements for PV power ramp-rate control. Solar Energy 99, 28–35.
- Gibson, T.L., and Kelly, N.A. (2010). Solar photovoltaic charging of lithium-ion batteries. J. Power Sources 195, 3928–3932.
- 4. Agbo, S.N., Merdzhanova, T., Yu, S., Tempel, H., Kungl, H., Eichel, R.-A., Rau, U., and Astakhov, O. (2016). Development towards cell-to-cell monolithic integration of a thin-film solar cell and lithium-ion accumulator. J. Power Sources 327, 340–344.
- Green, M.A., Ho-Baillie, A., and Snaith, H.J. (2014). The emergence of perovskite solar cells. Nat. Photonics 8, 506–514.
- Li, X., Bi, D., Yi, C., Décoppet, J.-D., Luo, J., Zakeeruddin, S.M., Hagfeldt, A., and Grätzel, M. (2016). A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells. Science 353, 58–62.
- Liu, M., Johnston, M.B., and Snaith, H.J. (2013). Efficient planar heterojunction perovskite solar cells by vapour deposition. Nature 501, 395–398.
- NREL. (2017). Best research-cell efficiencies. Available at: https://www.nrel.gov/pv/assets images/efficiency-chart.png (Accessed: 15<sup>th</sup> November 2017).
- Xu, J., Chen, Y., and Dai, L. (2015). Efficiently photo-charging lithium-ion battery by perovskite solar cell. Nat. Commun. 6, 8103.
- Gurung, A., Chen, K., Khan, R., Abdulkarim, S.S., Varnekar, G., Pathak, R., Naderi, R., and Qiao, Q. (2017). Highly efficient perovskite solar cell photocharging of lithium ion battery using DC-DC booster. Adv. Energy Mater. 7, 1602105.
- Murakami, T.N., Kawashima, N., and Miyasaka, T. (2005). A high-voltage dye-sensitized photocapacitor of a three-electrode system. Chem. Commun. 26, 3346–3348.
- Miyasaka, T., and Murakami, T.N. (2004). The photocapacitor: an efficient self-charging capacitor for direct storage of solar energy. Appl. Phys. Lett. 85, 3932–3934.
- Chen, X., Sun, H., Yang, Z., Guan, G., Zhang, Z., Qiu, L., and Peng, H. (2014). A novel "energy fiber" by coaxially integrating dye-sensitized solar cell and electrochemical capacitor. J. Mater. Chem. A 2, 1897–1902.
- Cohn, A.P., Erwin, W.R., Share, K., Oakes, L., Westover, A.S., Carter, R.E., Bardhan, R., and Pint, C.L. (2015). All silicon electrode photocapacitor for integrated energy storage and conversion. Nano Lett. 15, 2727–2731.
- Takshi, A., Yaghoubi, H., Tevi, T., and Bakhshi, S. (2015). Photoactive supercapacitors for solar energy harvesting and storage. J. Power Sources 275, 621–626.

- Zhang, X., Huang, X., Li, C., and Jiang, H. (2013). Dye-sensitized solar cell with energy storage function through PVDF/ZnO nanocomposite counter electrode. Adv. Mater. 25, 4093–4096.
- Chen, T., Qiu, L., Yang, Z., Cai, Z., Ren, J., Li, H., Lin, H., Sun, X., and Peng, H. (2012). An integrated "energy wire" for both photoelectric conversion and energy storage. Angew. Chem. Int. Ed. 51, 11977–11980.
- 18. Xu, J., Wu, H., Lu, L., Leung, S.-F., Chen, D., Chen, X., Fan, Z., Shen, G., and Li, D. (2014). Integrated photo-supercapacitor based on Bi-polar TiO<sub>2</sub> nanotube arrays with selective one-side plasma-assisted hydrogenation. Adv. Funct. Mater. 24, 1840–1846.
- 19. Yang, Z., Deng, J., Sun, H., Ren, J., Pan, S., and Peng, H. (2014). Self-powered energy fiber: energy conversion in the sheath and storage in the core. Adv. Mater. 26, 7038–7042.
- Fu, Y., Wu, H., Ye, S., Cai, X., Yu, X., Hou, S., Kafafy, H., and Zou, D. (2013). Integrated power fiber for energy conversion and storage. Energy Environ. Sci. 6, 805–812.
- Bae, J., Park, Y.J., Lee, M., Cha, S.N., Choi, Y.J., Lee, C.S., Kim, J.M., and Wang, Z.L. (2011). Single-fiber-based hybridization of energy converters and storage units using graphene as electrodes. Adv. Mater. 23, 3446– 2440
- Liang, J., Zhu, G., Wang, C., Wang, Y., Zhu, H., Hu, Y., Lv, H., Chen, R., Ma, L., Chen, T., et al. (2017). MoS<sub>2</sub>-based all-purpose fibrous electrode and self-powering energy fiber for efficient energy harvesting and storage. Adv. Energy Mater 7, 1601208.
- Xu, X., Li, S., Zhang, H., Shen, Y., Zakeeruddin, S.M., Graetzel, M., Cheng, Y.-B., and Wang, M.A. (2015). Power pack based on organometallic perovskite solar cell and supercapacitor. ACS Nano 9, 1782–1787.
- Xu, J., Ku, Z., Zhang, Y., Chao, D., and Fan, H.J. (2016). Integrated photo-supercapacitor based on PEDOT modified printable perovskite solar cell. Adv. Mater. Technol. 1, 1600074.
- Um, H.-D., Choi, K.-H., Hwang, I., Kim, S.-H., Seo, K., and Lee, S.-Y. (2017). Monolithically integrated, photo-rechargeable portable power sources based on miniaturized Si solar cells and printed solid-state lithium-ion batteries. Energy Environ. Sci. 10, 931–940.
- Paolella, A., Faure, C., Bertoni, G., Marras, S., Guerfi, A., Darwiche, A., Hovington, P., Commarieu, B., Wang, Z., and Prato, M. (2017) Light-assisted delithiation of lithium iron phosphate nanocrystals towards photorechargeable lithium ion batteries. Nat. Commun. 8, 14643.
- Guo, W., Xue, X., Wang, S., Lin, C., and Wang, Z.L. (2012). An integrated power pack of dyesensitized solar cell and Li battery based on double-sided TiO<sub>2</sub> nanotube arrays. Nano Lett. 12, 2520–2523.
- Li, N., Wang, Y., Tang, D., and Zhou, H. (2015). Integrating a photocatalyst into a hybrid lithium-sulfur battery for direct storage of solar energy. Angew. Chem. Int. Ed. 54, 9271–9274.

- Li, Q., Li, N., Ishida, M., and Zhou, H. (2015). Saving electric energy by integrating a photoelectrode into a Li-ion battery. J. Mater. Chem. A 3, 20903–20907.
- Yu, M., Ren, X., Ma, L., and Wu, Y. (2014). Integrating a redox-coupled dye-sensitized photoelectrode into a lithium-oxygen battery for photoassisted charging. Nat. Commun. 5, 5111.
- Yu, M., McCulloch, W.D., Beauchamp, D.R., Huang, Z., Ren, X., and Wu, Y. (2015). Aqueous lithium-iodine solar flow battery for the simultaneous conversion and storage of solar energy. J. Am. Chem. Soc. 137, 8332–8335.
- Li, B., and Liu, J. (2017). Progress and directions in low-cost redox-flow batteries for large-scale energy storage. Natl. Sci. Rev. 4, 91–105.
- Alotto, P., Guarnieri, M., and Moro, F. (2014). Redox flow batteries for the storage of renewable energy: a review. Renew. Sust. Energ. Rev. 29, 325–335.
- 34. Wang, W., Luo, Q., Li, B., Wei, X., Li, L., and Yang, Z. (2013). Recent progress in redox flow battery research and development. Adv. Funct. Mater. 23, 970–986.
- Liu, P., Cao, Y.L., Li, G.R., Gao, X.P., Ai, X.P., and Yang, H.X. (2013). A solar rechargeable flow battery based on photoregeneration of two soluble redox couples. ChemSusChem 6, 802–806.
- Yan, N.F., Li, G.R., and Gao, X.P. (2013). Solar rechargeable redox flow battery based on Li<sub>2</sub>WO<sub>4</sub>/Lil couples in dual-phase electrolytes. J. Mater. Chem. A 1, 7012–7015.
- Liao, S., Zong, X., Seger, B., Pedersen, T., Yao, T., Ding, C., Shi, J., Chen, J., and Li, C. (2016). Integrating a dual-silicon photoelectrochemical cell into a redox flow battery for unassisted photocharging. Nat. Commun. 7, 11474.
- 38. Wei, Z., Liu, D., Hsu, C., and Liu, F. (2014). All-vanadium redox photoelectrochemical cell: an approach to store solar energy. Electrochem. Commun. 45, 79–82.
- Shen, Y., Wei, Z., Liu, D., Almakrami, H., and Liu, F. (2017). All-vanadium photoelectrochemical storage cells using dye sensitized geometry-enhanced TiO<sub>2</sub> nanobelts. Mater. Res. Bull. 96, 431–436.
- 40. Liu, D., Wei, Z., Hsu, C.-J., Shen, Y., and Liu, F. (2014). Efficient solar energy storage using a TiO<sub>2</sub>/WO<sub>3</sub> tandem photoelectrode in an all-vanadium photoelectrochemical cell. Electrochim. Acta 136, 435–441.
- Wedege, K., Azevedo, J., Khataee, A., Bentien, A., and Mendes, A. (2016). Direct solar charging of an organic-inorganic, stable, and aqueous alkaline redox flow battery with a hematite photoanode. Angew. Chem. Int. Ed. 55, 7142– 7147.
- Li, W., Fu, H.-C., Li, L., Cabán-Acevedo, M., He, J.-H., and Jin, S. (2016). Integrated photoelectrochemical solar energy conversion and organic redox flow battery devices. Angew. Chem. Int. Ed. 55, 13104–13108.



- 43. Ostfeld, A.E., Gaikwad, A.M., Khan, Y., and Arias, A.C. (2016). High-performance flexible energy storage and harvesting system for wearable electronics. Sci. Rep. 6, 26122.
- 44. Chu, S., Cui, Y., and Liu, N. (2017). The path towards sustainable energy. Nat. Mater. 16,
- 45. Chakrapani, V., Rusli, F., Filler, M.A., and Kohl, P.A. (2012). A combined photovoltaic and Li ion battery device for continuous energy harvesting and storage. J. Power Sources 216,
- 46. Cheng, X.-B., Zhang, R., Zhao, C.-Z., and Zhang, Q. (2017). Toward safe lithium metal anode in rechargeable batteries: a review. Chem. Rev. 117, 10403-10473.
- 47. Lin, D., Liu, Y., and Cui, Y. (2017). Reviving the lithium metal anode for high-energy batteries. Nat. Nanotechnol. 12, 194.
- 48. Vicente, N., and Garcia-Belmonte, G. (2017). Methylammonium lead bromide perovskite battery anodes reversibly host high Li-ion concentrations. J. Phys. Chem. Lett. 8, 1371-
- 49. Mabrouk, S., Bahrami, B., Gurung, A., Reza, K.M., Adhikari, N., Dubey, A., Pathak, R., Yang, S., and Qiao, Q. (2017). Higher efficiency perovskite solar cells using additives of Lil, LiTFSI and BMImI in the PbI<sub>2</sub> precursor. Sustain. Energy Fuels 1, 2162-2171.
- 50. Ostfeld, A.E., and Arias, A.C. (2017). Flexible photovoltaic power systems: integration opportunities, challenges and advances. Flex. Print. Electron. 2, 013001.

- 51. Luo, J., Zhang, W., Yuan, H., Jin, C., Zhang, L., Huang, H., Liang, C., Xia, Y., Zhang, J., and Gan, Y. (2017). Pillared structure design of MXene with ultralarge interlayer spacing for high-performance lithium-ion capacitors. ACS Nano 11, 2459-2469.
- 52. Sun, Y., Tang, J., Qin, F., Yuan, J., Zhang, K., Li, J., Zhu, D.-M., and Qin, L. (2017). Hybrid lithium-ion capacitors with asymmetric graphene electrodes. J. Mater. Chem. A 5, 13601-13609.
- 53. Green, M.A., Hishikawa, Y., Dunlop, E.D., Levi, D.H., Hohl-Ebinger, J., and Ho-Baillie, A.W.Y (2018). Solar cell efficiency tables (version 51). Prog. Photovolt. Res. Appl. 26, 3-12.
- 54. Chen, J., Cai, X., Yang, D., Song, D., Wang, J., Jiang, J., Ma, A., Lv, S., Hu, M.Z., and Ni, C. (2017). Recent progress in stabilizing hybrid perovskites for solar cell applications. J. Power Sources 355, 98-133.
- 55. Wang, D., Wright, M., Elumalai, N.K., and Uddin, A. (2016). Stability of perovskite solar cells. Sol. Energy Mater. Sol. Cells 147, 255-275.
- 56. Asghar, M., Zhang, J., Wang, H., and Lund, P. (2017). Device stability of perovskite solar cells—a review. Renew. Sust. Energy Rev. 77,
- 57. Fan, L., Wei, S., Li, S., Li, Q., and Lu, Y. (2018). Recent progress of the solid-state electrolytes for high-energy metal-based batteries. Adv. Energy Mater. https://doi.org/10.1002/aenm. 201702657.

- 58. Manthiram, A., Yu, X., and Wang, S. (2017). Lithium battery chemistries enabled by solidstate electrolytes. Nat. Rev. Mater. 2, 16103.
- **59.** Yu, M., McCulloch, W.D., Huang, Z., Trang, B.B., Lu, J., Amine, K., and Wu, Y. (2016). Solarpowered electrochemical energy storage: an alternative to solar fuels. J. Mater. Chem. A 4, 2766-2782.
- 60. Altermatt, P.P. (2011). Models for numerical device simulations of crystalline silicon solar cells—a review. J. Comput. Electron 10, 314.
- 61. Neupane, U., Bahrami, B., Biesecker, M., Baroughi, M.F., and Qiao, Q. (2017). Kinetic Monte Carlo modeling on organic solar cells: domain size, donor-acceptor ratio and thickness. Nano Energy 35, 128-137.
- 62. Zhou, Y., and Gray-Weale, A. (2016). A numerical model for charge transport and energy conversion of perovskite solar cells. Phys. Chem. Chem. Phys. 18, 4476-4486.
- 63. Ye, Y., Shi, Y., Cai, N., Lee, J., and He, X. (2012). Electro-thermal modeling and experimental validation for lithium ion battery. J. Power Sources 199, 227-238.
- 64. Wang, M., Xiao, X., and Huang, X. (2017). A multiphysics microstructure-resolved model for silicon anode lithium-ion batteries. J. Power Sources 348, 66-79.
- 65. Chu, D., Li, X., and Zhang, S. (2016). A nonisothermal transient model for a metal-free quinone-bromide flow battery. Electrochim. Acta 90, 434-445.