Geometric Optimization of an Electrochemical Purification Cell to Prevent Corrosion in CSP Plants During Operation

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SolarPACES 2021
9/30/21

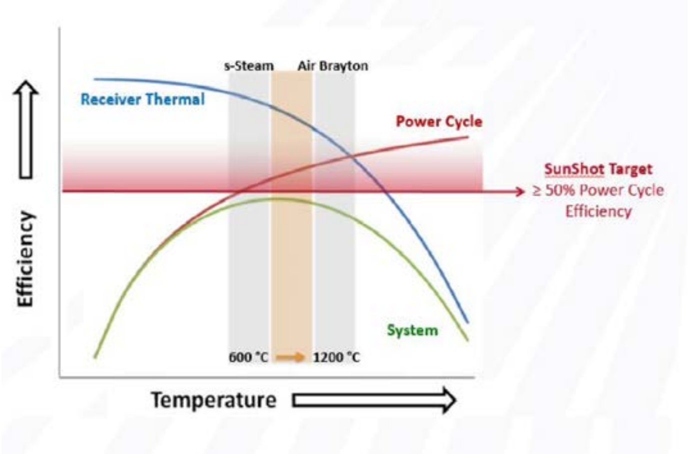
Molten Chloride Salt

Molten chloride salts are stable at higher temperatures than other molten salts

- Could enable more efficient operation of CSP plants, leading to lower LCOE
- Also useful for other reactors types (nuclear, electrochemical synthesis, etc.)

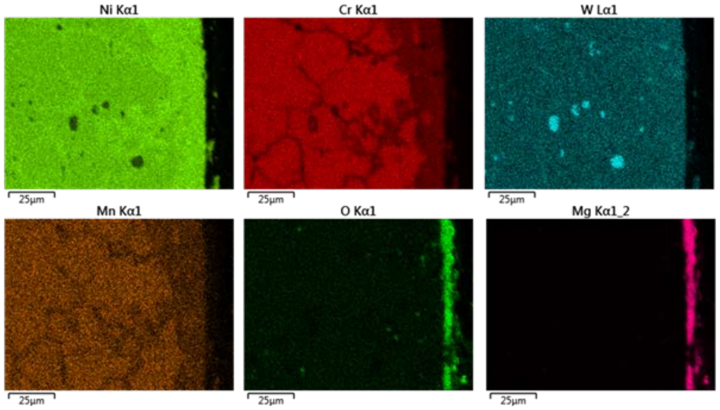
For this work, we are using a ternary NaCl/KCl/$MgCl_2$ salt

- Has favorable properties including low melting point
- Can be inexpensively sourced



Corrosion Problems

- ***Problem:*** Molten chloride salts are corrosive! The corrosive impurity MgOHCl forms in salt when exposed to H_2O.

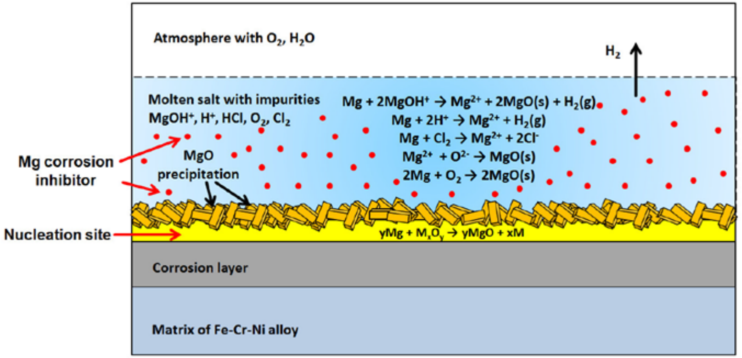


Elemental mapping by EDS at the same corrosion interface.

Alloy	OCP vs. pseudo-RE [mV]	E_{corr} vs. pseudo-RE [mV]	j_{corr} [μA/cm^2]	CR [mm/year]
650 °C				
SS347	–784±113	–847±91	713.00±30.74	7.49±0.32
SS310	–888±170	–938±218	626.16±38.72	6.42±0.40
In800H	–876±32	–910±22	573.79±34.19	5.94±0.33
IN625	–849±73	–856±57	233.00±94.68	2.80±0.38
700 °C				
SS310	–506±70	–571±75	1213.61±148.10	12.45±1.52
In800H	–453±5	–474±3	1387.79±131.96	14.31±1.36

Gomez-Vidal, J. C.; Tirawat, R., Solar Energy Materials and Solar Cells. **2016**

Salt Chemistry Control and Regeneration



- Corrosion depletes key alloying elements
- Example: oxidation of selective alloying elements such as Cr to Cr_2O_3 that is later fluxed to $CrCl_3$ by molten chlorides
- ***Controlling salt chemistry can mitigate corrosion***
- Salt-soluble *MgOHCl* in molten chlorides is one of the major species that reacts/corrodes metal *M* according to the reaction:

$$\mathbf{xMgOHCl + M \rightarrow xMgO + MCl_x + (x/2\ )H_2}$$

- Regenerating pure salts is important for plant operation

Corrosion Control

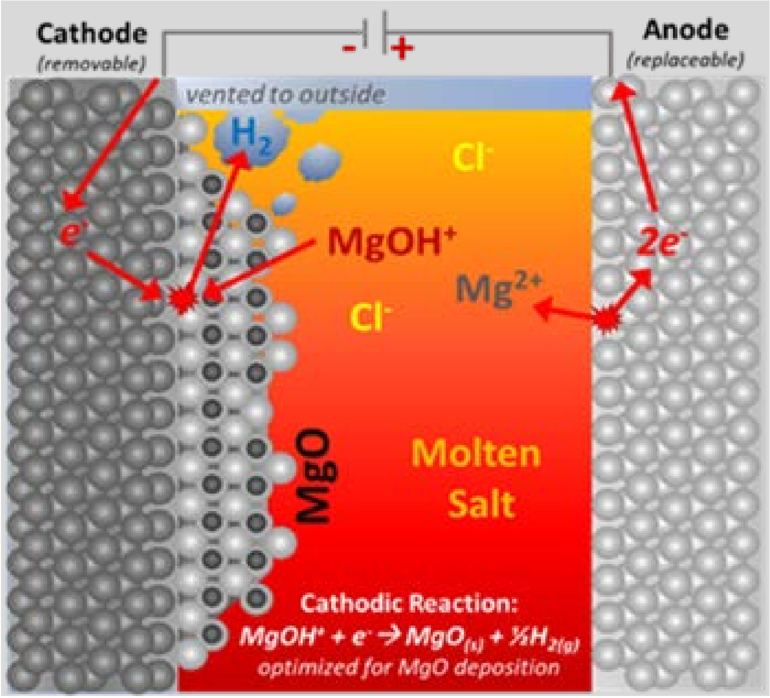
$$2MgOHCl \rightarrow 2MgOH^{+} + 2Cl^{-} \quad [\textit{molten salt}]$$
$$Mg^{2+} + 2Cl^{-} \rightarrow MgCl_2 \quad [\textit{molten salt}]$$
$$2MgOH^{+} + 2e^{-} \rightarrow 2MgO + H_2(g) \quad [\textit{cathode}]$$
$$\underline{Mg(s) \rightarrow Mg^{2+} + 2e^{-}} \quad [\textit{anode}]$$
$$2MgOHCl + Mg(s) \rightarrow MgCl_2 + 2MgO + H_2(g) \quad [\textit{overall reaction}]$$

Sealed/closed environment mitigates corrosive impurity formation

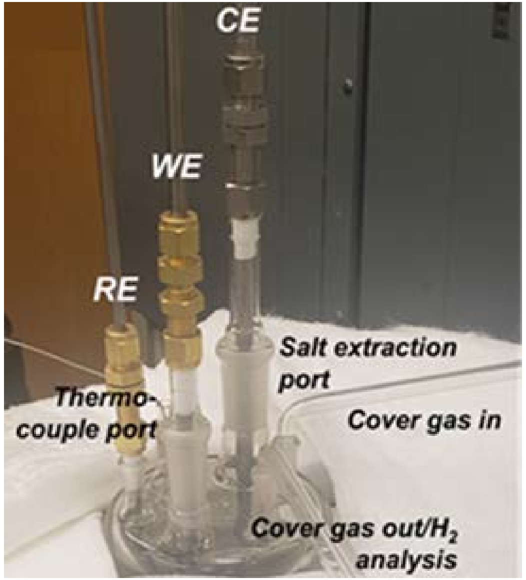
- MgOHCl forms when salt is exposed to moisture
- By preventing exposure to air and moisture, formation of corrosive MgOHCl can be minimized

Electrochemical purification used to remove corrosive impurities

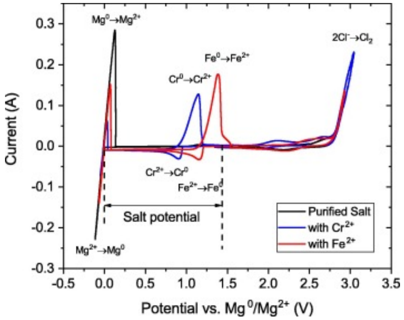
- Due to moisture in ullage gas and small leaks, some corrosive species will form even in sealed systems
- These can be controlled by electrochemical purification



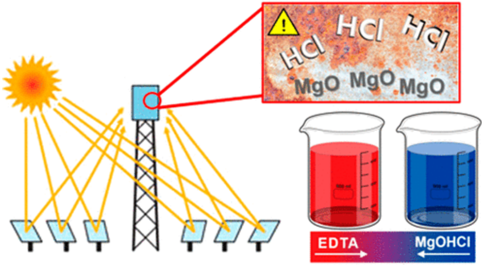
Lab-Scale Batch Electrochemical Purification



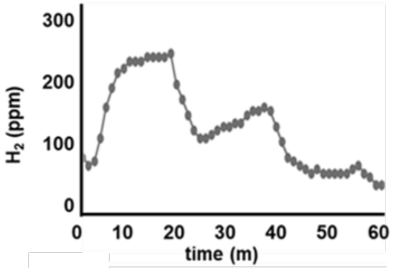
Salt Sensors



Titration



Gas Analysis



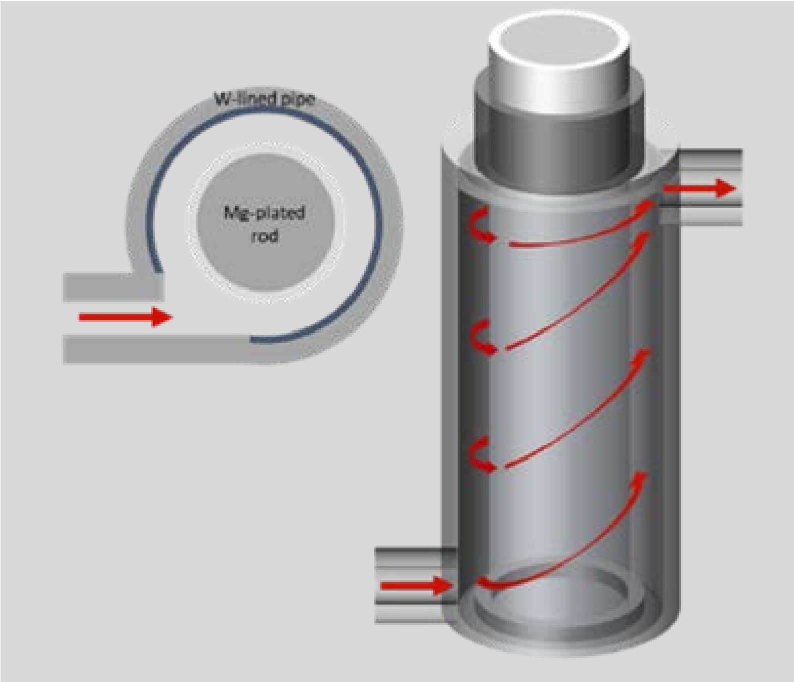
Klammer et al, *Analytical Chemistry*, 2020, 92, 3598-3604
Guo et al, *Journal of Electroanalytical Chemistry*, 2021, 115064

Goal: Design a Flow Cell for Use in CSP Plant

To be used ***in-situ*** in the CSP plant ***during operation***

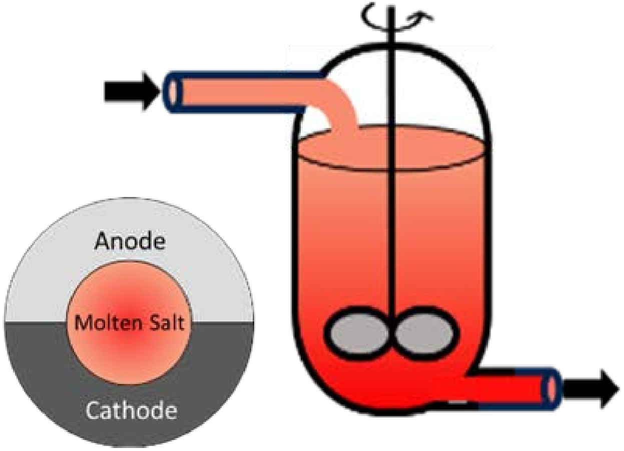
Corrosive ***MgOHCl will be removed as fast as it is formed***, so it will not build up and corrode alloys

Byproducts of purification, which are less harmful, will be removed via filtration and ullage gas sweep

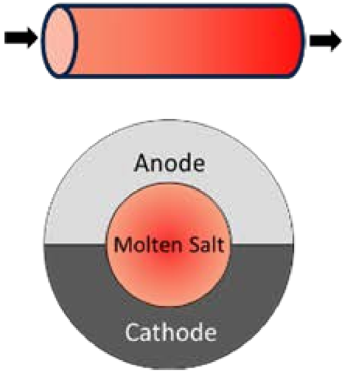


Reactor Types Considered

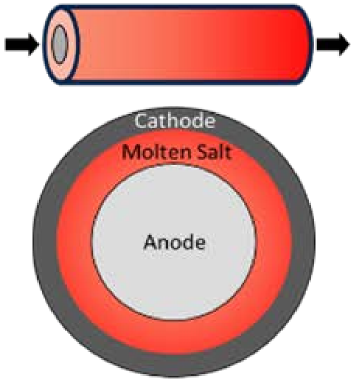
- Reactor must be a ***flow cell***
- More complex reactor types were considered but ruled out due to ***cost*** and ***manufacturability***



Continuous stirred tank reactor (CSTR)



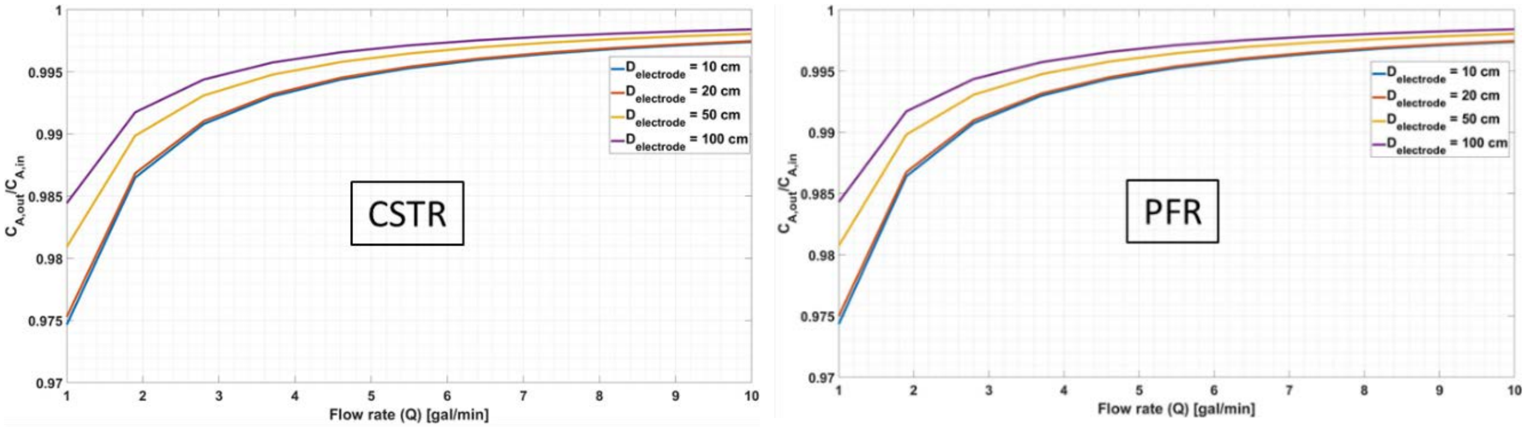
Plug flow reactor (PFR)



Annular plug flow reactor (annular PFR)

Analytical Modeling of CSTR and PFR – Starting Point

Reactor performance versus flow rate at various pipe diameters



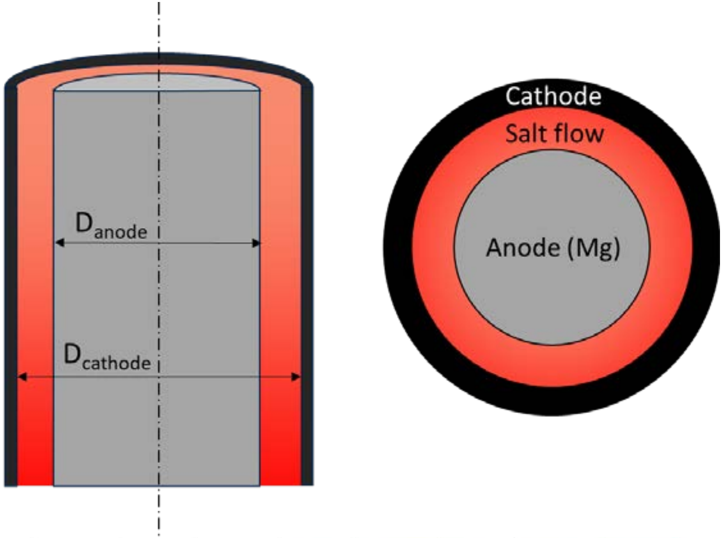
Reactor performance is unacceptable for both reactor types!

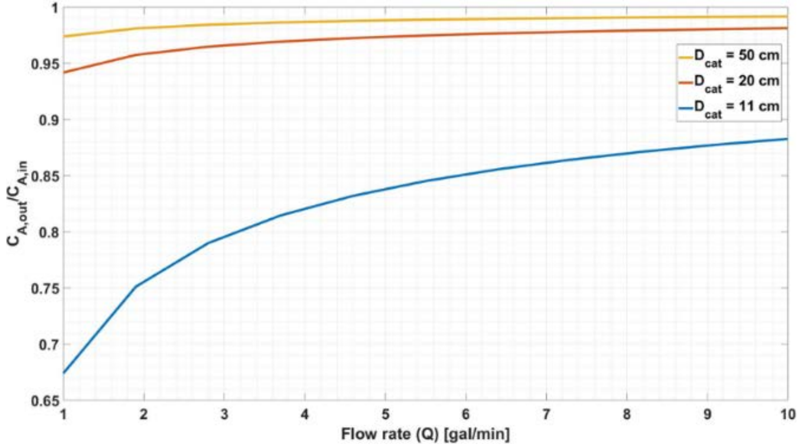
- CSTR Reactor length to achieve purification under a given set of conditions is ***over a kilometer long***
- PFR Reactor length to achieve purification under a given set of conditions is ***hundreds of meters long***

Insights/Shift to Annular PFR

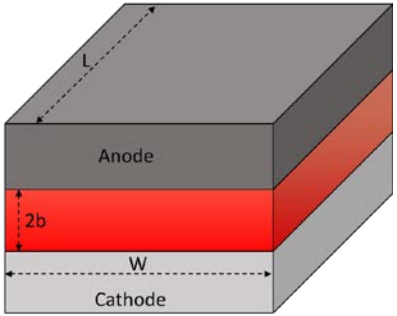
- Reactor design based on idealized plug flow reactor
- Annular shape reactor for three electrode system and provides high surface to volume ratio
- If anode radius approaches cathode radius, flow can be approximated as a plane slit

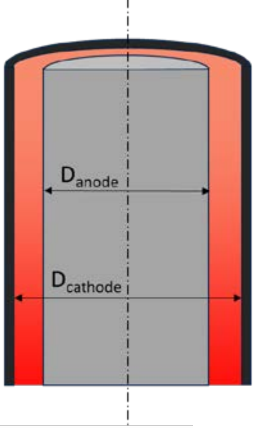
Reactor length to achieve purification is on the order of meters long



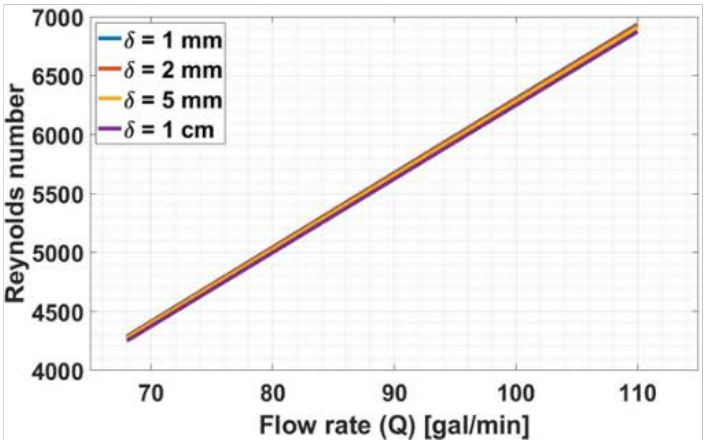


Performance Improved with Slit Flow



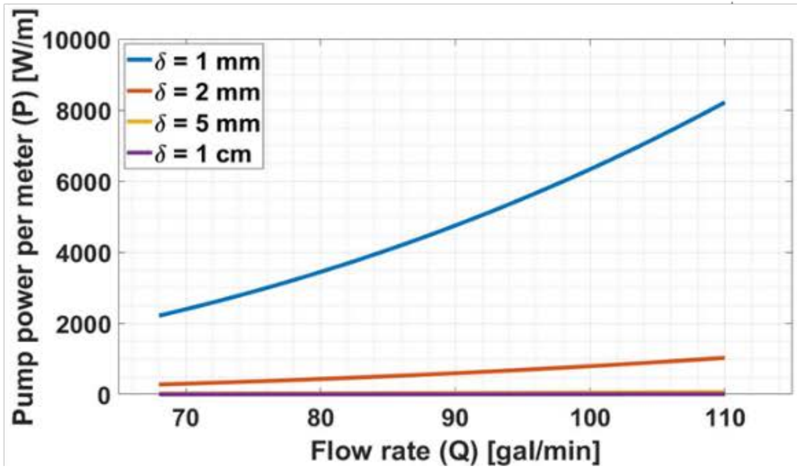


a



Reynolds number as a function of flow rate and electrode spacing

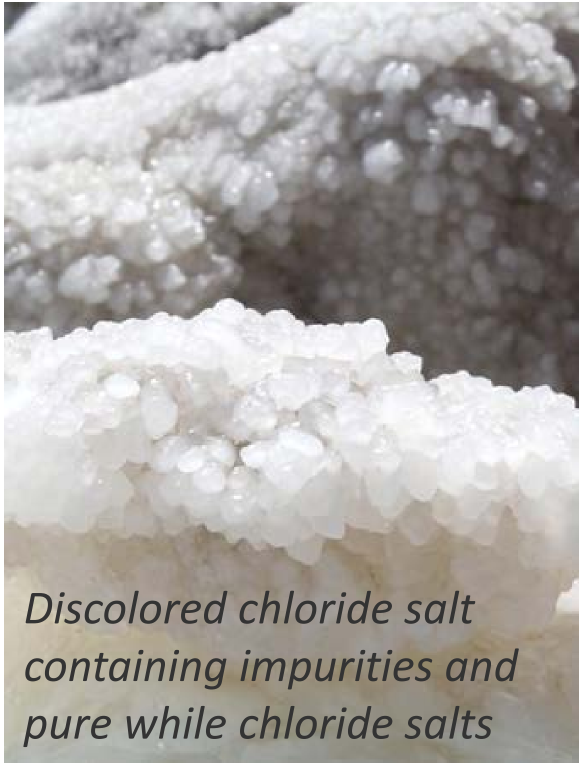
b



The increased pump power to overcome friction loss at various electrode spacings

Conclusion and Impact on System Resilience

- **We found that each successive design (CSTR → PFR → annular PFR) showed about an order of magnitude improvement**
- **Annular PFR can be further optimized and adapted to industrial conditions**
- **Currently in process of building a lab-scale annular PFR cell**
- **Purification cell will *substantially improve viability* of molten chloride salt-based systems**
  - It will ***decrease LCOE***
  - It will ***decrease maintenance*** costs
  - It will enable ***less expensive containment alloys*** to be used



Discolored chloride salt containing impurities and pure while chloride salts

Thank you for your attention!

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This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL/PR-5500-81438