Investigation of High-Temperature Latent Heat Storage Integrated with Supercritical CO_2 Brayton Cycle

By

Alok Kumar Ray

Submitted

in fulfillment of the requirements for the joint degree of

DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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THE UNIVERSITY OF QUEENSLAND

(June 2023)

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Dedicated to my family members

Supervisor Certification

This is to certify that the thesis entitled "**Investigation of High-Temperature Latent Heat Storage Integrated with Supercritical CO_2 Brayton Cycle**" being submitted by **Mr. Alok Kumar Ray** to the **Indian Institute of Technology Delhi, India, and The University of Queensland, Australia,** for the award of the degree of '**Doctor of Philosophy**' is a record of the bonafide research work carried out by him. Mr. Alok Kumar Ray has worked under our guidance and fulfilled the requirements for submitting this thesis, which has reached the requisite standard to our knowledge. The results in the thesis are original and have not been submitted, in part or full, to any other University or Institute to award any degree or diploma.

Prof. Hal Gurgenci	**Dr. Dibakar Rakshit**	**Dr. K. Ravi Kumar**
Emeritus Professor School of Mechanical and Mining Engineering, The University of Queensland St. Lucia, Australia - 4076	Associate Professor Department of Energy Science and Engineering Indian Institute of Technology Delhi Hauz Khas New Delhi, India - 110016	Associate Professor Department of Energy Science and Engineering Indian Institute of Technology Delhi Hauz Khas New Delhi, India - 110016

Abstract

The ever-increasing demand for energy and concern for environmental security has attracted considerable attention from researchers from fossil fuel technology towards renewable energy technology (e.g., solar energy, wind energy, etc.) and variable energy resources. Variable energy sources (e.g., Concentrating solar thermal systems, electricity spillage from PV and wind plants) can play significant roles in the complete transition to renewable energy resources. However, spatial and temporal intermittency is the major hindrance to the effective deployment of renewable energy technologies. Integrating thermal energy storage (TES) systems with renewable energy technologies can reduce the discrepancy between energy supply and demand, leading to continuous energy supply. However, the technologies need to evolve at higher operating temperatures (Thermal stability > 550°C) to enable the deployment of efficient thermodynamic cycles such as the supercritical CO_2 (sCO_2) cycle.

Among the various alternatives of TES technologies, high-temperature latent heat (HT-LHS) storage has significant benefits, such as isothermal operation, high energy storage density, and high exergetic efficiency. Moreover, high-temperature latent heat storage can be integrated with advanced power generation cycles or Thermionic photovoltaic (TIPV) systems to generate cost-effective heat and power. Hence, a critical analysis is imperative to investigate charging and discharging characteristics of the high-temperature latent heat storage. To demonstrate the utility of the HT-LHS system, numerical, theoretical, and experimental studies must be performed.

In this regard, a numerical investigation is conducted to study the thermo-hydraulic behavior during the melting/solidification of high-temperature metallic phase change material (silicon). A counter-clockwise circulation pattern is observed in the molten silicon, unlike clockwise pattern in molten conventional high-temperature PCM (sodium nitrate). The energy storage density and energy storage rates of silicon-based LHS are observed to be significantly higher than sodium nitrate ($NaNO_3$) based LHS. A suitable high-temperature metallic PCM is identified for HT-LHS system to be integrated with the sCO_2 Brayton cycle. Steady-state modeling of recompression sCO_2 Brayton cycle is performed to ascertain the effect of turbine inlet temperature on the thermodynamic efficiency. The thermodynamic efficiency reaches 50% at 700°C, which is significantly higher than the conventional Rankine cycle. The thermal efficiency is maximized at a split ratio of 0.75 for an air temperature of 30°C. Turbine inlet pressure and air

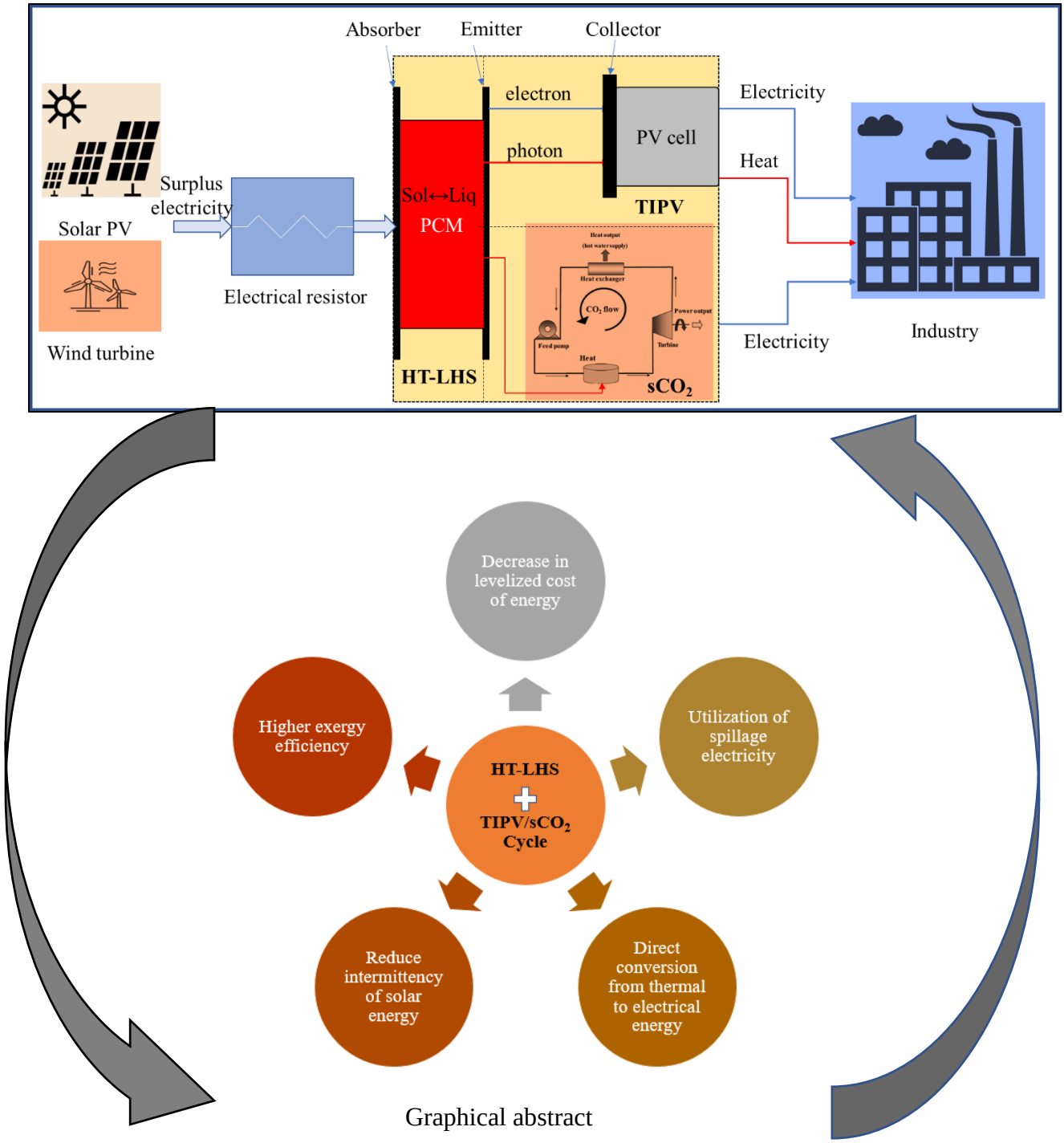
temperature are identified as the most and least sensitive parameters affecting cycle efficiency. A robust analytical model is developed for the discharge operation of the HT-LHS system in dimensionless form and solved to evaluate the discharge performance. Low heat transfer rate is the major technological challenge for HT-LHS systems with conventional inorganic salts. The individual and combined effects of passive heat transfer enhancement methods on the charging and discharging performance of HT-LHS systems are numerically studied. Commercial high-temperature inorganic salt (eutectic mixture of $NaNO_3$ and KNO_3) is considered as PCM in the concentric tube storage system. The combined effect on thermal performance is reported to be substantially higher than the individual effect. However, the combined effect of orientation and eccentricity results in a design anomaly for HT-LHS system. Eutectic mixture (60% $NaNO_3$,40% KNO_3) is synthesized using the common solvent method, and the thermal response of the synthesized sample is studied experimentally. A lab-scale prototype and experimental test facility are designed and developed to mimic the charging and discharging process of a concentric tube HT-LHS system. Moreover, results from the numerical model are validated against the experimental results. To further establish the inevitability of the HT-LHS system, a techno-economic comparative study is conducted between the HT-LHS system and Li-ion battery having the same capacity. The volumetric and gravimetric energy densities are observed to be significantly higher than the Li-ion battery. The charging and discharging durations for HT-LHS system are relatively smaller than the Li-ion battery. The abstract can be graphically depicted in the following Figure.

ऊर्जा की लगातार बढ़ती मांग और पर्यावरण सुरक्षा के चिंता ने फॉसिल ईंधन प्रौद्योगिकी से अधिकर ऊर्जा प्रौद्योगिकी (जैसे कि सौर ऊर्जा, पवन ऊर्जा, आदि) और परिवर्तनशील ऊर्जा संसाधनों की ओर से अध्ययनकर्ताओं को काफी ध्यान आकर्षित किया है। परिवर्तनशील ऊर्जा स्रोतों (जैसे कि संचालक सौर थर्मल प्रणालियाँ, पीवी और पवन प्लांट से बिजली बहाव) में पूरी तरह से आधारभूत ऊर्जा संसाधनों के लिए महत्वपूर्ण भूमिका निभा सकते हैं। हालांकि, स्थानिक और समयिक अनियमितता पर्यावरणीय ऊर्जा प्रौद्योगिकियों के प्रभावी निगमन में मुख्य बाधा है। ऊर्जा परिरक्षण तंत्र (टीईएस) प्रणालियों को ऊर्जा आपूर्ति और मांग के बीच अंतर को कम करके निरंतर ऊर्जा आपूर्ति के मार्ग की प्रमुख बाधाओं को कम करने के लिए परिवर्तनशील ऊर्जा प्रौद्योगिकियों के साथ एकीकृत करने की आवश्यकता होती है। हालांकि, प्रौद्योगिकियों को उच्च संचालन तापमानों (थर्मल स्थिरता > 550°C) पर विकसित करने की आवश्यकता होती है ताकि अत्यधिक उष्णमिति आधारित चक्र (सुपरक्रिटिकल सीओ2 (sCO_2) चक्र) जैसे कुशल थर्मोडायनामिक चक्रों को विस्तारित करने की संभावना हो।

टीईएस प्रौद्योगिकियों के विभिन्न विकल्पों में उच्च तापमान लटेंट ऊष्मा (एचटी-एलएचएस) संग्रह जैसे महत्वपूर्ण लाभ होते हैं, जैसे कि आइसोथर्मल संचालन, उच्च ऊष्मा संग्रह प्रतिष्ठा, और उच्च प्रदीपादी दक्षता। इसके अलावा, उच्च तापमान लटेंट ऊष्मा संग्रह को उन्नत बिजली प्रजनन चक्रों या थर्माइनिक फोटोवोल्टेक (टीआईपीवी) प्रणालियों के साथ समकालिक ताप और ऊर्जा उत्पन्न करने के लिए एकीकृत किया जा सकता है। इसलिए, उच्च तापमान लटेंट ऊष्मा संग्रह के चार्जिंग और डिस्चार्जिंग गुणधर्मों का विश्लेषण महत्वपूर्ण है। उच्च तापमान लटेंट ऊष्मा संग्रह के गुणधर्मों की प्रदर्शन की प्रतिष्ठ करने के लिए संख्यात्मक, सिद्धांतिक और प्रयोगात्मक अध्ययन किए जाने चाहिए।

इस संदर्भ में, एक संख्यात्मक अध्ययन किया जाता है उच्च तापमान धातुयुक्त ताप बदलने वाली सामग्री (सिलिकॉन) के गलन/कठोरी के दौरान थर्मो-हाइड्रोलिक व्यवहार का अध्ययन करने के लिए। गला हुआ सिलिकॉन में घुमावदार परिसंचार पैटर्न को देखा जाता है, जोकि घुले हुए पारंपरिक उच्च तापमान ताप बदलने वाली सामग्री (सोडियम नाइट्रेट) में घड़ी की दिशा के विपरीत है। सिलिकॉन पर आधारित एलएचएस की ऊष्मा संग्रह प्रतिष्ठा और ऊष्मा संग्रह दरें सोडियम नाइट्रेट (एनएनओ3) पर आधारित LHS से काफी अधिक होती हैं। एचटी-एलएचएस प्रणाली के लिए एक उपयुक्त उच्च तापमान धातुयुक्त पीसीएम चुना जाता है, जिसे sCO_2 ब्रेटन चक्र के साथ एकीकृत करने के लिए। रिकंठित स्थिरावस्था मॉडलिंग सीओ2 ब्रेटन चक्र पर

संघटित स्थानिकीय मॉडलिंग किया जाता है ताकि चरम थर्मोडायनामिक दक्षता पर टरबाइन प्रवेश तापमान का प्रभाव निश्चित किया जा सके। थर्मोडायनामिक दक्षता 700°C पर 50% तक पहुंचती है, जो पारंपरिक रैंकिन चक्र से काफी अधिक है। विद्युतचालितता एक साझी अनुपात 0.75 के लिए थर्मल दक्षता को अधिकतम किया जाता है, एक हवा के तापमान 30°C के लिए। चक्र की दक्षता पर प्रभाव डिस्चार्ज प्रदर्शन का मज़बूत विश्लेषण करने के लिए एक मजबूत व्याख्यात्मक मॉडल डिमेंशनलेस रूप में विकसित किया गया है और समाधान किया जाता है। पारंपरिक अनायासी नमकों के साथ HT-LHS प्रणालियों के लिए कम ऊष्मा पारंपरिक तकनीकी चुनौती है। अपेक्षाकृत ऊष्मा प्रदर्शन पर गतिशील ऊष्मा संग्रह तकनीकों के व्यक्तिगत और संयुक्त प्रभावों का संख्यात्मक अध्ययन किया जाता है। व्यावसायिक उच्च तापमान अनायासी नमक ($NaNO_3$ और KNO_3 के इयूटेक्टिक मिश्रण) को एक संरेखित ट्यूब संग्रह प्रणाली में पीसीएम के रूप में मान्यता प्राप्त किया जाता है. उष्मा प्रदर्शन पर संयुक्त प्रभाव को एकल प्रभाव से काफी अधिक बताया गया है। हालांकि, एचटी-एलएचएस प्रणाली के लिए अभिविन्यास और असंतुलन का संयुक्त प्रभाव एचटी-एलएचएस प्रणाली के लिए एक अभिकल्प अवस्था उत्पन्न करता है। (60% $NaNO_3$,40% KNO_3) इयूटेक्टिक मिश्रण को सामान्य विलयन पद्धति का उपयोग करके बनाया जाता है, और नमूने की थर्मल प्रतिक्रिया का प्रयोगात्मक अध्ययन किया जाता है। एक प्रयोगशाला-मापी विन्यास और प्रयोगात्मक परीक्षण सुविधा डिजाइन की जाती है जो एक संरेखित ट्यूब एचटी-एलएचएस प्रणाली की चार्ज और डिस्चार्ज प्रक्रिया का मिमिक करने के लिए बनाई और विकसित की गई है। इसके अलावा, संख्यात्मक मॉडल के परिणाम प्रयोगात्मक परिणामों के खिलाफ सत्यापित किए जाते हैं। एचटी-एलएचएस प्रणाली की अनिवार्यता को और बेहदी बटरी के साथ तकनीकी-आर्थिक तुलनात्मक अध्ययन द्वारा स्थापित करने के लिए एक तकनीकी-आर्थिक तुलनात्मक अध्ययन किया जाता है जिसमें समान क मता होती है। आपयामी और भारमापी ऊष्मा घनत्व लिथियम-आयन बैटरी से काफी अधिक होते हैं। अवधारणा निम्न चित्र में ग्राफिक रूप में दिखाई जा सकती है।



Graphical abstract

Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution of others to jointly authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support, and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

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Publications included in the thesis

International Journal Articles

1. **A. K. Ray**, D. Rakshit, K. Ravi Kumar, and H. Gurgenci, "Silicon as high-temperature phase-change medium for latent heat storage: A thermo-hydraulic study," Sustain. Energy Technol. Assessments, vol.46, no. September 2020, pp. 101249, 2021.

2. **A. K. Ray**, D. Rakshit, and K. Ravikumar, "High-temperature latent thermal storage system for solar power: Materials, concepts, and challenges," Clean.Eng. Technol., vol. 4, pp. 100155, 2021.

3. **A. K. Ray**, D. Rakshit, K. Ravikumar, and H. Gurgenci"A comparative study of high-temperature latent heat storage systems", *Energies* **2021**, *14*, 68-86.

4. **A. K. Ray**, D. Rakshit, K. Ravikumar, and H. Gurgenci, "Strength-Weakness-Opportunities-Threats-Unusual (SWOT-U) behavior analysis of Silicon as phase change material for high-temperature latent heat storage" Thermal Science and Engineering Progress Volume 38, 1, February 2023, 101627.

5. **Alok K.Ray**, Sumer Singh, Dibakar Rakshit, Udayraj̃, Comparative study of cooling performance for portable cold storage box using phase change medium" Thermal Science and Engineering Progress Volume 27, 1 January 2022, 101146

International Conference Articles

1. **Ray, AK**, Dibakar, R., Kumar, R., Gurgenci, H., a comparative study of melting performance for ultra-high temperature latent storage system. 9th Eur. Conf. Ren. Energy Sys. 21-23 April 2021, Istanbul, Turkey

2. **A. K. Ray**, D. Rakshit, K. Ravikumar, and H. Gurgenci ", A Numerical Investigation of Charging a high-Temperature Latent Heat Storage Unit: AVariable Domain Methodology. Proceedings of the 26th National and 4th International ISHMT-ASTFE Heat and Mass Transfer Conference, December 17-20,2021, IIT Madras, Chennai-600036, Tamil Nadu, India

3. **A. K. Ray**, D. Rakshit, K. Ravikumar, and H. Gurgenci, 'Thermal performance of eccentric high-temperature latent heat storage system: passive heat transfer enhancement strategy'EuroSun 2022, Kassel, Germany.

4. R. Mochahari, **A.K. Ray** , K. Ravi Kumar and D. Rakshit,"Thermal performance of a supercritical CO_2 based central receiver"THIRD International Conference on Future Technologies in Manufacturing, Automation, Design & Energy, ICoFT 2022, December 14-16, NIT Puducherry.

Book Chapter

Ray, AK, Vashist, S, Joy, J.M, and Rakshit, D, "Comparison Between Ultra-High-Temperature Thermal Battery and Li-Ion Battery", Recent Advances in Fluid Dynamics, Chapter 39, ISBN-978-981-19-3378-3.

Submitted manuscripts included in this thesis

1. A. K. Ray, D. Rakshit, K. Ravikumar, and H. Gurgenci, "A paradox: Passive heat transfer enhancement strategies enhance thermal performance of high-temperature latent heat storage"

2. A. K. Ray, D. Rakshit, K. Ravikumar, and H. Gurgenci, "Transient discharge performance of high-temperature latent storage system itegrated with supercritical CO_2 Brayton cycle: A combined analytical and numerical study"

Contributions by others to the thesis

All chapters

Editorial suggestions were provided by the candidate's supervisors, Prof. Hal Gurgenci, Dr. Dibakar Rakshit, Dr. K. Ravi Kumar and PhD committee members, Prof. Anil Verma, Dr. Anand Veeraragavan and Dr. Kaushik Saha.

Statement of parts of the thesis submitted to qualify for the award of another degree

No works submitted towards another degree have been included in this thesis.

Research involving human or animal subjects

No animal or human subjects were involved in this research.

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Keywords

Phase change material, High-temperature, latent heat storage, Silicon, Supercritical CO_2 cycle, TIPV, Renewable energy resources

Australian and New Zealand standard research classifications (ANZSRC)

ANZSRC code: 091501, Computational Fluid Dynamics, 40%

ANZSRC code: 091305, Energy Generation, Conversion and Storage Engineering,40%

ANZSRC code: 091599 Interdisciplinary Engineering not elsewhere classified, 20%

Fields of research classification

FoR code: 4012, Fluid Mechanics and Thermal Engineering, 60%

FoR code: 4099, Other Engineering, 30%

FoR code: 4017, Mechanical Engineering, 10%

Contents

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Nomenclature

Abbreviations

AR	Aspect ratio	NTU	Number of transfer units
CCW	Counterclockwise	Nu	Nusselt number
CST	Concentrated solar thermal	PCM	Phase change medium
DSC	Differential scanning calorimetry	Pr	Prandtl number
DSG	Direct steam generation	PV	Photovoltaic
EHC	Effective heat capacity	Ra	Rayleigh number
Fo	Fourier number	Re	Reynold's number
Gr	Grashoff number	RER	Renewable energy resources
HTF	Heat transfer fluid	sCO_2	Supercritical carbon dioxide
HT	High temperature	SEM	Scanning electron microscope
lpm	Liter per minute	SHS	Sensible heat storage
LCoE	Levelized cost of energy	Ste	Stefan number
LDF	Latent discharge fraction	TCHS	Thermochemcial heat storage
LHS	Latent heat storage	TES	Thermal energy storage
LSF	Latent storage fraction	TGA	Thermo-gravimetric analysis
MF	Melting fraction	TIPV	Thermionic photovoltaic

Greek symbols

α (m^2/s)	Thermal diffusivity	Φ (ev)	Workfunction
β	Liquid fraction/melt fraction	λ (μm)	Wavelength
δ	Solid fraction	μ (Pa.s)	Dynamic viscosity
$\vec{\nabla}.$	Divergence	ρ (kg/m^3)	Density
ε	effectiveness	∇	Gradient
η	efficiency	θ (°)	Inclination

Symbols

A (kg/s)	Mushy zone constant	ΔH_r (kJ/mol)	Enthalpy of reaction
a_r	Percentage of conversion	j_{ECH}	Volumetric current transfer rate
As (m^2)	Surface area	k (W/mK)	Thermal conductivity
c_p(kJ/kgK)	Specific heat capacity	K (D)	Permeability
D(T)	Darcy term	k_T(1/K)	Coefficient of thermal expansion
e (mm)	eccentricity	q" (W/m^2)	Heat flux
E (kJ)	Energy stored/released	S	Shape factor
f	Friction factor	$\dot{q}$ (kJ/m^3)	Heat generateion rate
flc2hs	Heavyside function	S_{dis} (kJ/m^3)	Energy dissipation
h (kJ)	Sensible enthalpy	S(β) (kg/s)	Source term in N-S equation
h_{sl} (kJ/kg)	Latent heat of fusion/solidification	U (W/m^2K)	Overall heat transfer coefficient
H(kJ)	Total enthalpy	U (V)	Open circuit voltage

Subscripts

T_i (K)	Initial temperature	ε_{avg}	Average effectiveness
T_f (K)	Final temperature	e_x (mm)	Horizontal eccentricity
T_s/T_{Solid} (K)	Solidification temperature	e_y (mm)	Vertical eccentricity
T_l/T_{liq} (K)	Liquidus temperature	Φ_e (eV)	Emitter work function
C_{eff} (J/kgK)	Effective heat capacity	Φ_c (eV)	Collector work function
η_{Tur}	Turbine efficiency	Q_{el} (kJ)	Energy transfer through electron
η_{comp}	Compressor efficiency	Q_{ph} (kJ)	Energy transfer through photon
ε_{Recup}	Recuperator effectiveness	ρ_{mod} (kg/m^3)	Modified density
T_m (K)	Melting point	$E_{discharge}$ (kJ)	Energy discharged
d_o (mm)	Outer diameter	d_i (mm)	Inner diameter
e_r (mm)	Radial eccentricity	d_m (mm)	Mean diameter