

4f-5d orbital tag-team catalysis empowers high-loading zinc–iodine batteries

Corresponding Author: Professor Quan-Hong Yang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this work, Chen et al. present a compelling demonstration of f-d orbital synergy in cerium single-atom catalysts for high-loading zinc-iodine batteries. The study stands out for its sophisticated integration of machine learning guidance with deep orbital-level analysis, offering a coherent strategy to overcome the persistent adsorption–activation dilemma in conversion-type cathodes. The proposed "tag-team" mechanism is well-supported by a combination of theoretical calculations and experimental validations, and the achievement of record-high iodine loading and areal capacity in practical pouch cells underscores the practical relevance of this fundamental insight. I therefore recommend acceptance in Nat Commun after the following points are considered.

1. A more detailed comparison with other f-block SACs (e.g., La, Sm) would help clarify the unique advantages of Ce and strengthen the rationale behind its selection.
2. The discussion on mechanical degradation at loadings $>10 \text{ mg cm}^{-2}$ is mentioned. A further analysis of electrode architecture or strategies to mitigate stress heterogeneity could strengthen the practical narrative.
3. The XPS data indicates a mixture of Ce^{3+} and Ce^{4+} . In-depth discussion on their respective roles in the catalytic cycle would provide deeper mechanistic insight, e.g., which state is more critical for adsorption vs. charge transfer?
4. The variable-temperature EIS analysis, used to determine activation energies, requires the equivalent circuit model and fitting errors to be included in the SI to ensure methodological rigor.
5. Several experimental details are suggested to be added for reproducibility: the electrolyte volume in coin and pouch cells, and the specific configuration for the in situ Raman/UV-vis cells.
6. Direct visualization of cycled separators (e.g., through photographs or SEM) would provide additional convincing evidence for the suppressed shuttle effect in Ce SAC-based cells.
7. The reported specific capacity ($\sim 242 \text{ mAh g}^{-1}$) exceeds the theoretical value for the I_2/I^- redox couple (211 mAh g^{-1}). The authors should clarify the origin of this excess capacity (e.g., contribution from carbon, normalization method, or other redox processes).
8. For the high-loading pouch cell, a calculation of the iodine utilization rate (areal capacity / theoretical capacity based on I_2 loading) would help quantify the efficiency of active material use.

Reviewer #2

(Remarks to the Author)

Chen et al. report an article titled "4f-5d orbital tag-team catalysis empowers high-loading zinc–iodine batteries". The authors use ML to identify Ce single atom catalysts (SACs) that interact with iodine. From their analyses, the authors argue that their new material is practical for batteries.

Although this article is probably publishable after major revisions, there are some imprecisions that should be cleared up prior to publication:

Major comments:

1. The authors introduce the terminology of "tag team" catalysts. I think such terminology should be clarified. I had not heard this term before. It seems the authors are introducing this new terminology to describe f/d interactions.
2. In their results section, the authors state "Unlike conventional approaches that focus primarily on thermodynamic outputs (e.g., adsorption energy or free energy), our method establishes physically meaningful descriptors that characterize the

binding strength between the catalyst and iodine, as well as the ability to activate I-I bonds, thereby providing a more universal basis for catalyst screening" and then immediately follow this up with "These descriptors were used to predict two reaction-relevant properties: the adsorption energy of iodine species (ΔE^*I), related to iodine immobilization and shuttle suppression, and the I-I bond length in I_3^* , reflecting bond cleavage efficiency." Is the point that the authors are trying to make that understanding *why* the adsorption energy from a chemical perspective is what they are doing? I would argue that what the authors have done here is not that different, because neither the Bader charge nor the number of d/f electrons near the Fermi level can be readily be controlled.

3. There is a lot of description around Zn-I batteries, but then the article talks mainly about Ce-SACs. I am no battery expert, but how these two are related is not clear to me from the early parts of the article. The first time where this is discussed is on page 14. I would urge the authors to give some background on this.

4. "Moreover, the two descriptors vary independently and are associated with distinct aspects of the reaction mechanism (Fig. 1d)". To me, it appears that these descriptors are highly correlated, at least in rank. Thus, saying that they vary independently appears incorrect.

5. For Co SACs and other SACs with 3d metals, the authors need to consider open shell electron configurations, which are likely and probable for 3d metals. The work of Kulik has done this on SACs.

6. When the authors consider SACs computationally, they assume certain coordination environments. There is no direct proof that the synthesized SACs have these coordination environments. Do the authors have reasoning for this?

7. The authors should provide all their calculated geometries on Zenodo, instead of the images they currently provide.

Reviewer #3

(Remarks to the Author)

This manuscript presents a comprehensive study on the design of a cerium single-atom catalyst (Ce SAC) for high-loading zinc-iodine batteries, addressing the trade-off between adsorption strength and redox kinetics, which is a fundamental challenge in conversion-type cathodes. The proposed "f-d orbital tag-team catalysis" mechanism is innovative and well-supported by a combination of machine learning screening and DFT calculations. The experimental results, particularly the high areal capacity and pouch cell demonstration, are impressive and highlight the practical relevance of the work. Overall, this manuscript is well-organized with solid data presented, contributing to the understanding of f-block catalysts and designing of high-loading conversion-type cathodes. I recommend its publication in Nature Communications with the following suggestions:

1. To further strengthen the proposed "f-d orbital tag-team" mechanism, it would be helpful to provide additional theoretical analysis, such as charge density difference or Bader charge calculations, to more directly quantify the contribution of Ce 4f orbitals during I-I bond cleavage.
2. Equivalent circuit fitting of the EIS data, along with relevant parameters and error analysis, would help better support the conclusions regarding charge transfer resistance and interface evolution.
3. Clarifying the physical state of iodine (e.g., crystalline or amorphous) within the carbon host through XRD or Raman spectroscopy. In addition, quantifying the capacity contribution from the carbon substrate itself would help accurately attribute the electrochemical performance to iodine redox.
4. Including the UV-Vis calibration curve and fitting details used for polyiodide concentration analysis in the Supplementary Information would improve the reproducibility and reliability of the adsorption measurements.
5. Have the authors explored how different Ce SAC loadings influence the iodine redox kinetics? A correlation between catalyst loading and electrochemical performance could provide valuable insight for further optimizing the material design.
6. SEM or TEM images of the cathode before and after cycling would be useful to evaluate the morphological and structural stability of the electrode under operating conditions.
7. To better situate the high-loading performance within a practical context, it would be beneficial to include cycling stability and efficiency data at moderate loadings (e.g., 2–10 mg cm⁻²).
8. A direct performance comparison with other recently reported Zn-I₂ systems (particularly in terms of areal capacity, mass loading, and cycling stability) would help readers better appreciate the advances made in this work.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors revised the manuscript accordingly, it is publishable in the present form.

Reviewer #2

(Remarks to the Author)

The reviewers have adequately addressed my comments.

Reviewer #3

(Remarks to the Author)

All my concerns have been addressed and the manuscript can be accepted now.

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Point-by-point response to the reviewers' comments

Reviewer #1:

In this work, Chen et al. present a compelling demonstration of f-d orbital synergy in cerium single-atom catalysts for high-loading zinc-iodine batteries. The study stands out for its sophisticated integration of machine learning guidance with deep orbital-level analysis, offering a coherent strategy to overcome the persistent adsorption–activation dilemma in conversion-type cathodes. The proposed "tag-team" mechanism is well-supported by a combination of theoretical calculations and experimental validations, and the achievement of record-high iodine loading and areal capacity in practical pouch cells underscores the practical relevance of this fundamental insight. I therefore recommend acceptance in Nat Commun after the following points are considered.

Reply: We sincerely appreciate the reviewer's positive evaluation and constructive feedback. Below are our detailed responses to each comment.

1. A more detailed comparison with other f-block SACs (e.g., La, Sm) would help clarify the unique advantages of Ce and strengthen the rationale behind its selection.

Reply: We thank the reviewer for this insightful comment. To clarify the differences among f-block SACs and to justify the choice of Ce, we performed a detailed comparison of how the d- and f-orbital characteristics of Ce, La, and Sm govern their catalytic behavior toward I₂ activation. As shown in Fig. R1a–c, Ce exhibits the highest d-band center among the tested f-block metals, giving adsorption energies for I₂^{*}, I₃^{*}, and I^{*} that fall within the Sabatier optimum. In contrast, La binds these intermediates too weakly, while Sm over-stabilizes them and hinders turnover.

Crucially, the enhanced activity of Ce originates from its partially filled and moderately delocalized 4f¹ orbital. As revealed by the orbital composition (Fig. R1e), Ce is the only metal whose 4f orbital directly participates in the I₃^{*} interaction. This participation introduces a significant f-orbital antibonding component, which weakens the I–I bond within I₃^{*}, lowers the transition-state energy, and facilitates I–I activation. La lacks such an f channel (4f⁰), while the

highly localized Sm 4f⁵ orbital cannot contribute effectively.

This mechanism is supported by the Mayer bond orders (Fig. R1f), which show that Ce maintains the optimal M–I bond strength. In addition, the reaction enthalpy diagram (Fig. R1d) further confirms this trend by revealing the lowest overall energy barrier for Ce.

Together, these results demonstrate that Ce uniquely combines a favorable *d*-band position with an f-orbital-derived antibonding interaction, making it the most active f-block SAC for I₂ activation.

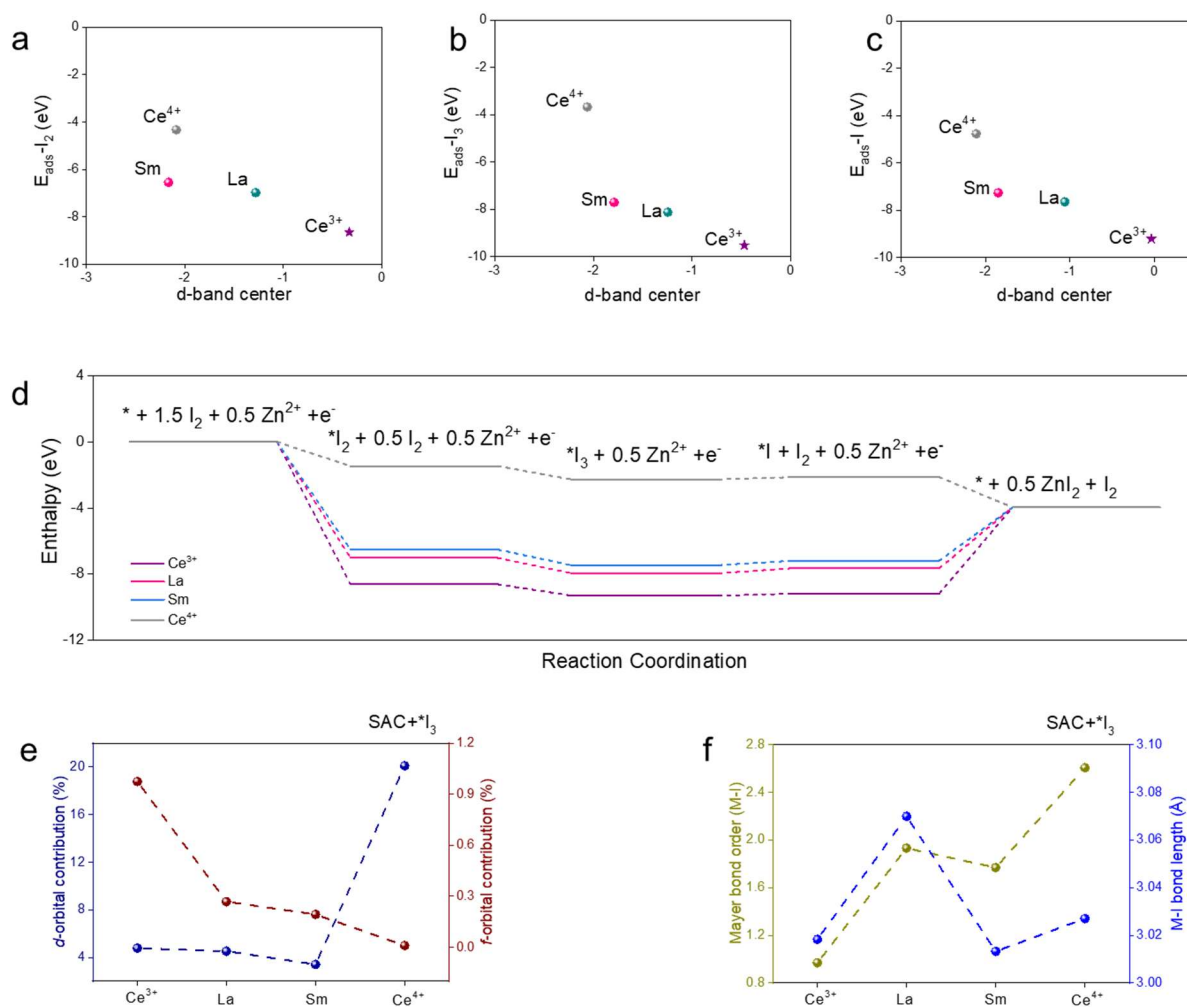


Figure R1. a–c, Correlation between the d-band centers of Ce SAC with Ce³⁺, La SAC, Sm SAC, and Ce SAC with Ce⁴⁺ and the adsorption energies for I₂^{*} (a), I₃^{*} (b) and I^{*} (c) intermediates. d, Enthalpy diagram for the I₂ reduction reaction on the above SACs. e, Orbital composition of the above metal d and f states and f, total Mayer bond orders in SAC+I₃^{*} structures, as the rate-determining step.

2. The discussion on mechanical degradation at loadings $>10 \text{ mg cm}^{-2}$ is mentioned. A further analysis of electrode architecture or strategies to mitigate stress heterogeneity could strengthen the practical narrative.

Reply: We thank the reviewer for this valuable suggestion. We agree that a deeper analysis of strategies to mitigate stress heterogeneity is crucial for practical high-loading electrodes. The post-cycling SEM analysis revealed that the significant performance decay at high mass loadings ($>10 \text{ mg cm}^{-2}$) is primarily due to micro-crack formation within the thick electrode (Figure R2). This is caused by the repeated volume changes and stress concentration during cycling, which is exacerbated when the electrode thickness increases without a proportional adjustment in the stack pressure. These cracks degrade the ionic/electrical contact pathways, leading to increased impedance and rapid failure.

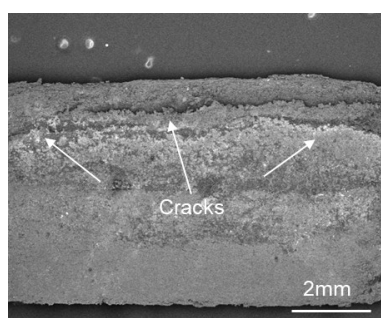


Figure R2. SEM image of the Ce SACs/I₂ cathode cross-section.

3. The XPS data indicates a mixture of Ce^{3+} and Ce^{4+} . In-depth discussion on their respective roles in the catalytic cycle would provide deeper mechanistic insight, e.g., which state is more critical for adsorption vs. charge transfer?

Reply: We thank the reviewer for this important point. The coexistence of Ce^{3+} and Ce^{4+} in XPS is expected for *f*-block systems with flexible valence states. DFT calculations enable us to distinguish their mechanistic roles.

Ce^{3+} is the catalytically active state for iodine adsorption and I–I bond activation. As shown in Fig. R1a–c, Ce^{3+} exhibits a higher d-band center and therefore provides moderate, optimally balanced adsorption energies for I_2^* , I_3^* , and I^* . More importantly, Ce^{3+} retains a partially filled and moderately delocalized $4f^n$ orbital. Orbital composition analysis (Fig. R1e) reveals that this $4f^n$ state directly contributes an antibonding interaction with the I–I fragment in I_3^* , exerting

tunable electronic repulsion that weakens the I–I bond and lowers the transition-state barrier. This f -orbital antibonding effect is unique to Ce^{3+} and is responsible for efficient charge redistribution during I–I activation.

In contrast, Ce^{4+} plays a minimal catalytic role. The Ce^{4+} state lacks $4f$ electrons ($4f^0$ configuration), resulting in no f -orbital overlap with I_3^* . Its d -band center is also significantly lower, leading to weaker and less effective adsorption. Consistently, the reaction enthalpy diagram (Fig. R1d) shows that Ce^{4+} has substantially higher barriers and cannot stabilize the key I_3^* intermediates. Thus, Ce^{4+} primarily acts as a spectator state rather than an active site for charge transfer or bond activation.

Overall, Ce^{3+} provides both (i) an optimal adsorption strength arising from its elevated $5d$ states and (ii) a crucial charge-transfer pathway enabled by its near-Fermi-level $4f^1$ antibonding interaction, making it the catalytically dominant state. In contrast, Ce^{4+} does not significantly contribute to either function. These results clearly show that the catalytic function of the Ce center is governed predominantly by the Ce^{3+} state.

4. The variable-temperature EIS analysis, used to determine activation energies, requires the equivalent circuit model and fitting errors to be included in the SI to ensure methodological rigor.

Reply: We greatly appreciate the reviewer's comment. In the revised manuscript, we have included the equivalent circuit diagram, detailed the testing parameters, and reported the fitting errors. These additions provide a clearer understanding of the activation energy calculations.

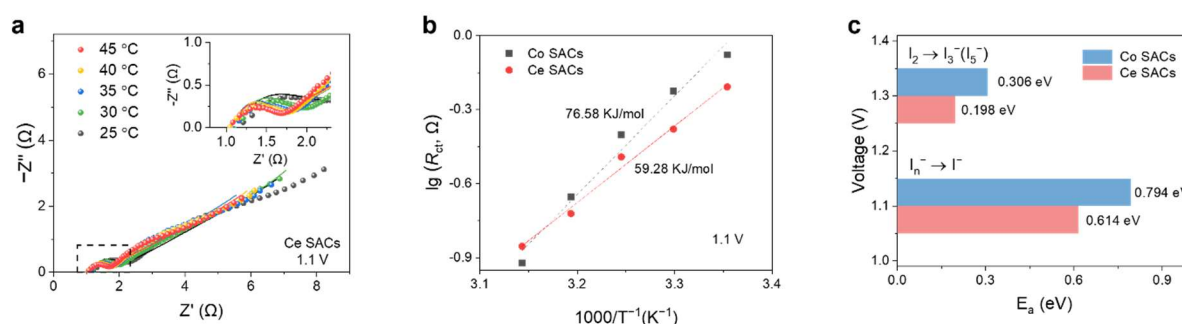


Figure R3. a, Temperature-dependent EIS of Ce SACs/ I_2 cathode at 1.1 V. b, Activation energies derived from Arrhenius plots of Ce SACs/ I_2 and Co SAC/ I_2 cathodes at 1.1 V. c, Activation energies for Ce SACs/ I_2 and Co SAC/ I_2 cathodes at 1.3 V and 1.1 V, respectively.

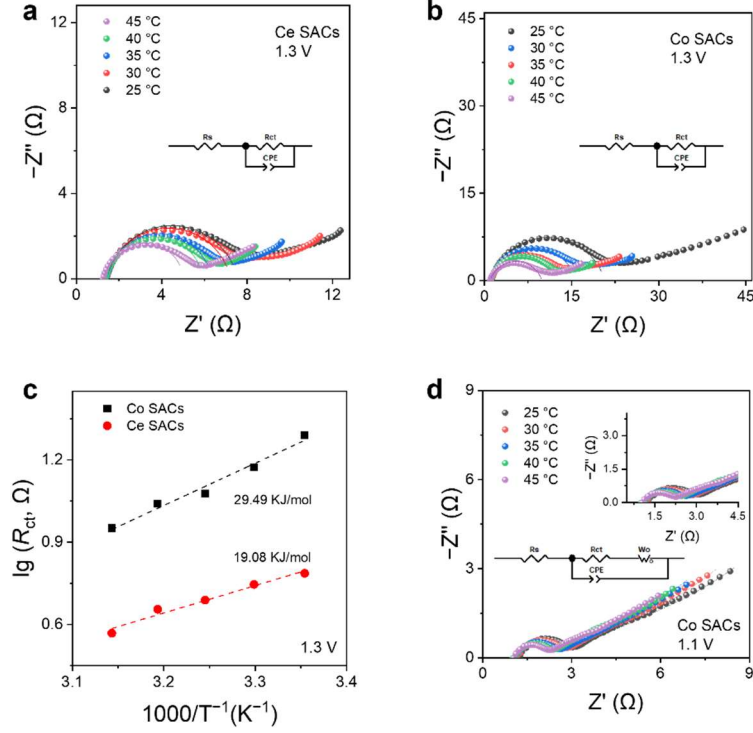


Figure R4. Temperature-dependent electrochemical impedance and activation energy analysis. a, b, Nyquist plots and equivalent circuits of Ce SACs (a) and Co SACs (b) at 1.3 V vs. Zn²⁺/Zn under varying temperatures (25–45 °C). c, Arrhenius plots derived from EIS data at 1.3 V. d, Nyquist plots of Co SACs at 1.1 V vs. Zn²⁺/Zn under varying temperatures (25–45 °C).

Table R1. Fitted R_{ct} values for Zn-I₂ cells with Ce SACs/I₂ and Co SACs/I₂ electrodes at 1.1 V and 1.3 V under different temperatures.

Temperature		25°C	30°C	35°C	40°C	45°C
Ce SACs (1.3V)	R_{ct} (Ω)	6.11	5.57	4.88	4.52	3.70
	Error(%)	3.69	4.33	4.30	4.34	5.74
Co SACs (1.3V)	R_{ct} (Ω)	19.49	14.87	11.92	10.97	8.92
	Error(%)	2.48	2.75	2.79	2.66	3.05
Ce SACs (1.1V)	R_{ct} (Ω)	0.62	0.42	0.32	0.19	0.14
	Error(%)	3.08	2.84	4.12	4.96	6.54
Co SACs (1.1V)	R_{ct} (Ω)	0.84	0.59	0.40	0.22	0.12
	Error(%)	2.45	2.05	3.79	5.84	6.70

Updates in the Revised Manuscript:

We have supplemented the equivalent circuits in the Revised Manuscript and the Revised Supporting Information.

Line 180-183, Page 10: “To unveil the underlying kinetic limitations, temperature-dependent EIS analysis was conducted to quantify the activation energy (E_a) of iodine reduction reactions (IRR) at different potential (Figs. 3c–e, Supplementary Fig. 12 and Supplementary Table 5).”

5. Several experimental details are suggested to be added for reproducibility: the electrolyte volume in coin and pouch cells, and the specific configuration for the in situ Raman/UV-vis cells.

Reply: We thank the reviewer for carefully noting these details. The revised Experimental Section now specifies the electrolyte volumes for both coin and pouch cells, as well as the concentration and path length used in UV–vis analysis.

Updates in the Revised Manuscript:

Page 23 in the Revised Manuscript: The electrolyte used was a 2M ZnSO₄ aqueous solution, with a volume of 80 μL per 2 mg cm^{-2} of cathode mass loading, and this ratio was scaled accordingly for different loadings.

Page 24 in the Revised Manuscript: In situ Raman spectroscopy was acquired using a confocal Raman microscope (LabRAM HR Evolution, Horiba, Japan) with a 532 nm laser, by monitoring the SACs/I₂ cathode surface through the quartz window of a custom two-electrode cell (IVIUM, Netherlands) during galvanostatic charge-discharge cycles.

Page 24 in the Revised Manuscript: In situ UV-vis spectroscopy was conducted on an Evolution 220 spectrophotometer (Thermo Fisher, USA) using a 1 cm path length quartz cuvette as the electrochemical cell, with the cathode and anode secured on opposite sides, ensuring absorbance values were within the optimal linear range.

6. Direct visualization of cycled separators (e.g., through photographs or SEM) would provide additional convincing evidence for the suppressed shuttle effect in Ce SAC-based cells.

Reply: We thank the reviewer for this insightful suggestion. To directly verify the suppression

of the shuttle effect, we have conducted additional cycling tests and captured optical images of the separators from cells with and without the Ce SACs catalyst. As shown in Figure R5, the separator in the Ce SACs-based cell remains significantly lighter, indicating less polyiodide permeation.

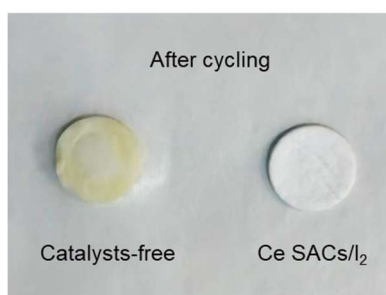


Figure R5. Optical images of separators disassembled from cells with Ce SACs/I₂ and catalyst-free electrodes.

Updates in the Revised Manuscript:

We have supplemented the testing details in the revised Supporting Information.

Line 280-283, Page 16: “Notably, when Co SACs or no catalysts were used, severe surface corrosion on the zinc surface was observed, indicative of rampant polyiodide shuttling. In contrast, smooth morphology with negligible byproduct was detected on zinc anode paired with Ce SACs/I₂ cathode (Supplementary Fig. 23).”

7. The reported specific capacity ($\sim 242 \text{ mAh g}^{-1}$) exceeds the theoretical value for the I_2/I^- redox couple (211 mAh g^{-1}). The authors should clarify the origin of this excess capacity (e.g., contribution from carbon, normalization method, or other redox processes).

Reply: We thank the reviewer for this insightful suggestion. To directly verify the extra capacity contribution, we have conducted additional rate tests of the porous carbon. As shown in Figure R6, the porous carbon matrix contributes less than 50 mAh g^{-1} of non-faradaic capacity.

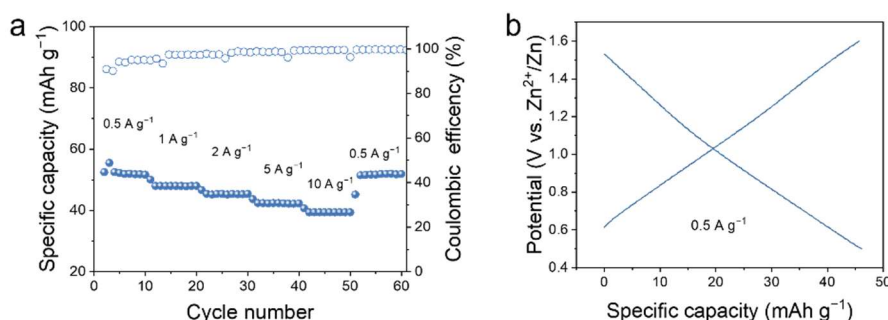


Figure R6. Electrochemical performance of the porous carbon host. (a) Rate capability and corresponding Coulombic efficiency at various current densities. (b) Galvanostatic charge-discharge voltage profiles at a current density of 0.5 A g^{-1} .

8. For the high-loading pouch cell, a calculation of the iodine utilization rate (areal capacity / theoretical capacity based on I_2 loading) would help quantify the efficiency of active material use.

Reply: We sincerely thank the reviewer for highlighting this important point. We thank the reviewer for this important suggestion. Based on the measured areal capacity ($\sim 6 \text{ mAh cm}^{-2}$) and iodine loading (28.8 mg cm^{-2}), the calculated specific capacity of the pouch cell is 205 mAh g^{-1} , corresponding to an iodine utilization efficiency of approximately 97% relative to the theoretical capacity of iodine (211 mAh g^{-1}). We have incorporated this quantitative analysis into the Revised Manuscript to emphasize the practical significance of our tag-team catalysis strategy.

Updates in the Revised Manuscript:

Line 255-258, Page 14: “At a high loading of 28.8 mg cm^{-2} ($\sim 2.4 \text{ C}$), Ce SACs/ I_2 cells exhibit exceptional stability, retaining 97% iodine utilization over 100 cycles with a near-unity Coulombic efficiency (99.9%) and stable voltage plateaus (Fig. 4i and Supplementary Fig. 21a).”

Reviewer #2:

Chen et al. report an article titled “4f-5d orbital tag-team catalysis empowers high-loading zinc–iodine batteries”. The authors use ML to identify Ce single atom catalysts (SACs) that interact with iodine. From their analyses, the authors argue that their new material is practical for batteries. Although this article is probably publishable after major revisions, there are some imprecisions that should be cleared up prior to publication:

Reply: We sincerely appreciate the reviewer’s positive evaluation and constructive feedback. Below are our detailed responses to each comment.

Major comments:

1. The authors introduce the terminology of “tag team” catalysts. I think such terminology should be clarified. I had not heard this term before. It seems the authors are introducing this new terminology to describe f/d interactions.

Reply: Thank you for this insightful comment. The term "tag-team catalysis" is introduced to describe a mechanistic paradigm, referenced in our manuscript (*Nature* **456**, 841 (2008); *Science* **322**, 77-80 (2008)), where discrete catalytic components function cooperatively yet address distinct mechanistic steps.

In our study, this concept is extended to the orbital level. The "*f-d* orbital tag-team" mechanism describes the functional decoupling of two critical aspects in iodine electrochemistry: The Ce 5*d* orbitals drive strong chemisorption of polyiodides, essential for suppressing the shuttle effect, while the Ce 4*f* orbitals facilitate I-I bond activation by antibonding interactions near the Fermi level, enabling fast conversion kinetics.

Unlike conventional synergism, which often enhances a single function, this “orbital tag-team” mechanism resolves the inherent competition between strong adsorption and facile activation. This division of labor allows the catalyst to bypass the Sabatier-type dilemma, where strong adsorption typically poisons active sites. Consequently, simultaneous immobilization and efficient conversion of intermediates are achieved, which is pivotal for the high-loading performance demonstrated.

Updates in the Revised Manuscript:

Line 68-71, Page 4: “This data-driven screening led to the discovery of a unique f - d orbital tag-team effect^{1,2} in Ce SACs, **a mechanism characterized by the functional decoupling of adsorption and activation into distinct orbital tasks.**”

2. In their results section, the authors state “Unlike conventional approaches that focus primarily on thermodynamic outputs (e.g., adsorption energy or free energy), our method establishes physically meaningful descriptors that characterize the binding strength between the catalyst and iodine, as well as the ability to activate I-I bonds, thereby providing a more universal basis for catalyst screening” and then immediately follow this up with “These descriptors were used to predict two reaction-relevant properties: the adsorption energy of iodine species (ΔE^*I), related to iodine immobilization and shuttle suppression, and the I-I bond length in $^*I_3$, reflecting bond cleavage efficiency.” Is the point that the authors are trying to make that understanding **why** the adsorption energy from a chemical perspective is what they are doing? I would argue that what the authors have done here is not that different, because neither the bader charge nor the number of d/f electrons near the fermi level can be readily be controlled.

Reply: Thank you for raising this important point, which allows us to clarify the conceptual advancement of our work. The primary contribution of our study lies in establishing and validating a **predictive framework** that directly correlates intrinsic electronic properties with catalytic performance for iodine redox in Zn-I₂ batteries, moving beyond traditional post-hoc thermodynamic analysis.

While conventional screening requires computing ΔE^*I for each candidate through demanding adsorption-state calculations, **our framework demonstrates that the intrinsic electronic structure of the pristine catalyst can reliably predict both adsorption energy and bond activation capability.** This enables rapid performance estimation without requiring full adsorption-state computations for each new candidate, significantly accelerating the discovery process.

Regarding descriptor controllability, while fundamental atomic properties are fixed, the electronic environment of a catalytic site can be effectively modulated through coordination engineering. **Our descriptors serve as quantitative indicators of this tunable electronic**

environment, wherein variations in coordination number (e.g., M–N₄ to M–N₃) or the introduction of heteroatoms (e.g., S/O ligands) alter both Bader charge and local electron density. **This tunability underpins the broader applicability of our framework**, suggesting its potential extension not only to other coordination motifs but also to related conversion-type systems such as lithium–sulfur and lithium–selenium batteries, where similar adsorption–activation challenges exist, though further validation would be required.

In summary, our descriptor framework enables the prediction of key catalytic properties directly from a pristine catalyst's electronic structure, bypassing intensive adsorption calculations and enabling a more rational design strategy.

3. There is a lot of description around Zn-I batteries, but then the article talks mainly about Ce-SACs. I am no battery expert, but how these two are related is not clear to me from the early parts of the article. The first time where this is discussed is on page 14. I would urge the authors to give some background on this.

Reply: Thank you for raising this important point regarding the connection between Zn-I₂ batteries and our focus on Ce-SACs. The single-atom catalysts (SACs) are precisely the key component engineered into the cathode of the Zn-I₂ battery to address the core challenges of iodine electrochemistry (shuttle effect and slow reaction kinetics) that we discussed. In response, we have revised the introduction and description of Fig. 1e, f (and Figure R7) to better illustrate the linkage from the very beginning.

Specifically, the introduction now establishes the following context on page 3: “Recent advances have explored the use of 3d-metal single-atom catalysts (SACs) (e.g., Fe, Co) to modulate iodine redox pathways through *d-p* orbital hybridization, a concept previously validated in sulfur reduction catalysis. However, these catalysts face a fundamental constraint well-known as “Sabatier principle”, i.e., insufficient adsorption hinders I–I bond activation while excessive binding over-stabilizes intermediates and impedes catalytic turnover.” This background directly motivates our machine learning (ML) approach to discover more optimal catalysts like Ce-SACs that can overcome this limitation.

Furthermore, to make this contrast visually immediate, we have revised the description of

Figs. 1e and f to explicitly compare a typical 3d-metal SAC (Co–N₄) with our target 4f-metal SAC (Ce–N₄) in the context of polyiodide conversion. The revised description on page 7 is as follows: “We compare the electronic structures and polyiodide adsorption/conversion behaviors of a typical 3d metal SAC (Co–N₄) with 4f metal SAC (Ce–N₄) to elucidate a catalyst design strategy for overcoming the key challenges in Zn–I₂ batteries (Figs. 1e, f). Co–N₄, dominated by localized d orbitals, suffers from insufficient charge transfer to the coordinating N atoms (1.17 |e|), resulting in weak adsorption and sluggish conversion of polyiodides. In contrast, Ce–N₄ engages in tag-team catalysis through the complementary and synergistic interactions of the d/f orbitals with iodine species, enabling stronger adsorption and more favorable redox behavior of polyiodides”.

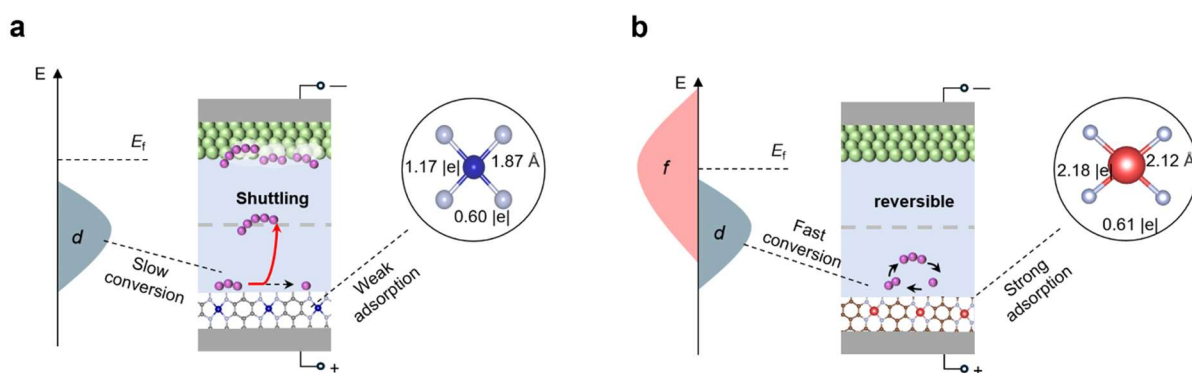


Figure R7. a, b, Schematic illustration of polyiodide adsorption and conversion on Co SACs (a) and Ce SACs (b), respectively.

4. “Moreover, the two descriptors vary independently and are associated with distinct aspects of the reaction mechanism (Fig. 1d)”. To me, it appears that these descriptors are highly correlated, at least in rank. Thus, saying that they vary independently appears incorrect.

Reply: Thank you for this insightful comment. We should agree that the two descriptors are not fully independent (Figure R8), but are not “highly correlated”, either. More quantitatively, the two descriptors (total *d/f* electron count and metal-ligand charge polarization) have a moderate correlation with an *R*² of 0.6. Crucially, we find that they are functionally distinct and effectively link to independent aspects of the reaction mechanism. Our conclusion is based on the following evidence:

N_d+*N_f* (total *d/f* electron count) is the primary descriptor for the I–I bond activation step,

showing a strong correlation with the I–I bond length ($R^2=0.81$) but a much weaker one with adsorption energy ($R^2=0.58$).

Conversely, $\Delta\text{Bader}-N_f$ (metal-ligand charge polarization) is the dominant descriptor for the adsorption step, strongly predicting adsorption energy ($\Delta E^*_{\text{I}}, R^2=0.89$) while poorly predicting the I–I bond length ($R^2=0.48$) in Figure R9. It underscores that the descriptors, while somewhat correlated, are associated with distinct and non-interchangeable aspects of the catalytic process.

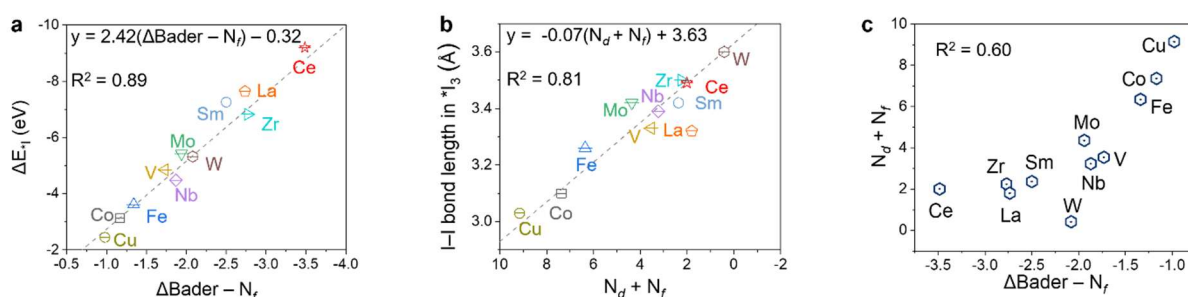


Figure R8. a, Correlation between the adsorption energy of I^- (ΔE^*_{I}) and $\Delta\text{Bader} - N_f$ for different SACs. b, Correlation between the I–I bond length in $^*\text{I}_3$ and $N_d + N_f$ for different SACs. c, The relationship between two descriptors: $N_d + N_f$ and $\Delta\text{Bader} - N_f$.

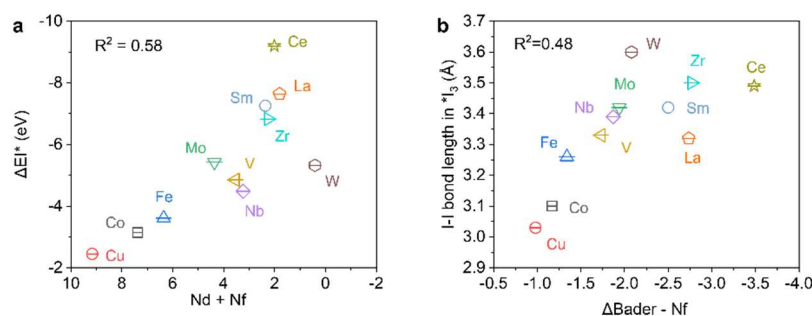


Figure R9. (a) Correlation between the adsorption energy of I^- (ΔE^*_{I}) and $N_d + N_f$ for different SACs. (b) Correlation between the I–I bond length in $^*\text{I}_3$ and $\Delta\text{Bader} - N_f$ for different SACs.

We have revised the relevant sentence to include the quantitative correlation coefficient ($R^2 = 0.6$), providing a more precise description of the descriptor relationship.

Updates in the Revised Manuscript:

Line 110-112, Page 6: “Moreover, while the two descriptors are correlated (Fig. 1d, $R^2=0.6$),

they are linked to distinct aspects of the reaction mechanism (Supplementary Fig. 4), allowing separate regulation of adsorption strength and bond activation.”

5. For Co SACs and other SACs with 3d metals, the authors need to consider open shell electron configurations, which are likely and probable for 3d metals. The work of Kulik has done this on SACs.

Reply: Thank you for raising this critical point regarding the importance of open-shell configurations for 3d-metal SACs. Using open-shell configurations in SAC calculations is critical for correctly describing systems with unpaired electrons. **We would like to clarify that all our DFT calculations for Co and other 3d-metal single-atom sites were performed exactly using spin-polarized, open-shell configurations, just as you commented.** For clearance, we have now explicitly stated this point in the section of computational details in the revised manuscript. Furthermore, we have duly cited the references from Prof. Kulik's group and others on open-shell 3d-metal SACs.

Updates in the Revised Manuscript:

Line 453-463, Page 24: “Spin-polarized DFT calculations were performed using VASP with projector augmented wave (PAW). The Perdew-Burke-Ernzerhof (PBE) functional within the Generalized Gradient Approximation (GGA) was used to represent the exchange correlation potential. The cutoff energy of the plane wave basis is set to 520 eV, and a $6\times6\times1$ Monkhorst-Pack k-point mesh were applied. A vacuum spacing of 25 Å was introduced along the z direction to avoid spurious interactions. The electronic and ionic convergence thresholds were set to 1.0×10^{-5} eV/atom and 1.0×10^{-2} eV/Å, respectively. van der Waals interactions between the substrate and iodine species were treated using the DFT-D3 method with Becke–Johnson damping. All geometric optimizations, adsorption energies, thermodynamic corrections, and *d*-band center calculations were obtained from the spin-polarized ground state, ensuring a physically accurate description of the open-shell configurations commonly exhibited by transition-metal SACs^{47,48}.”

Line 470-481, Page 25: “The differential enthalpy of adsorption for the different surfaces were calculated using the DFT total energies and the thermal correction to enthalpy change ($\Delta H_{\text{corr}}(\text{T})$)

at a specific temperature T:

$$\Delta H = \Delta E_{ads} + \Delta H_{corr(T)} \quad (3)$$

For bonding analyses, including crystal orbital Hamilton populations (COHPs), projected density of states (PDOS), and natural adaptive orbitals (NAdOs) calculations, the optimized spin-polarized structures were placed into a $2 \times 1 \times 1$ supercell and evaluated in a closed-shell configuration during post-processing, as implemented in the CP2K simulation package and MultiWFN program^{51,52}. This step is necessary because the NAdO method operates on spin-paired density matrices and does not support open-shell wavefunctions⁵³. No further structural optimization was carried out under the closed-shell setting, and the qualitative bonding trends were confirmed to be consistent with the spin-polarized electronic structures.”

References

- 47 Leung, K., Nielsen, I. M. B., Sai, N., Medforth, C. & Shelnutt, J. A. Cobalt–porphyrin catalyzed electrochemical reduction of carbon dioxide in water. 2. mechanism from first principles. *J. Phys. Chem. A* **114**, 10174-10184 (2010).
- 48 Nandy, A. & Kulik, H. J. Why conventional design rules for C–H activation fail for open-shell transition-metal catalysts. *ACS Catal.* **10**, 15033-15047 (2020).
- 51 Kühne, T. D. *et al.* CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations. *J. Chem. Phys.* **152**, 194103 (2020).
- 52 Lu, T. & Chen, F. Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **33**, 580-592 (2012).
- 53 Casals-Sainz, J. L., Fernández-Alarcón, A., Francisco, E., Costales, A. & Martín Pendás, Á. Bond Order Densities in Real Space. *J. Phys. Chem. A* **124**, 339-352 (2020).

6. When the authors consider SACs computationally, they assume certain coordination environments. There is no direct proof that the synthesized SACs have these coordination environments. Do the authors have reasoning for this?

Reply: Thank you for raising this important point. The coordination environments in our computational models are based on experimental evidence. For the representative Co and Ce

SACs presented in this work, we performed synchrotron X-ray absorption spectroscopy (XAS) analysis. Specifically, the fitting of the Extended X-ray Absorption Fine Structure (EXAFS) spectra, as shown in Figure R10b and d, provides direct evidence for the first coordination shell. The results confirm a coordination number of approximately 4 for both metals, which directly validates our tetra-coordinated computational models. For other metal SACs studied computationally, while not directly characterized here, extensive literature on the molten-salt annealing method consistently confirms that it predominantly yields tetra-coordinated (M-N₄) single-atom structures^{31,32}. In summary, our computational models are grounded in both direct experimental validation and consistent literature reports, ensuring their relevance to the synthesized SACs.

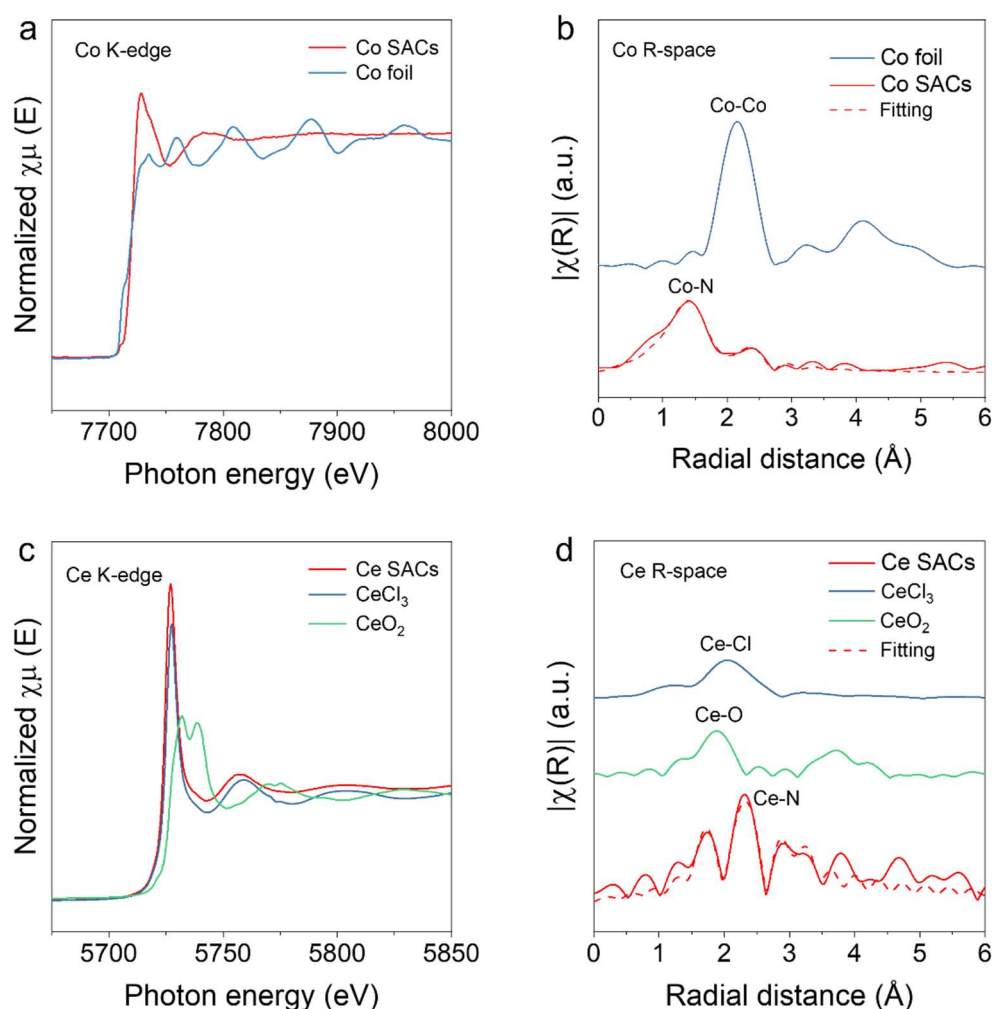


Figure R10. a. Synchrotron radiation analysis of Co and Ce SACs. (a, c) X-ray absorption near-edge structure (XANES) spectra for Co and Ce SACs, respectively. (b, d) Extended X-ray absorption fine structure (EXAFS) spectra for Co and Ce SACs, respectively.

Table R2. Curve fit parameters of Co K-edge EXAFS for Co SACs.

Sample	Path	N	R/(Å)	$\sigma^2/\text{\AA}^2$	$\Delta E/\text{eV}$	R factor
Co SACs	Co-N	4.00	1.946	0.015	0.077	0.009

Table R3. Curve fit parameters of Ce K-edge EXAFS for Ce SACs.

Sample	Path	N	R/(Å)	$\sigma^2/\text{\AA}^2$	$\Delta E/\text{eV}$	R factor
Ce SACs	Ce-N	4.00	2.021	0.010	-0.100	0.020

Updates in the Revised Manuscript:

We have supplemented the experimentally determined coordination structures of the Co and Ce SACs from XAS analysis in the revised Manuscript and Supplementary information.

Line 156-161, Page 9: “Furthermore, to determine the local coordination environment of these isolated atoms, we performed synchrotron-based X-ray absorption spectroscopy (XAS). Quantitative analysis of the extended X-ray absorption fine structure (EXAFS) spectra confirms the dominant presence of a four-coordinate configuration for the metal centers (Supplementary Fig. 8 and Tables 3, 4), which is consistent with our computational models.”

References

- 31 Han, L. *et al.* A single-atom library for guided monometallic and concentration-complex multimetallic designs. *Nat. Mater.* **21**, 681-688 (2022).
- 32 Xiong, Y. *et al.* Gram-scale synthesis of high-loading single-atomic-site fe catalysts for effective epoxidation of styrene. *Adv. Mater.* **32**, 2000896 (2020).

7. The authors should provide all their calculated geometries on zenodo, instead of the images they currently provide.

Reply: Thank you for this valuable suggestion. In response, we have uploaded the key computational geometries from this work to a Zenodo repository. This dataset includes the optimized structures of the M-N-C single-atom sites and relevant adsorption intermediates in VASP format (CONTCAR files). The repository is publicly available at <https://doi.org/10.5281/zenodo.17629945>. A corresponding data availability statement,

including this DOI link, has been added to the revised manuscript.

Updates in the Revised Manuscript:

Line 501-503, Page 26: “The VASP-format optimized structures of the M-N-C catalysts and the relevant adsorption intermediates that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.17629945>.”

Reviewer #3 (Remarks to the Author):

This manuscript presents a comprehensive study on the design of a cerium single-atom catalyst (Ce SAC) for high-loading zinc-iodine batteries, addressing the trade-off between adsorption strength and redox kinetics, which is a fundamental challenge in conversion-type cathodes. The proposed “f-d orbital tag-team catalysis” mechanism is innovative and well-supported by a combination of machine learning screening and DFT calculations. The experimental results, particularly the high areal capacity and pouch cell demonstration, are impressive and highlight the practical relevance of the work. Overall, this manuscript is well-organized with solid data presented, contributing to the understanding of f-block catalysts and designing of high-loading conversion-type cathodes. I recommend its publication in Nature Communications with the following suggestions:

Reply: We sincerely appreciate the reviewer’s positive evaluation and constructive feedback. Below are our detailed responses to each comment.

1. To further strengthen the proposed "f-d orbital tag-team" mechanism, it would be helpful to provide additional theoretical analysis, such as charge density difference or Bader charge calculations, to more directly quantify the contribution of Ce 4f orbitals during I-I bond cleavage.

Reply: We thank the reviewer for this insightful suggestion. Following the comment, we added the charge density difference plots in Fig. R11 to visualize the real-space electron rearrangement during adsorption of I_2^* , I_3^* , and I^* on Ce SAC. Although Ce exhibits some electron depletion in all three cases, which reflects normal metal–iodine polarization, the spatial pattern of this redistribution differs markedly among the intermediates. For I_2^* and I^* , the electron depletion around Ce is relatively isotropic, reflecting conventional adsorption mainly governed by Ce-5d polarization. In contrast, the I_3^* complex shows a distinctly directional and fragmented redistribution of electrons along the I-I axis. This anisotropic pattern is consistent with the participation of Ce 4f orbitals, whose localized nature promotes directional antibonding interactions that weaken the I-I bond.

Importantly, the magnitude of electron gain on I_3^* is smaller than in I_2^* and I^* , indicating that I-I activation in I_3^* is not driven by simple charge transfer. Instead, it arises from a local orbital-driven antibonding interaction, consistent with the proposed f - d orbital tag-team mechanism. This interpretation is supported by the PDOS and COHP analyses (Fig. 5 in Manuscript), which distinguish the contributions of Ce $5d$ and $4f$ states. The charge density difference plots further confirm the unique directional electron redistribution in the I_3^* configuration.

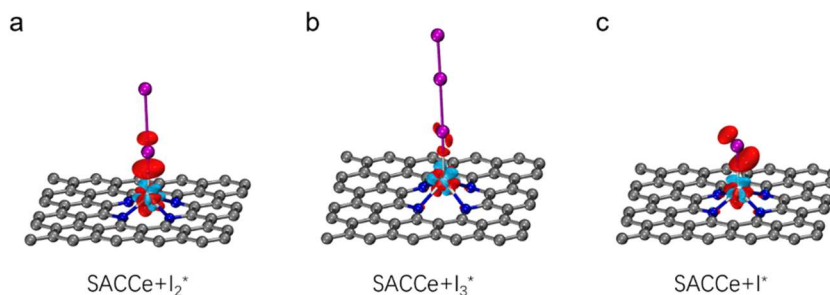


Figure R11. Charge density difference plots for SACCe interacting with (a) I_2^* , (b) I_3^* , and (c) I , where red and blue denote electron accumulation and depletion, respectively.

2. Equivalent circuit fitting of the EIS data, along with relevant parameters and error analysis, would help better support the conclusions regarding charge transfer resistance and interface evolution.

Reply: We greatly appreciate the reviewer's comment. In the revised manuscript, we have included the equivalent circuit diagram, detailed the testing parameters, and reported the fitting errors. These additions provide a clearer understanding of the activation energy calculations.

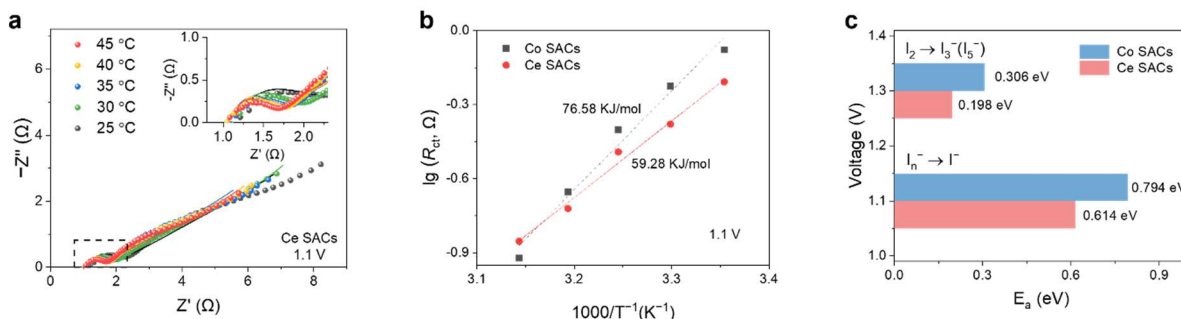


Figure R12. a, Temperature-dependent EIS of Ce SACs/ I_2 cathode at 1.1 V. b, Activation energies derived from Arrhenius plots of Ce SACs/ I_2 and Co SAC/ I_2 cathodes at 1.1 V. c, Activation energies for Ce SACs/ I_2 and Co SAC/ I_2 cathodes at 1.3 V and 1.1 V, respectively.

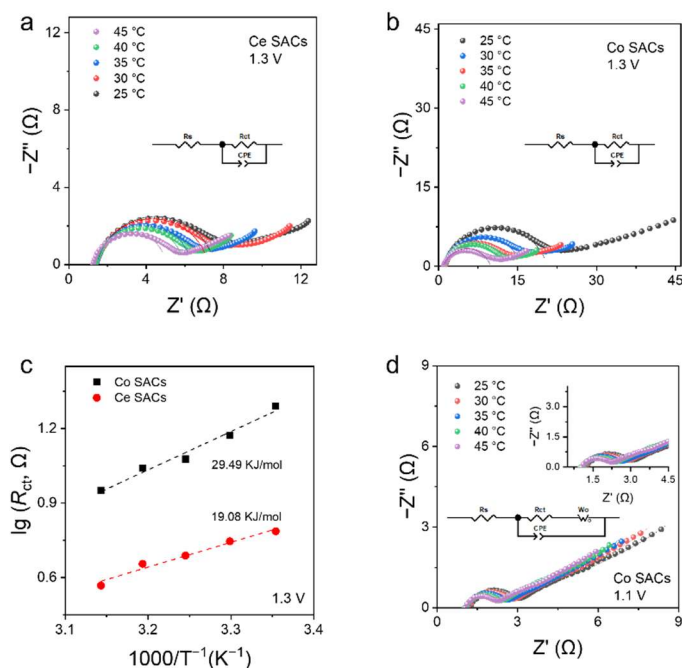


Figure R13. Temperature-dependent electrochemical impedance and activation energy analysis. a, b, Nyquist plots and equivalent circuits of Ce SACs (a) and Co SACs (b) at 1.3 V vs. Zn^{2+}/Zn under varying temperatures (25–45 °C). c, Arrhenius plots derived from EIS data at 1.3 V. d, Nyquist plots of Co SACs at 1.1 V vs. Zn^{2+}/Zn under varying temperatures (25–45 °C).

Table R4. Fitted R_{ct} values for Zn- I_2 cells with Ce SACs/ I_2 and Co SACs/ I_2 electrodes at 1.1 V and 1.3 V under different temperatures.

	Temperature	25°C	30°C	35°C	40°C	45°C
Ce SACs (1.3V)	$R_{\text{ct}} (\Omega)$	6.11	5.57	4.88	4.52	3.70
	Error(%)	3.69	4.33	4.30	4.34	5.74
Co SACs (1.3V)	$R_{\text{ct}} (\Omega)$	19.49	14.87	11.92	10.97	8.92
	Error(%)	2.48	2.75	2.79	2.66	3.05
Ce SACs (1.1V)	$R_{\text{ct}} (\Omega)$	0.62	0.42	0.32	0.19	0.14
	Error(%)	3.08	2.84	4.12	4.96	6.54
Co SACs (1.1V)	$R_{\text{ct}} (\Omega)$	0.84	0.59	0.40	0.22	0.12
	Error(%)	2.45	2.05	3.79	5.84	6.70

Updates in the Revised Manuscript:

We have supplemented the equivalent circuits in the Revised Manuscript and the Revised Supporting Information.

Line 180-183=3, Page 10: “To unveil the underlying kinetic limitations, temperature-dependent EIS analysis was conducted to quantify the activation energy (E_a) of iodine reduction reactions (IRR) at different potential (Figs. 3c–e, Supplementary Fig. 12 and Supplementary Table 5).”

3. Clarifying the physical state of iodine (e.g., crystalline or amorphous) within the carbon host through XRD or Raman spectroscopy. In addition, quantifying the capacity contribution from the carbon substrate itself would help accurately attribute the electrochemical performance to iodine redox.

Reply: We thank the reviewer for this insightful suggestion. To directly verify the physical state of iodine and the extra capacity contribution, we have conducted XRD analysis and additional rate tests of the porous carbon. As shown in Figure R14 and Figure R15, the iodine is in an amorphous form within the porous carbon, and the porous carbon matrix contributes less than 50 mAh g⁻¹ of non-faradaic capacity.

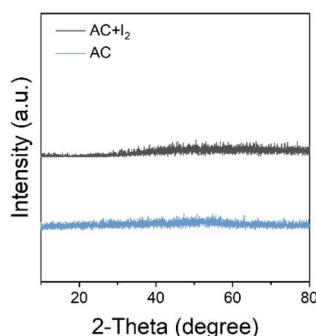


Figure R14. XRD patterns of pristine activated carbon (AC) and iodine-loaded activated carbon (AC+I₂).

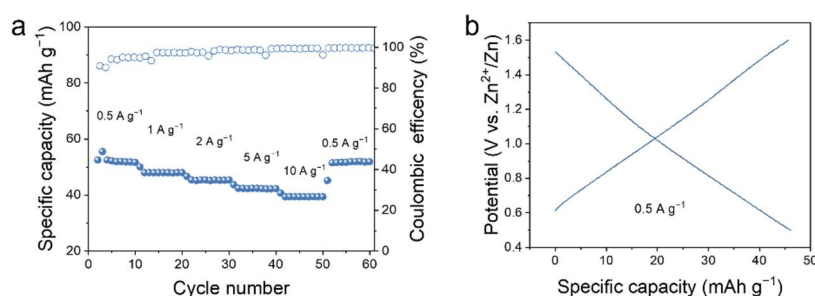


Figure R15. Electrochemical performance of the porous carbon host. a, Rate capability and corresponding Coulombic efficiency at various current densities. b, Galvanostatic charge-discharge voltage profiles at a current density of 0.5 A g^{-1} .

4. Including the UV-Vis calibration curve and fitting details used for polyiodide concentration analysis in the Supplementary Information would improve the reproducibility and reliability of the adsorption measurements.

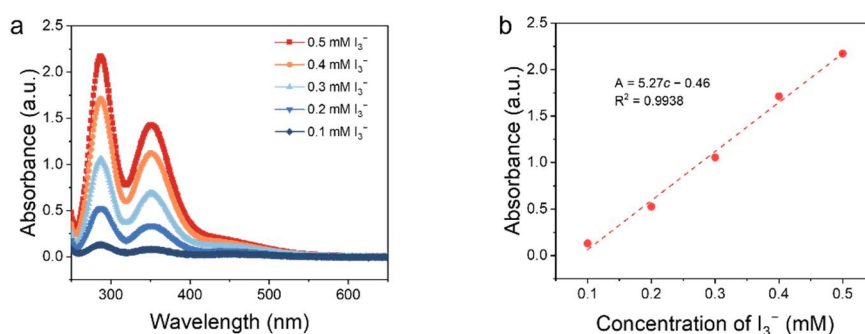


Figure R16. a, UV-Vis absorption spectra of the solution. b, The standard calibration curve of I_3^- concentration.

Updates in the Revised Manuscript:

We have supplemented the calibration curve in the Revised Supporting Information.

Line 166-169, Page 10: UV-vis spectra quantified this phenomenon, revealing that the characteristic I_3^- absorption peaks at 288 nm and 350 nm, were significantly weakened in Ce SAC-treated solutions compared to the control samples (Supplementary Figs. 9a-c).

5. Have the authors explored how different Ce SAC loadings influence the iodine redox kinetics? A correlation between catalyst loading and electrochemical performance could provide valuable insight for further optimizing the material design.

Reply: We thank the reviewer for this insightful suggestion. We performed cyclic voltammetry (CV) measurements with I_2 cathodes at different Ce SAC loadings (4 wt%, 8 wt%, and 16 wt%). The corresponding CV curves are presented in **Figure R 17**. The 8 wt% Ce loading demonstrated the smallest polarization and the highest current density, confirming it as the optimal loading for iodine redox kinetics.

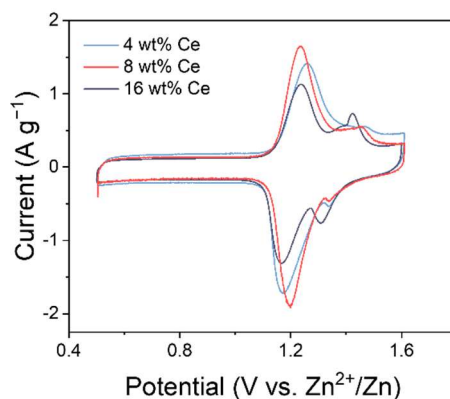


Figure R17. Cyclic voltammetry (CV) curves of cathodes with different Ce SAC loadings at scan rate of 0.2 mV/s.

6. SEM or TEM images of the cathode before and after cycling would be useful to evaluate the morphological and structural stability of the electrode under operating conditions.

Reply: We thank the reviewer for this valuable suggestion. The SEM images show well-preserved electrode morphology after cycling, demonstrating excellent structural stability with no visible degradation.

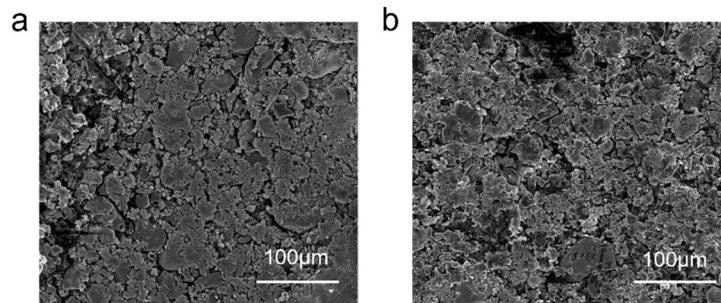


Figure R18. SEM images of the Ce SACs/I₂ cathode (a) before cycling and (b) after 100 cycles at 2 A g⁻¹.

Updates in the Revised Manuscript:

We have supplemented the testing details in the revised Supporting Information.

Line 280-283, Page 16: “Notably, when Co SACs or no catalysts were used, severe surface corrosion on the zinc surface was observed, indicative of rampant polyiodide shuttling. In contrast, smooth morphology with negligible byproduct was detected on zinc anode paired with Ce SACs/I₂ cathode (Supplementary Fig. 23).”

7. To better situate the high-loading performance within a practical context, it would be

beneficial to include cycling stability and efficiency data at moderate loadings (e.g., 2–10 mg cm⁻²).

Reply: We thank the reviewer for this valuable suggestion. To address it directly, we have conducted additional cycling stability tests under moderate mass loadings, specifically at **4 mg cm⁻²** (under current densities of 0.5, 2, and 10 A g⁻¹) and at **8 mg cm⁻²** (under 0.5 and 2 A g⁻¹). As shown in the new figure below, the cells exhibit exceptional long-term cycling stability over 30,000 cycles. These comprehensive data, combined with our previously reported high-loading performance, provide a complete view of our material's capability across various practical scenarios and firmly underscore its robustness and high-rate potential.

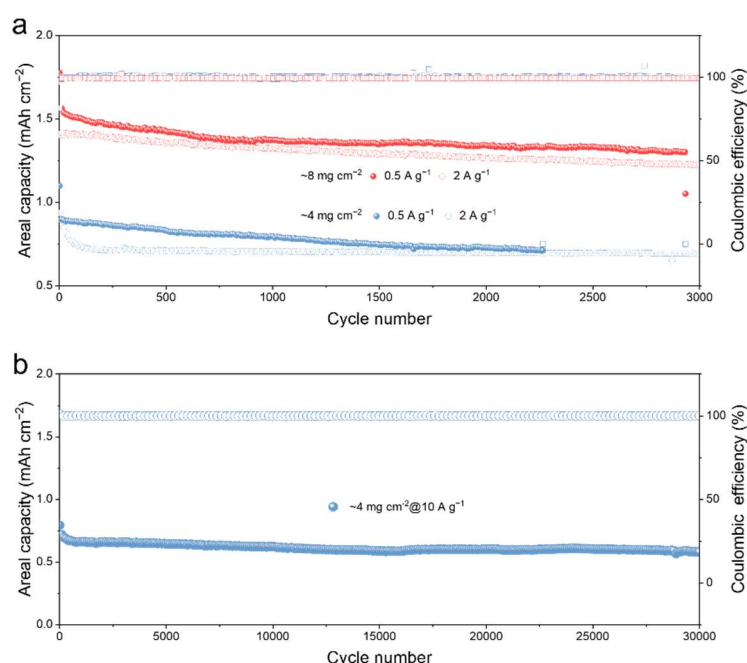


Figure R19. a, Cycling stability and Coulombic efficiency of the electrode at a moderate mass loading of 4 mg cm⁻² under various current densities (0.5, 2, and 10 A g⁻¹). b, The areal capacity retention over 30,000 cycles at a high current density of 10 A g⁻¹ and a mass loading of 4 mg cm⁻².

Updates in the Revised Manuscript:

We have supplemented the testing details in the revised Supporting Information.

Line 242-245, Page 13: “Addressing the practical challenge of high iodine loading, Ce SACs/I₂ cathode sustain nearly linear scaling with areal capacity increasing from 1.75 to 10.06 mg cm⁻².

Moreover, well-defined redox plateaus were preserved across a broad current range (0.5–10 A g⁻¹) (Supplementary Fig. 19).”

8. A direct performance comparison with other recently reported Zn–I₂ systems (particularly in terms of areal capacity, mass loading, and cycling stability) would help readers better appreciate the advances made in this work.

Reply: We thank the reviewer for this valuable suggestion. As recommended, we have now included a direct performance comparison with other state-of-the-art Zn–I₂ systems in the revised supplementary manuscript, which is presented in Supplementary Table 7.

Table R5. Summary of the electrochemical performance of Ce SACs/I₂ in comparison with previous reports, with a focus on mass loading, current density, areal capacity, capacity retention, and cycling stability.

Cathode	Mass loading (mg cm ⁻²)	Current density (A g ⁻¹)	Areal capacity (mAh cm ⁻²)	Capacity retention (%)	Cycling number	Ref.
Ce SACs/I₂	35	0.5	6.1	96	137	This work
	4	10	0.8	74	31700	
B-Fe-NC/I ₂	1	2.11	0.2	99	10000	[2]
I ₂ /PNC-1000	3	0.2	0.7	95	10000	[3]
PAH-PCH gel	3	1.68	0.3	85.6	18000	[4]
Fe SAC-MNC/I ₂	1.2-1.8	0.5	0.2-0.3	81	50000	[5]
SACu@NKB	2	0.2	0.4	92	5000	[6]
I ₂ /NiSAs-HPC	1	1	0.2	94	10000	[7]
Carbon cloth/I ₂	3.2	20	0.7	90	200	[8]
I ₂ /OSTC	1.5-2.5	1	0.3-0.5	85	10000	[9]

G/PVP@ZnI ₂	4.0-5.0	0.2	0.6-0.7	80	1000	[10]
Starch	3	10	0.2	90	50000	[11]
CMK-3@I ₂	1.2-1.5	0.2	0.2	86	10000	[12]
Fe-SAs@BNCF/I ₂	8.2	1	1.3	80	100	[13]
Ferrocene/ferrocenium	30.3	0.1	5	95	200	[14]
NZ-aNC@I ₂	5.5	5	0.8	93	1500	[15]
I ₂ /CCTF-TPMB	3	5	0.5	93.9	30000	[16]

Updates in the Revised Manuscript:

We have supplemented the testing details in the revised Supporting Information.

Line 265-267, Page 14: “These results demonstrate that the *f*–*d* orbital tag team in Ce SACs alleviates key limitations at high iodine loading and offers a promising pathway toward scalable Zn–I₂ batteries for grid-level energy storage (Supplementary Table 7).”