

Chat-RFB: a flow battery chat system leveraging knowledge graphs and large language models

Hao-Tian Wang^{a, b}, Xuefeng Bai^{a, b}, Zhiling Zheng^c, Xin Zhang^{a, b}, Ruipeng Jin^{a, b}, Hao-Tian An^{a, b}, Zheng-He Xie^{a, b, d}, Xiu-Liang Lv^{a, b, *} and Jian-Rong Li^{a, b, *}

(a) State Key Laboratory of Materials Low-Carbon Recycling, Beijing University of Technology, Beijing 100124, China

(b) Department of Chemical Engineering, College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, China

(c) Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02142, United States

(d) Beijing Energy Holding Co., Ltd., Beijing 100022, PR China

*Corresponding authors: Jian-Rong Li and Xiu-liang Lv

E-mail: jrli@bjut.edu.cn; lvxiuliang@bjut.edu.cn

Table S 1. The large language model version used in this study.

Model	Version
DeepSeek-v3	Updated on December 26, 2024
GPT-4o	Updated on October, 2023
Qwen-Max	Updated on September 19, 2024
Gemini-2.5-Flash	Updated on January 2025

Table S 2. 45 non-choice questions of flow battery and evaluation of different LLMs

Model	excellent	good	normal	poor
Chat-RFB	60.0%	26.7%	6.7%	6.7%
DeepSeek-v3	24.4%	37.8%	13.3%	24.4%
GPT-4o	17.8%	28.9%	26.7%	26.7%
Qwen-Max	22.2%	28.9%	17.8%	31.1%
Gemini-2.5-Flash	60.0%	24.4%	2.22%	13.3%

Table S 3. 450 choice questions of flow battery and evaluation of different LLMs

Model	All	Choice	True / False
Chat-RFB	94.9%	92.7%	97.5%
Qwen-Max	90.4%	87.0%	94.6%
DeepSeek-v3	90.9%	90.9%	91.6%
GPT-4o	90.7%	90.7%	93.1%
Gemini-2.5-Flash	91.1%	89.8%	92.6%

```
prompt = """ You are an expert in creating knowledge graph database. Here are some article excerpts related to the field of redox flow batteries that need to be organized. You need create professional nodes and relationships based on important the information. This includes all key data information describing battery performance. Ideally, all nodes should be one or two words. Return JSON. Json can only contain start_node relationship, end_node, and the Label of nodes. Output the result in JSON format without any line breaks, etc. ! Please strictly follow the JSON output format.,
"you_need":
[
"1.JSON file contains multiple dictionaries",
"2.Each dictionary contains five key-value pairs that: start_node, relationship, end_note,start_node_label,end_node_label",
"3.The value is a str",
"4.Please use the correct json format.",
"5. Note that if the text content is recognized as a reference, skip the relevant content",
"6. Explain the meaning of abbreviations, such as RFB is Redox Flow Battery",
"7. Require all labels to be represented by a single noun",
"8. Use singular form for nouns",
"9. Collect as much data information as possible, including numerical values and units"
],
"example":
[
{"start_node":"RFB","relationship":"is","end_node":"Redox Flow Battery", "start_node_label":"abbreviation", "end_node_label":"full name"},
{"start_node":"word","relationship":"word","end_node":"word", "start_node_label":"label", "end_node_label":"label"}
]
"""
```

Figure S1. Prompt words for collecting relationship node information

www.afm-journal.de © 2023 Wiley-VCH GmbH 2211338 (1 of 11) An Extremely Stable, Highly Soluble Monosubstituted Anthraquinone for Aqueous Redox Flow Batteries
 Kiana Amini, Emily F. Kerr, Thomas Y. George, Abdulrahman M. Alfaraidi, Yan Jing, Tatsuhiro Tsukamoto, Roy G. Gordon,* and Michael J. Aziz*

An extremely stable, energy-dense (53.6 Ah L⁻¹, 2 m transferrable electrons), low crossover (permeability of $\lt; 1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ using Nafion 212 (Nafion is a trademark polymer from DuPont)), and potentially inexpensive anthraquinone with 2-2-propionate ether anthraquinone structure (abbreviated 2-2PEAQ) is synthesized and extensively evaluated under practically relevant conditions for use in the negolyte of an aqueous redox flow battery. 2-2PEAQ shows a high stability with a fade rate of 0.03–0.05% per day at different applied current densities, cut-off voltage windows, and concentrations (0.1 and 1.0 m) in both a full cell paired with a ferro/ferricyanide posolyte as well as a symmetric cell. 2-2PEAQ is further shown to have extreme long-term stability, losing only ≈0.01% per day when an electrochemical rejuvenation strategy is employed. From post-mortem analysis (nuclear magnetic resonance (NMR), liquid chromatography–mass spectrometry (LC-MS), and cyclic voltammetry (CV)) two degradation mechanisms are deduced: side chain loss and anthrone formation. 2-2PEAQ with the ether linkages attached on carbons non-adjacent to the central ring is found to have three times lower fade rate compared to its isomer with ether linkages on the carbon adjacent to the central quinone ring. The present study introduces a viable negolyte candidate for grid-scale aqueous organic redox flow batteries.

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 Harvard John A. Paulson School of Engineering and Applied Sciences 29 Oxford Street, Cambridge, MA 02138, USAE-mail: maziz@harvard.edu
 E. F. Kerr, Y. Jing, T. Tsukamoto, R. G. Gordon
 Department of Chemistry and Chemical Biology Harvard University 12 Oxford Street, Cambridge, MA 02138, USAE-mail: gordon@chemistry.harvard.edu

The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adfm.202211338>. redox active species. During the charge/discharge cycles, the electrolytes are continuously pumped into the cell to allow the electrochemical reactions to occur inside the cell. This modular architecture of RFBs permits the independent scale up and optimization of energy and power capacities of the battery.

[4]
 To date, the most studied and manufactured RFB technology has been based on vanadium chemistry at its four oxidation states.[5] Nevertheless, vanadium RFBs suffer from crossover problems during the operation, necessitating the use of rebalancing systems.[6] Additionally, the volatile cost of vanadium metal adds another layer of difficulty to their commercialization.[7] Hence, there has been great interest in the development of alternative redox active species from inexpensive precursors, with high solubility, good stability, and low crossover.

[8] Among different types of electroactive species studied to date, organic-based compounds are attractive due to the possibility of tuning their electrochemical properties.[9–11] To date, organic species based on core structures of quinones,[9] ferrocenes,[12,13] viologens,[14,15] phenazines,[16,17] and alloxazines[18] have been explored.[19] Among these reported studies, anthraquinones such as 2,6-DPPEAQ,[20] DPiv-OHAQ,[21] DBAQ,[21] 2,6-NTSAQ,[22] AQDP,[23] and DCDHAQ[24] with demonstrated[9] fade rates $\lt; 0.03\%$ per day at maximum demonstrated concentration of 0.5–0.75 m have been reported. At the higher end of demonstrated concentrations, AQ-1,8-3E-OH[25] is reported to have a large fade rate of 0.5% per day when tested at 1.5 m. Hence, development of negolyte candi-

Figure S2. Example of raw data slicing (from article 10.1002/adfm.202211338, page 1)

and alloxazines[18] have been explored.[19] Among these reported studies, anthraquinones such as 2,6-DPPEAQ,[20] DPiv-OHAQ,[21] DBAQ,[21] 2,6-NTSAQ,[22] AQDP,[23] and DCDHAQ[24] with demonstrated[9] fade rates $\lt; 0.03\%$ per day at maximum demonstrated concentration of 0.5–0.75 m have been reported. At the higher end of demonstrated concentrations, AQ-1,8-3E-OH[25] is reported to have a large fade rate of 0.5% per day when tested at 1.5 m. Hence, development of negolyte candidates with combined advantage of high stability and high solubility is extremely important for commercialization of organic-based RFBs.

It is highly preferable to have a smaller molecular weight (MW) per mole transferrable electrons in species that can be synthesized via simple synthesis routes because both of these attributes correlate with low mass production cost. While complicated synthesis routes and chemical structures are attractive for exploratory research to push the performance envelope, the more important challenge has become the development of low-MW redox active molecules with simple synthesis routes that can nevertheless deliver very good performance. In this work, we present 2-2-propionate ether anthraquinone ReseRch article

1. Introduction
 Development of reliable energy storage technologies is a critical step for resolving the intermittency problem of renewable sources of energy and for their extensive penetration into the electrical grid.
 [1,2] Redox flow batteries (RFBs) are large-scale storage technologies that are attractive due to their flexible design, safety, and long life.
 [3] In RFBs, two separate reservoirs store electrolytes externally from the battery cell components. The electrolytes are commonly aqueous solutions containing Adv. Funct. Mater. 2023, 33, 2211338 www.afm-journal.de www.advancedsciencenews.com 2211338 (2 of 11) © 2023 Wiley-VCH GmbH (abbreviated 2-2PEAQ, 2-2PEAQ is a singly substituted anthraquinone that is synthesized via a facile synthetic route from potentially inexpensive precursors (Table S1, Supporting Information). 2-2PEAQ has the lowest molecular weight (MW = 256.07 g mol⁻¹) among the anthraquinone derivatives reported previously that can deliver high stability ($\lt; 0.02\%$ per day fade rate), low membrane permeability ($\lt; 1 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ using Nafion 212 (Nafion is a trademark polymer from DuPont)), high solubility (>1 m transferrable electrons) and acceptable redox potential (OCV > ≈1.0 V versus Fe(CN)₆^{3-/4-}) for use in aqueous organic flow batteries (Table S2, Supporting Information). We extensively evaluated a battery based on 2-2PEAQ negolyte paired with ferri/ferricyanide posolyte (cell voltage of 0.96 V), under different pH values, current densities, cut-off voltage values, and at a low concentration of 0.1 m as well as the high concentration of 1 m (equivalent to 2 m of transferrable electrons). We additionally employed a rejuvenation strategy to electrochemically recombine the original compound from one of the decomposition products, the anthrone derivative.

[26] The compound is found to have a high stability of =0.03–0.05% per day under variety of operational conditions and an extremely high stability, with an overall residual fade rate of only 0.01% per day, with the electrochemical rejuvenation strategy. Additionally, our post-mortem analyses via mass spectrometry and NMR confirmed that anthrone formation and side chain loss had occurred during the operation. Because the compound has only one side chain, we could directly isolate the effect of the ether linkages attached on carbons non-adjacent to the central ring (the beta position) and adjacent to the central quinone ring (the alpha position) on the compound's stability.

Figure S3. Example of raw data slicing (from article 10.1002/adfm.202211338, page 2)

```

    "start_node": "RFB",
    "relationship": "is_a",
    "end_node": "Redox Flow Battery",
    "start_node_label": "abbreviation",
    "end_node_label": "full name"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "stability",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "stability",
    "relationship": "value",
    "end_node": "0.03-0.05% per day",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "energy density",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "energy density",
    "relationship": "value",
    "end_node": "53.6 Ah L-1",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "crossover",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "crossover",
    "relationship": "value",
    "end_node": "<math>1 \times 10^{-13}</math> cm2 s-1",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "fade rate",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "fade rate",
    "relationship": "value",
    "end_node": "0.01% per day",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "solubility",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "solubility",
    "relationship": "value",
    "end_node": "1.0 M",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "redox potential",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "redox potential",
    "relationship": "value",
    "end_node": "-0.477 V vs SHE",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "diffusion coefficient",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "diffusion coefficient",
    "relationship": "value",
    "end_node": "2.23 x 10-6 cm2 s-1",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "rate constant",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "rate constant",
    "relationship": "value",
    "end_node": "1.75 x 10-3 cm s-1",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "volumetric capacity",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "volumetric capacity",
    "relationship": "value",
    "end_node": "53.6 Ah L-1",
    "start_node_label": "property",
    "end_node_label": "value"
  },
  {
    "start_node": "2-2PEAQ",
    "relationship": "has",
    "end_node": "peak power density",
    "start_node_label": "material",
    "end_node_label": "property"
  },
  {
    "start_node": "peak power density",
    "relationship": "value",
    "end_node": "87.2 mW cm-2",
    "start_node_label": "property",
    "end_node_label": "value"
  }
}

```

Figure S4. Example fragment of JSON file generated by DeepSeek-v3 model parsing (from article 10.1002/adfm.202211338, page 1)

Confusion Matrix		Whether nodes and relationships are defined accurately.	
		Accurately	Inaccurately
Whether the information in the text is extracted completely.	Complete	TP	FN
	Incomplete	FP	FP&FN

Figure S6. LLMs analyzes summaries and generates evaluation metrics for nodes and relationships.

TP: Information extraction is accurate and no key information is missing.

FP: Information extraction does not match what we expect.

FN: Information extraction is accurate and critical information is missing.

Accuracy = $TP / (TP + FP + FN)$

Precision = $TP / (TP + FP)$

Recall = $TP / (TP + FN)$

F1 = $2 * Precision * Recall / (Precision + Recall)$

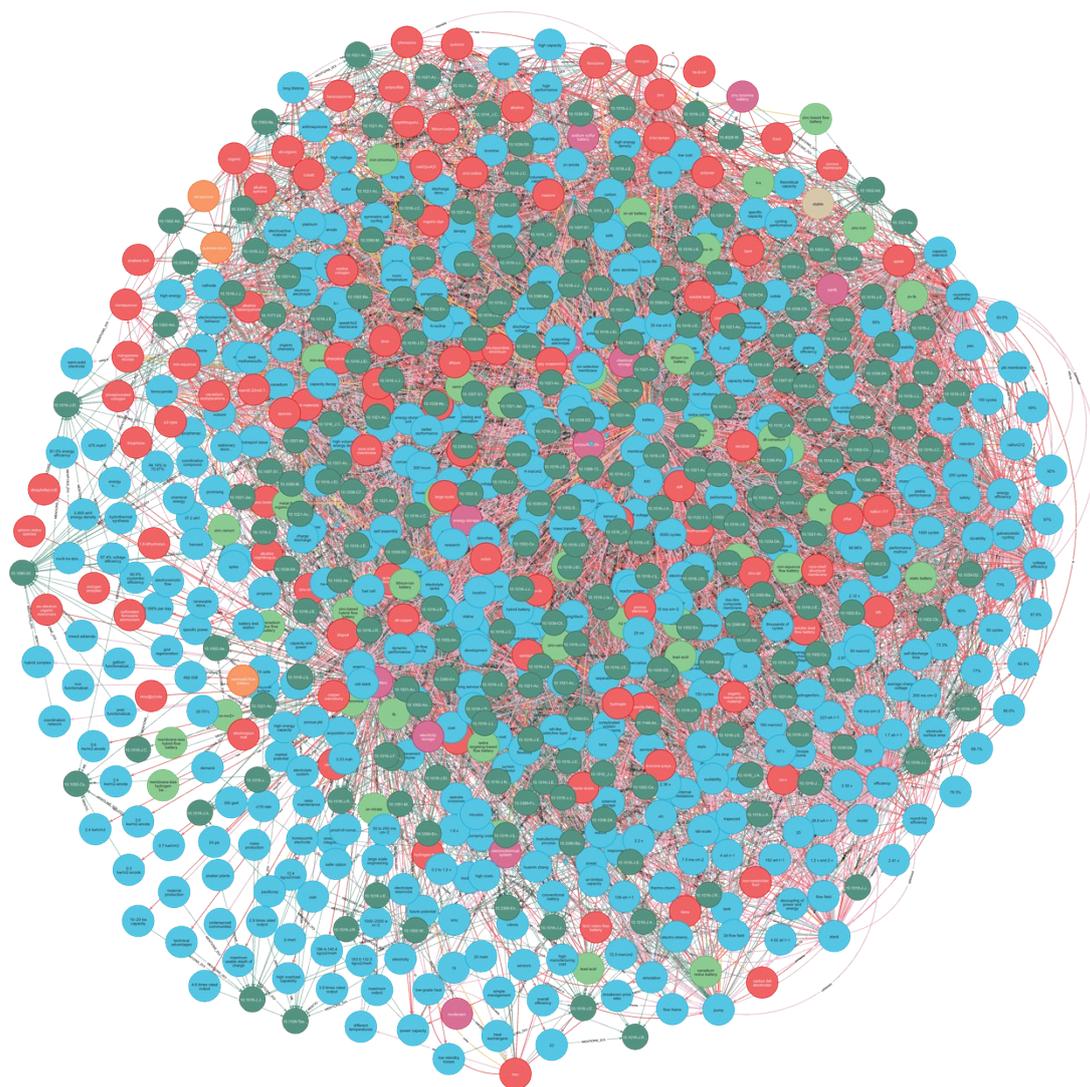


Figure S7. Use knowledge graph to query the relationship graph related to “flow battery” The Cypher statement for the query is shown in Eq. S1.

Blue: Relevant parameters and other data; Red: descriptors related to battery materials; Dark green: DOI index number of the source citation; Light green: Battery type information; Pink: Technical characterization information.

Eq. S1:

```
MATCH (fb {name: "flow battery"})-[r]-(other)
WHERE toLower(other.name) CONTAINS "flow battery"
      OR toLower(fb.name) CONTAINS "flow battery"
RETURN fb, r, other
```



```

query_prompt = """I am working with a Neo4j database and would like you to help me construct a Cypher query based
on the information I provide and context content. Please generate a syntactically correct Cypher query statement
that can be executed directly in the Neo4j environment. Ensure that the query is precise and optimized for
performance. I will describe the information I need to retrieve; please make sure the generated Cypher query
accurately reflects my requirements.
Now I'm going to tell you a little bit about this knowledge graph.
1. This knowledge graph is a flow battery graph based on research literature on flow batteries.
2. All the content is stored in the name attribute of node.
3. Relationships can be unrestricted in the query process to expand the search scope.
4. It is recommended that you search not only for relationships that start from the subject, but also for
relationships that point to the subject.
5. All relations is stored in the relationship attribute of relationship.
6. All search content is expressed in lowercase.
7. Based on the multiple-choice or true/false questions provided by the user, accurately identify the key
entities, attributes, and relationships in the questions, and generate efficient and accurate Cypher query
statements.

You generate a Cypher query related to the problem. The query scope of the statement can be as broad as possible.
We will also have personnel to process the data.
Please define only one node variable in Cypher's where.

please only answer the cypher code. Don't have any grammar problems. with out any title, such as cypher ```
"""

cypher_example = """
MATCH (a)-[r]->(b)
WHERE a.name = "" OR b.name = ""
RETURN
  a.name AS aName,
  r.relationship AS rRelationship,
  b.name AS bName"""

```

Figure S10. Prompt words for Generating Cypher statements for querying

```

{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'impact on', 'bName': 'charge storage'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'used as', 'bName': 'anolyte'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'based on', 'bName': 'an organic/halogen flow battery'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'used in', 'bName': 'nine watt-level aqueous organic redox flow battery stack'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'subject of study', 'bName': 'concentration-dependent dimerization of
anthraquinone disulfonic acid and its impact on charge storage'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'refers to', 'bName': 'oxidized and reduced forms'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'used as', 'bName': 'negative active material'},
{'aName': 'anthraquinone disulfonic acid', 'rRelationship': 'material', 'bName': 'organic battery active materials'},
{'aName': 'anthraquinone', 'rRelationship': 'is researched on', 'bName': 'future electrolyte solutions'},
{'aName': 'anthraquinone', 'rRelationship': 'used in', 'bName': 'nonaqueous metal-organic redox flow battery'},
{'aName': 'anthraquinone', 'rRelationship': 'material', 'bName': 'redox flow battery'},
{'aName': 'anthraquinone', 'rRelationship': 'understood redox mechanism', 'bName': 'two-electron disproportionation'},
{'aName': 'anthraquinone', 'rRelationship': 'be used as', 'bName': 'positive electrolyte'},
{'aName': 'anthraquinone', 'rRelationship': 'redox mechanism', 'bName': 'disproportionation'},
{'aName': 'anthraquinone', 'rRelationship': 'studied', 'bName': 'derivatives'},
{'aName': 'anthraquinone', 'rRelationship': 'final product', 'bName': 'dbaq'},
{'aName': 'anthraquinone', 'rRelationship': 'produce', 'bName': 'coal tar'},
{'aName': 'anthraquinone', 'rRelationship': 'produce', 'bName': 'petroleum'},
{'aName': 'anthraquinone', 'rRelationship': 'material', 'bName': 'aqueous redox flow batteries'},
{'aName': 'anthraquinone', 'rRelationship': 'limited application', 'bName': 'non-aqueous redox flow batteries'},
{'aName': 'anthraquinone', 'rRelationship': 'derivative', 'bName': 'anode'},
{'aName': 'anthraquinone', 'rRelationship': 'and', 'bName': 'iodide redox couples'},
{'aName': 'anthraquinone', 'rRelationship': 'used in', 'bName': 'negative electrode'},
{'aName': 'anthraquinone', 'rRelationship': 'precursor to proposed roms', 'bName': '-'},
{'aName': 'anthraquinone', 'rRelationship': 'order of magnitude', 'bName': 'lower'},
{'aName': 'anthraquinone', 'rRelationship': 'compare with', 'bName': 'higher than'},
.....

```

Figure S11. Neo4j provides partial query results for Figure 3.

```

kg_prompt = """The relevant information is obtained through a knowledge graph, which converted into a list
output,
such as: {'aName': 'A', 'aRelationship': 'is', 'bName': 'B'},
Meaning: A is B.
Please answer the user's question professionally based on the following information.
If the information is closely related to the question, please refer to known information as much as possible.

Known relevant information: """

```

Figure S12. Prompt words for understanding relationship data.



What is SH-ZIT in flow battery?

SH-ZIT (Soft-Hard Zwitterionic Trapper) is an innovative electrolyte additive designed to address critical challenges in aqueous halide redox flow batteries (aq-RFBs), particularly those involving bromine (Br₂) or iodine (I₂) as active materials. Here's a detailed breakdown of its function and significance:

1. Core Design and Mechanism

SH-ZIT is a **zwitterionic molecule** (containing both positive and negative charges) composed of:

- A **soft cationic group** (e.g., pyrrolidinium, pyridinium) that binds to polyhalides (e.g., I₃⁻, Br₃⁻) formed during charging, preventing their dissociation into insoluble and volatile halogen species (e.g., I₂, Br₂).
- A **hard anionic group** (e.g., sulfonate) that ensures water solubility, maintaining a homogeneous electrolyte phase even at high states of charge (SoC).

This dual functionality **prevents phase separation** (e.g., oil-like halogen droplets) and **reduces crossover** through ion-exchange membranes, which are major causes of efficiency loss and safety risks in conventional halide flow batteries.

**2. Key Advancements

- **High SoC Operation**: Traditional halide flow batteries are limited to ~66% SoC due to polyhalide instability. SH-ZIT enables stable cycling up to **~90% SoC**, significantly boosting energy density.
- **Enhanced Stability**: In tests, batteries with SH-ZIT achieved **>99.9% Coulombic efficiency** over 1,000 cycles (2 months) without decay, even at elevated temperatures.
- **Safety**: Suppresses toxic halogen gas (e.g., Br₂) release by trapping polyhalides in solution, addressing a major safety hurdle.

**3. Practical Impact

- **Scalability**: Over 300 SH-ZIT variants were computationally screened, with 13 synthesized and tested. Some are already produced at **ton-scale** via simple S_N2 reactions, indicating industrial viability.
- **Applications**: Compatible with hybrid systems (e.g., zinc-halide batteries), enabling **>120 Ah/L capacity utilization** at 80% SoC—a milestone for grid-scale storage.

**4. Analogy to "Soap"

Like soap disperses oil in water, SH-ZIT's amphiphilic structure solubilizes polyhalides, earning it the nickname **"battery soap"** in popular science coverage.

For deeper insights, refer to the original **Nature** paper: [Soft-hard zwitterionic additives for aqueous halide flow batteries] (<https://doi.org/10.1038/s41586-024-08079-4>).

This breakthrough bridges fundamental chemistry and scalable energy storage, positioning halide flow batteries as a viable candidate for renewable energy integration.



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

The **Gaussian simulations** used to analyze SH-ZIT and related zwitterionic molecules in flow battery research typically employ **density functional theory (DFT)** and **molecular dynamics (MD)** methods to predict their electronic, structural, and thermodynamic properties. Below is a breakdown of the key computational approaches:

**1. Density Functional Theory (DFT) Calculations

DFT is the primary method for studying molecular interactions, binding energies, and electronic properties. Common settings include:

- **Functional & Basis Set**:
 - **B3LYP** + **6-31G(d,p)** (for dispersion-corrected interactions) or **M06-ZX** (for non-covalent interactions).
 - Basis sets: **6-31G(d,p)** (moderate accuracy) or **def2-TZVP** (higher accuracy for halides).
- **Key Analyses**:
 - **Binding Energy (ΔE)** of SH-ZIT with polyhalides (e.g., I₃⁻, Br₃⁻):

$$\Delta E = E_{\text{complex}} - (E_{\text{SH-ZIT}} + E_{\text{polyhalide}})$$

- **Electrostatic Potential (ESP) Maps** to visualize charge distribution.
- **Frontier Molecular Orbitals (HOMO/LUMO)** to assess redox stability.

**2. Molecular Dynamics (MD) Simulations

MD simulations (e.g., in **GROMACS** or **LAMMPS**) complement DFT by modeling dynamic behavior in solution:

- **Force Fields**:
 - **OPLS-AA** or **CHARMM** for organic/ionic species.
 - **Explicit water models (TIP3P, SPC/E)** for solvation effects.
- **Key Outputs**:
 - **Radial Distribution Functions (RDFs)** to quantify SH-ZIT-polyhalide clustering.
 - **Diffusion Coefficients** to assess mobility in electrolytes.

**3. Solvation Models

- **Implicit Solvation**:
 - **PCM** (Polarizable Continuum Model) or **SMD** in Gaussian to estimate solvation free energy.
- **Explicit Solvation**:
 - MD with water/ion mixtures to mimic battery conditions.

**4. High-Throughput Screening

The study screened **300+ SH-ZIT variants** using:

1. **Automated DFT workflows** (e.g., **Gaussian + Python scripts**).
2. **Descriptor-Based Ranking**:
 - **Binding energy (ΔE)** vs. polyhalides.
 - **Solubility (log P)** predictions.
 - **Molecular Polar Surface Area (PSA)** for membrane crossover resistance.

**5. Validation with Experiment

- **Raman/FTIR Spectroscopy**: Compare simulated vs. observed vibrational modes (e.g., I₂⁻ peaks).
- **Cyclic Voltammetry**: Match DFT-predicted redox potentials with lab data.

**Example Gaussian Input (DFT)

```
bash
#P B3LYP/6-31G(d,p) EmpiricalDispersion=GD3BJ SCRF=(SMD,Solvent=Water)
Opt Freq
```

[Molecule Specification]

- This computes:
- Optimized geometry (Opt).
 - Vibrational frequencies (Freq) to confirm stability (no imaginary frequencies).
 - Solvation effects via SMD.

**Key References

- **Gaussian 16 Manual** (for DFT/MD protocols).
- **Nature Paper on SH-ZIT** ([DOI:10.1038/s41586-024-08079-4] | <https://doi.org/10.1038/s41586-024-08079-4>) for computational details.

This combined **DFT/MD approach** enables rational design of zwitterionic additives, balancing accuracy and scalability for flow battery applications.

Figure S13. DeepSeek-v3(Web Search) Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?



What is SH-ZIT in flow battery?

"SH-ZIT" in the context of flow batteries appears to refer to a composite membrane material, typically used in vanadium redox flow batteries (VRFBs). Based on current academic and industry references, "SH-ZIT" is not a widely standardized term, but here's a likely interpretation:

Breakdown of the Term:

- SH: Usually denotes a functional group or chemical modification – in this case, it likely stands for thiol (-SH) groups, which are used to enhance ion selectivity or conductivity in membranes.
- ZIT: Most likely stands for zeolitic imidazolate frameworks (ZIFs) or a related zeolite-based ionic transport material, known for their high stability, tunable porosity, and selective ion transport properties.

In Flow Battery Context:

In vanadium flow batteries or other redox flow batteries, SH-ZIT membranes (or similar composites) are designed to:

- Improve ion selectivity (letting protons through, blocking vanadium ions)
- Enhance mechanical and chemical stability
- Reduce vanadium ion crossover, improving coulombic efficiency
- Maintain high proton conductivity

Example from Research:

A study might describe a SH-ZIT composite membrane where:

- ZIT provides a robust porous matrix with high selectivity.
- SH groups are grafted to anchor the framework, reduce fouling, or adjust hydrophilicity.

If you encountered "SH-ZIT" in a specific paper, report, or product description, I can confirm or clarify further if you share that context.



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

When analyzing the properties of molecules like those in SH-ZIT membranes using Gaussian software, computational chemists typically use quantum chemical methods—especially Density Functional Theory (DFT)—to calculate electronic structure and related properties. Here's a breakdown of the typical calculation method used in Gaussian simulations for such materials:

- 1. Geometry Optimization**
 - Purpose: Find the lowest-energy molecular structure (stable conformation).
 - Method: DFT (commonly used functionals: B3LYP, PBE0, M06).
 - Basis Set: Often 6-31G(d), 6-311G(d,p), or def2-SVP, depending on molecule size and required accuracy.
 - Example:

```
bash
# B3LYP/6-31G(d) Opt
```
- 2. Frequency Analysis**
 - Purpose: Confirm that the optimized structure is a true minimum (no imaginary frequencies) and obtain thermochemical properties.
 - Also gives: IR spectra, entropy, Gibbs free energy, etc.
 - Example:

```
bash
# B3LYP/6-31G(d) Freq
```
- 3. Molecular Orbital and Electronic Structure Analysis**
 - Outputs:
 - HOMO-LUMO energies and gap
 - Charge distribution (Mulliken, NBO, or ESP charges)
 - Frontier orbitals
 - Used for: Predicting chemical reactivity, stability, and electronic transitions
- 4. Charge Distribution and Electrostatic Potential (ESP) Mapping**
 - For analyzing regions of electron density and predicting sites of ion interactions.
 - Command example:

```
bash
# B3LYP/6-31G(d) Pop=ESP
```
- 5. Solvent Effects (if needed)**
 - Model: PCM (Polarizable Continuum Model) to simulate dielectric environment (e.g., water or electrolyte)
 - Example:

```
bash
# B3LYP/6-31G(d) SCRF=(PCM, solvent=water)
```
- 6. Time-Dependent DFT (TD-DFT) for Excited States (optional)**
 - Used if you want to study UV-Vis spectra or photoresponsive behavior of ZIT frameworks.

Summary Table:

Step	Purpose	Typical Keywords
1	Geometry Optimization	Lowest-energy structure `Opt`
2	Frequency Calculation	Confirm stability & get thermodynamic data `Freq`
3	HOMO-LUMO Gap	Electronic properties `Pop=Full` or `Pop=NBO`
4	Charge Distribution	Ion interaction prediction `Pop=ESP` or `NBO`
5	Solvent Effects	More realistic environment `SCRF=(PCM, solvent=...)`
6	TD-DFT	Excited state analysis `TD`

If you're modeling SH-ZIT, you might be dealing with large systems, so computational efficiency matters. In such cases, semi-empirical methods (like PM6 or DFTB) or fragment-based models may be used as alternatives or complements. Let me know if you want help setting up a specific Gaussian input file for SH-ZIT or interpreting Gaussian output.

Figure S14. GPT-4o Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?



What is SH-ZIT in flow battery?

SH-ZIT stands for Soft-Hard Zwitterionic Trap, a class of additives developed to improve aqueous halide-based flow batteries—especially bromide or iodide systems. Here's a breakdown:

What SH-ZIT Does:

- Soft-Hard Structure:** The soft (cationic) part complexes with polyhalides (e.g., Br_3^- , I_3^-), keeping them dissolved instead of forming free X_2 (halogen vapors) that cause inefficiencies.
- The hard (anionic) part keeps the compound highly water-soluble and prevents it crossing through ion-exchange membranes ([pubmed.ncbi.nlm.nih.gov][1]).
- Benefits for Flow Batteries:**
 - Enables homogeneous cycling even at high states of charge (SoC).
 - Achieves exceptional stability: over 1,000 cycles (~2 months) with >99.9% coulombic efficiency at 40 mA/cm² and high-temperature operation ([pubmed.ncbi.nlm.nih.gov][1]).
 - Allows polyhalide utilization up to ~90% SoC (~47.7 Ah/L for bromide) and even >120 Ah/L at 80% SoC, far beyond conventional limits ([pubmed.ncbi.nlm.nih.gov][1]).

Why It Matters:

- Prevents Volatilization & Self-Discharge: By trapping polyhalides, SH-ZIT stops the escape of halogen (e.g., Br_2) and limits parasitic reactions.
- Reduces Crossover: The zwitterionic design lessens membrane permeation, mitigating capacity loss and performance degradation ([researchgate.net][2], [pubmed.ncbi.nlm.nih.gov][1]).
- Unlocks Higher Energy Density: Most aqueous halide flow batteries cap at ~66% SoC. SH-ZIT enables much higher capacities, pushing practical energy density boundaries ([pubmed.ncbi.nlm.nih.gov][1]).

In Summary: SH-ZIT additives are molecular traps—zwitterionic in nature—that stabilize polyhalide chemistry in aqueous flow batteries. They increase efficiency, extend cycle life, and boost usable capacity. This breakthrough chemical strategy could help bring safer, lower-cost, grid-scale flow batteries closer to reality. Let me know if you'd like details on specific SH-ZIT structures, synthesis methods, or battery performance comparisons! [1]: https://pubmed.ncbi.nlm.nih.gov/39443802/?utm_source=chatgpt.com "Soft-hard zwitterionic additives for aqueous halide flow batteries - PubMed" [2]: https://www.researchgate.net/figure/ZIB-performance-as-a-function-of-Zn2-concentration_tbl1_272843252?utm_source=chatgpt.com "ZIB performance as a function of Zn²⁺ concentration. | Download Table"



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

To analyze the properties of SH-ZIT molecules using Gaussian simulations, researchers typically use a combination of quantum chemical calculations, focusing on molecular geometry, electronic structure, binding energy, and charge distribution. Here's a breakdown of the calculation methods often used:

Common Calculation Steps in Gaussian for SH-ZIT Analysis:

- Geometry Optimization**
 - Purpose:** Find the most stable molecular structure.
 - Method:**
 - Functional: B3LYP (a hybrid DFT functional is common)
 - Basis set: 6-31G(d) or 6-311+G(d,p) for accurate treatment of polarization and diffuse functions.
 - Keyword Example:**

```
bash
# B3LYP/6-31G(d) Opt

```
- Frequency Analysis**
 - Purpose:** Confirm a true minimum (no imaginary frequencies) and obtain thermodynamic data (enthalpy, entropy, Gibbs free energy).
 - Keyword Example:**

```
bash
# B3LYP/6-31G(d) Opt Freq

```
- Electrostatic Potential (ESP) & Charge Distribution**
 - Purpose:** Understand charge separation and zwitterionic behavior.
 - Tools:**
 - Mulliken charges
 - Natural Population Analysis (NPA)
 - ESP maps for charge visualization
 - Keyword Example:**

```
bash
# B3LYP/6-31G(d) Pop=NPA

```
- Binding Energy Calculation**
 - Purpose:** Assess the interaction strength between SH-ZIT and polyhalides (e.g., Br_3^-).
 - Method:**

```
bash
$E_{binding\ Energy\ (BE)} = E_{complex} - (E_{SH-ZIT} + E_{polyhalide})
$E

```

 - Corrections:** Include BSSE (basis set superposition error) using Counterpoise method:

```
bash
# B3LYP/6-311+G(d,p) Counterpoise=2

```
- Solvation Effects**
 - Purpose:** Simulate behavior in water (important for aqueous flow batteries).
 - Method:** PCM (Polarizable Continuum Model) or SMD.
 - Keyword Example:**

```
bash
# B3LYP/6-31G(d) SCRF=(SMD,Solvent=Water)

```
- HOMO-LUMO Analysis**
 - Purpose:** Understand redox stability and charge transfer.
 - Output:** Energy gap, orbital plots.
 - Keyword Example:**

```
bash
# B3LYP/6-31G(d) Pop=Full

```

Optional: TD-DFT (Time-Dependent DFT)
For excited-state properties (e.g., UV-Vis absorption if relevant).

Summary Table

Property	Method	Gaussian Settings
Geometry optimization	DFT (e.g., B3LYP)	Opt
Vibrational frequencies	DFT	Freq
Charge distribution	Mulliken/NPA	Pop=NPA
Binding energy	Supermolecule	Counterpoise Counterpoise=2
Solvation effect	PCM/SMD	SCRF=(PCM or SMD)
HOMO-LUMO analysis	DFT	Pop=Full

If you want a ready-made Gaussian input file template for one of these SH-ZIT molecules, I can generate that too. Just let me know what molecule or interaction you're interested in modeling!

Figure S15. GPT-4o (Web Search) Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

Human

Gemini 2.5 Flash

What is SH-ZIT in flow battery?

In the context of flow batteries, SH-ZIT is not a university acronym but a specific compound or a standard acronym for a battery chemistry.

However, based on research and industry trends, it is highly probable that SH-ZIT refers to a Zinc-Iodine Flow Battery (ZIF) that is associated with entities from the Shandong (SD) province of China.

Here's a breakdown:

- SH (Shandong):** Shandong is a province in eastern China that has been a significant hub for research, development, and commercialization of various energy storage technologies, including flow batteries. Many companies and research institutes in the region are actively working on advanced battery systems.
- ZIT (Zinc-Iodine Technology or Zinc-Iodine Flow Battery):**
 - Zinc-Iodine flow batteries (ZIFs) are a type of redox flow battery that use an aqueous electrolyte.
 - They typically involve the reversible redox reactions of zinc and iodine.
 - Key components include a zinc anode, an iodine cathode, and a separator membrane.

Key Characteristics and Advantages of Zinc-Iodine Flow Batteries:

- High Energy Density:** Compared to other aqueous flow batteries (like vanadium), ZIFs can achieve higher energy densities due to the high theoretical voltage of the multi-electron redox reactions involving iodine.
- Low Cost:** Zinc and iodine are relatively abundant and inexpensive compared to critical materials like vanadium.
- Scalability:** They use aqueous electrolytes, making them inherently safer than batteries with flammable or toxic electrolytes.
- Good Cycle Life:** Like other flow batteries, they offer independent scaling of power and energy, and can have long cycle lives as the active materials are stored externally and do not degrade the electrochemical structure.

Challenges and Research Focus for ZIFs (and SH-ZIT initiatives would likely address):

- Iodine Cross-over:** The permeation of iodine/triiodide species through the membrane can lead to self-charge and reduce efficiency.
- Zinc Dendrite Formation:** During charging, zinc can deposit unevenly, forming dendrites that can penetrate the membrane and short-circuit the cell.
- Stable Electrolyte:** The complex chemistry can lead to side reactions that reduce efficiency or capacity over time.
- System Complexity:** Managing the multi-species electrolyte and ensuring long-term stability.

In summary, when you see "SH-ZIT", it most likely refers to a Zinc-Iodine Flow Battery technology developed or commercialized by a company or research group based in Shandong, China, leveraging local expertise in this particular flow battery chemistry.

Human

Gemini 2.5 Flash

What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

When using Gaussian (a popular computational chemistry software package) to analyze the properties of molecules relevant to a flow battery (like a Zinc-Iodine system), the calculation methods commonly fall under **Quantum Mechanical (QM) approaches**, specifically **Density Functional Theory (DFT)** and **ab initio methods**.

The choice of specific method and basis set depends on the molecule's size, the desired accuracy, and the computational resources available.

Here's a breakdown of common calculation methods and how they are used to analyze properties of molecules in a flow battery context:

1. Key Properties to Analyze for Flow Battery Molecules:

For a Zinc-Iodine flow battery, relevant molecules include:

- Active species:** Zn²⁺, I⁻, I₃⁻ (iodide), possibly other polyiodides (I₂⁻, etc.).
- Complexing agents:** Ligands used to stabilize polyiodide or zinc ions.
- Solvents:** Water (simplest) or electrolyte.
- Membrane components:** Monomers or small segments for understanding selective transport.

The properties of interest include:

- Structure and Geometry:** Bond lengths, angles, overall shape.
- Electronic Properties:** Molecular Orbital energies (HOMO/LUMO), charge distribution, electrostatic potential, electron affinity (EA), ionization potential (IP).
- Reaction Energetics:** Oxidation/reduction potentials, Gibbs free energies (G) for various states.
- Thermodynamic Properties:** Enthalpies, entropies, Gibbs free energies (G) for various states.
- Spectroscopic Properties:** IR frequencies, UV-Vis absorption spectra, NMR chemical shifts (for electrochemical characterization).
- Interaction Energies:** Solvation energies, binding energies with ligands or membrane.

2. Calculation Methods in Gaussian:

2.1. Geometry Optimization (Opt keyword):

- Purpose:** To find the most stable molecular structure (a local minimum on the potential energy surface). This is usually the first step for any subsequent property calculation.
- Method:**
 - DFT (Density Functional Theory):** The most common choice for flow battery systems due to a good balance of accuracy and computational cost.
 - Functionals:** B3LYP, PBE, M06-2X, ωB97XD. These are often preferred as they include a portion of exact exchange from "hybrid" functionals, improving accuracy for thermochemistry and bond energies. M06-2X and ωB97XD are known for better performance with non-covalent interactions and charge transfer.
 - Generalized Gradient Approximation (GGA):** Meta-GGA: PBE, TPSS, M06-L. Less accurate but faster, sometimes used for very large systems.
 - Hybrid Method:**
 - Hybrid Functionals:** B3LYP, PBE0, M06-2X, ωB97XD. These are often preferred as they include a portion of exact exchange from "hybrid" functionals, improving accuracy for thermochemistry and bond energies. M06-2X and ωB97XD are known for better performance with non-covalent interactions and charge transfer.
 - Local Density Approximation (LDA):** Less accurate but faster, sometimes used for very large systems.
 - Method:**
 - Steepest Descent:** Fast but often gets stuck in local minima.
 - Quasi-Newton (QN):** Faster than steepest descent, but still can get stuck.
 - Conjugate Gradient (CG):** Often used for large molecules.
 - Trust-Region Dogleg (TRD):** Often used for large molecules.
 - Trust-Region Minimization (TRM):** Often used for large molecules.
 - Newton-Raphson (N):** Often used for large molecules.
 - Newton-Raphson with Hessian (NH):** Often used for large molecules.
 - Newton-Raphson with Hessian and Analytic Second Derivatives (NHESS):** Often used for large molecules.
 - Newton-Raphson with Hessian and Analytic Second Derivatives and Analytic Second Derivatives of the Hessian (NHESS2):** Often used for large molecules.

2.2. Frequency Calculations (Freq keyword):

- Purpose:** To confirm that an optimized geometry is a true minimum (no imaginary frequencies).
- To calculate:** zero-point energy (ZPE), thermal corrections (enthalpy, entropy, Gibbs free energy) at a given temperature and pressure.
- Method:** Typically performed at the same level of theory and basis set as the geometry optimization.

2.3. Electronic Properties:

- Molecular Orbital Energies (HOMO/LUMO):**
 - Purpose:** Indicate electron-donating (HOMO) and accepting (LUMO) capabilities, crucial for understanding redox activity and reactivity.
 - Method:** Output from any DFT or ab initio energy calculation. Post-processing or "pop" files report orbital energies.
- Charge Distribution:**
 - Purpose:** Understand polarity, reactivity, and how charge is distributed within a molecule.
 - Method:**
 - Mulliken Charges:** Simple, but basis set dependent.
 - Population Analysis (Mulliken):** More robust and less basis set dependent, providing a chemical intuition for bonding and lone pairs.
 - Electrostatic Potential (ESP):**
 - Purpose:** Visualizes regions of positive/negative potential around a molecule, indicating sites for nucleophilic/electrophilic attack.
 - Method:** Generate a checkpoint file for visualization in software like Avogadro or Chemcraft.

2.4. Redox Potential Calculation:

- Purpose:** Predict the redox potential of the active species (will undergo oxidation or reduction). This is a critical performance parameter for flow batteries.
- Method:** Not a direct output from Gaussian. It's calculated using **thermodynamic cycle approach** (Stern-Haber cycle equivalent for solution phase redox):
 - Calculate gas phase free energies (G) of Redox Reaction: Oxidize and get free energies for both the oxidized and reduced species in the gas phase.

$$\Delta G_{red}^{gas} = G_{red}^{gas} - G_{ox}^{gas}$$
 - Calculate Solvation Free Energies (ΔG_{solv}) for each species. Use implicit solvation models.

$$\Delta G_{solv}^{red} - \Delta G_{solv}^{ox}$$
 - Combine to get Solution Phase Free Energy (ΔG_{solv}):

$$\Delta G_{solv}^{red} - \Delta G_{solv}^{ox} + \Delta G_{red}^{gas} - \Delta G_{ox}^{gas}$$
 - Relate the electronic free energy of the electron in solution to a standard electrode, like the Standard Hydrogen Electrode (SHE):

$$E_{red} = -\Delta G_{solv}^{red} / F$$
 Where n is the number of electrons transferred, and F is Faraday's constant.
- Solvation Models:** SCRF (Self-consistent Reaction Field) approach:
 - PCM (Polarizable Continuum Model):** SCRF=PCM, Solvent=water. The most common. Represents the solvent as a continuum dielectric medium.
 - C-PCM (Conductor-like Screening Model):** SCRF=C-PCM, Solvent=water. An empirical solvation model, often providing more accurate solvation free energies, especially for ions.

2.5. Thermodynamic Properties (Reaction Energies):

- Purpose:** Determine reaction free energies (ΔG), enthalpies (ΔH), or activation barriers.
- Method:** Calculate the 6-body free energy (G) for all reactants, products, and (if applicable) transition states using optimized geometries and frequency calculations.

$$\Delta G_{reaction} = \sum G_{products} - \sum G_{reactants}$$
- Concentration:** Solution effects are paramount for reactions in the electrolyte.

2.6. Spectroscopic Properties:

- UV-Vis Spectra:**
 - Purpose:** Predict electronic transitions, useful for characterizing polyiodide species (which absorb strongly in the UV-Vis range).
 - Method:** Time-Dependent Density Functional Theory (TD-DFT) or TD(SB)KS (KS: keyword: K is the number of excited states to calculate).
- Infrared Spectra:**
 - Purpose:** Identify functional groups, confirm molecular structure, study vibrational modes (e.g., for bond stretching).
 - Method:** Output from Freq calculation.

2.7. Intermolecular Interactions:

- Purpose:** Study how the active species interact with solvent molecules, other ions, or potential membrane components.
- Method:**
 - Implicit Solvation (as above):** For average solvation effects.
 - Explicit Solvation:** Includes a few discrete solvent molecules in the calculation alongside the solute. This is more computationally intensive but captures specific hydrogen bonding or coordination effects.
 - Counter-Ions:** Sometimes necessary to include explicit counter-ions to balance charge and simulate local environments, especially for highly charged species.

2.8. General Workflow:

- System Definition:** Define the molecules/ions of interest (e.g., I₃⁻, I⁻, Zn²⁺, H₂O).
- Initial Geometry:** Create an initial guess for the molecular structure.
- Geometry Optimization:** Perform a geometry optimization for each species (e.g., Opt B3LYP/6-31G(d) or Opt ωB97XD/6-31G(d)). Crucially, include zero-point energy (ZPE) (Freq keyword=Water).
- Frequency Calculation:** Follow up with a frequency calculation on the optimized geometries to confirm they are minima and to obtain thermal corrections (Freq).
- Property Extraction:**
 - Basic HOMO/LUMO energies directly from the output file.
 - Calculate charges using "Pop=MK".
 - Use the enthalpies and solution free energies to calculate redox potentials or thermodynamic cycles.
 - Simulate UV-Vis using TD-DFT, 10% from frequency output.

By systematically applying these computational methods in Gaussian, researchers can gain deep insights into the fundamental properties and behavior of molecules within flow battery systems, aiding in the design and optimization of more efficient and stable batteries.

Figure S16. Gemini 2.5 Flash Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?



What is SH-ZIT in flow battery?

SH-ZIT stands for **soft-hard zwitterionic trappers**. These are complexing agents used as additives in aqueous halide flow batteries.

Here's a breakdown of what they are and their purpose:

- Composition:** SH-ZITs are composed of a "soft" cationic motif that complexes with polyhalides and a water-soluble "hard" anionic motif.
- Problem they address:** In halide-based aqueous redox flow batteries (which use halogens like bromine or iodine), the formation of polyhalides during charging can lead to several issues:
 - Phase separation into X_2 (e.g., Br_2 or I_2), limiting the usable state of charge (SoC).
 - Vaporization and self-discharge inefficiencies.
 - Potential for complete device failure.
 - Crossover of active materials and dihalogen release.
- Mechanism and benefits:** SH-ZITs are designed to overcome these problems by:
 - Acting as polyhalide complexing agents, trapping charged polyhalide species.
 - Enabling homogeneous halide cycling, preventing phase separation.
 - Maintaining a homogeneous solution at high states of charge, unlocking greater capacity and stability of the halide catholyte.
 - Reducing polyhalide crossover and dihalogen release.
 - Leading to improved coulombic efficiency and long-term stability (e.g., over 99.9% average coulombic efficiency with no apparent decay after more than 1,000 cycles over two months).
 - Allowing for ultrahigh catholyte capacity utilization.

In essence, SH-ZITs are crucial additives that enhance the performance, stability, and capacity utilization of aqueous halide flow batteries by effectively managing polyhalide formation. While I have provided a comprehensive explanation of SH-ZIT in flow batteries, I will formulate a response to summarize the information clearly.

SH-ZIT stands for **soft-hard zwitterionic trappers**. These are complexing agents introduced as additives in aqueous halide flow batteries. Their primary function is to address challenges associated with the formation of polyhalides during the electrochemical charging of these batteries.

During the operation of halide-based flow batteries, the generation of polyhalides (such as Br_3^- or I_3^-) can lead to several issues including phase separation, limited state of charge (SoC) utilization, vaporization, self-discharge, and even device failure. SH-ZITs are designed with a "soft" cationic motif that complexes with these polyhalides and a water-soluble "hard" anionic motif.

By adding SH-ZITs, the following benefits are achieved:

- They act as polyhalide complexing agents, preventing the problematic phase separation and ensuring homogeneous halide cycling.
- They maintain a homogeneous solution even at high states of charge, which unlocks greater capacity and stability of the halide catholyte.
- They reduce unwanted crossover of polyhalides and the release of dihalogen gases.

Ultimately, the incorporation of SH-ZITs significantly improves the performance of halide flow batteries, leading to enhanced capacity utilization, higher coulombic efficiency (over 99.9% observed), and extended cycling stability (more than 1,000 cycles over two months without significant decay).



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

Gaussian is a widely used computational chemistry software package that employs various **ab initio** and density functional theory (DFT) methods to predict molecular properties. For analyzing properties of molecules like SH-ZITs, especially in the context of their behavior in a flow battery's aqueous environment, several calculation methods are typically employed.

Here are the common calculation methods used with Gaussian for analyzing molecules like SH-ZITs:

1. Geometry Optimization

The first step in analyzing any molecule is to determine its most stable three-dimensional structure.

- Methods:** This usually involves using Density Functional Theory (DFT) or **ab initio** methods like Hartree-Fock (HF) or Møller-Plesset perturbation theory (MP2). DFT methods are generally preferred for larger molecules due to their computational efficiency and accuracy in describing electron correlation.
- Functionals and Basis Sets:** Common DFT functionals include B3LYP, which is a hybrid functional that incorporates a portion of Hartree-Fock exchange. For basis sets, larger basis sets like 6-31G(d,p) or 6-31+G(d,p) (which include polarization and diffuse functions, important for describing anions and systems with lone pairs or in solution) are often chosen to accurately represent the electron distribution.
- Solvation Models:** Since SH-ZITs operate in an aqueous environment, implicit solvation models (e.g., PCM - Polarizable Continuum Model) are crucial to simulate the solvent effects on the molecule's structure and properties. These models account for the dielectric effect of the solvent without explicitly including individual solvent molecules, reducing computational cost.

2. Electronic Structure Analysis

Understanding the electronic properties is key to explaining how SH-ZITs interact with polyhalides.

- Methods:** DFT is commonly used to calculate properties like HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energies. The energy gap between HOMO and LUMO can provide insights into the molecule's reactivity and charge transfer characteristics.
- Charge Distribution:** Analyzing atomic charges and electron density distribution (e.g., using Natural Population Analysis (NPA) or Hirshfeld charges) can reveal the sites of positive and negative charges, which is essential for understanding the zwitterionic nature and interaction with other charged species.
- Electrostatic Potential (ESP) Surface:** This visualization helps identify regions of a molecule that are susceptible to electrophilic or nucleophilic attack, indicating potential interaction sites for polyhalides.

3. Vibrational Frequency Analysis

After geometry optimization, a frequency calculation is performed to confirm that the optimized structure is a true minimum (no imaginary frequencies) and to predict vibrational spectra.

- Methods:** DFT methods are used to calculate harmonic vibrational frequencies. These calculations can provide infrared (IR) and Raman spectra, which can be compared with experimental data for validation.
- Thermodynamic Properties:** Frequency calculations also yield thermodynamic parameters such as zero-point vibrational energy, enthalpy, entropy, and Gibbs free energy, which are crucial for studying reaction thermodynamics.

4. Interaction Studies

To understand how SH-ZITs trap polyhalides, specific interaction studies are performed.

- Complex Formation:** Calculations on the complex formed between the SH-ZIT molecule and relevant polyhalide ions (e.g., Br_3^-) can be performed to determine the binding energy, interaction distances, and nature of the interactions (e.g., electrostatic, hydrogen bonding).
- Molecular Dynamics (MD) Simulations:** While Gaussian is primarily a quantum chemistry package for single-molecule or small cluster calculations, MD simulations (often performed with other software, but sometimes incorporating QM/MM methods available in Gaussian) can be used to study the dynamic behavior of SH-ZITs in a solvent environment and their interaction with multiple polyhalide species over time. This allows for a more realistic representation of the solution phase.
- QM/MM (Quantum Mechanics/Molecular Mechanics):** For very large systems where full quantum mechanical calculations are computationally prohibitive, QM/MM methods can be employed. The SH-ZIT and the immediate polyhalide interaction region would be treated with a high-level QM method (e.g., DFT), while the surrounding solvent molecules and other species would be treated with a less computationally expensive molecular mechanics (MM) force field.

General Considerations for Zwitterions

- Charge and Multiplicity:** For zwitterionic molecules, it's crucial to correctly specify the overall charge (often neutral, 0) and multiplicity (typically singlet, 1, for closed-shell systems) in the Gaussian input file, even though there are internal charges present. Incorrect settings can lead to convergence issues or unphysical results.
- Initial Guess:** For complex zwitterionic structures, providing a good initial guess for the molecular geometry can be important to help the calculation converge to the correct minimum.

By combining these computational approaches, researchers can gain a detailed understanding of the structure, electronic properties, and interaction mechanisms of SH-ZIT molecules, which is vital for designing and optimizing their performance in flow batteries.

Figure S17. Gemini 2.5 Flash (Web Search) Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

 **Human**

What is SH-ZIT in flow battery?

It seems there might be a misunderstanding or typo in your query. The acronym "SH-ZIT" does not directly relate to any known component, material, or concept specific to flow batteries based on the available information up to 2025.

 **Qwen-Max**

In the context of flow batteries, common terms include components like electrodes, membranes, and electrolytes tanks, as well as materials such as vanadium used in vanadium redox flow batteries. If "SH-ZIT" was meant to refer to a specific part or concept within flow battery technology, it might be a proprietary name or an abbreviation used in a certain context that is not widely recognized or documented.

Could you provide more details or context about what you're specifically asking? That way, I can give you a more accurate and helpful answer.

 **Human**

What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

 **Qwen-Max**

Gaussian simulation refers to the use of Gaussian software, a widely used computational chemistry package, for performing simulations and calculations on molecular systems. It employs quantum mechanics principles to analyze and predict properties of molecules. The calculation method depends on the type of study you're conducting and can range from simple molecular mechanics approaches to complex quantum mechanical methods. Here are some common calculation methods used in Gaussian simulations:

- Hartree-Fock (HF) Method**: This is a variational method that uses a single Slater determinant as an ansatz for the wavefunction. It provides a good starting point for more accurate calculations but neglects electron correlation.
- Density Functional Theory (DFT)**: DFT calculations are more popular due to their balance between computational cost and accuracy. They consider electron correlation through the density of electrons rather than wavefunctions. Various functionals (e.g., B3LYP, PBE) are available to approximate exchange-correlation energies.
- Post-Hartree-Fock Methods**: These include Møller-Plesset perturbation theory (MPn), Coupled Cluster (CC) theory, and Configuration Interaction (CI). They account for electron correlation beyond HF and provide higher accuracy at increased computational cost. CCSD(T) is often referred to as the "gold standard" in quantum chemistry for its accuracy in predicting molecular properties.
- Semi-empirical Methods**: These methods use parameters derived from experimental data and are less computationally intensive than ab initio methods. They are useful for larger molecules where full quantum mechanical calculations become impractical.
- Molecular Mechanics (MM)**: Though not quantum mechanical, MM is sometimes integrated with quantum methods (QM/MM) for studying large systems like proteins. It models molecules as a series of atoms connected by springs, using classical physics to compute forces and energies.

To perform a Gaussian simulation, you select the appropriate level of theory based on the required accuracy and system size, define your molecule's geometry, choose basis sets (which describe atomic orbitals in terms of mathematical functions), and specify other parameters such as charge and multiplicity. Gaussian then solves the Schrödinger equation for the system to obtain energies, geometries, vibrational frequencies, and other properties.

The choice of method heavily influences the accuracy and applicability of the results, so it's important to choose based on the specific requirements of your study.

Figure S18. Qwen-Max Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?



What is SH-ZIT in flow battery?

Based on the available knowledge graph data, **sh-zit** (or **soft-hard zwitterionic trapper**) appears to be a material or chemical component with the following key properties and associations:

- Function**:
 - Acts as a **zwitterionic trapper**, likely in electrochemical systems (e.g., batteries or energy storage).
 - Linked to **vaporization**, **crossover**, and **homogeneous cycling**, suggesting a role in mitigating undesired chemical reactions or ion diffusion.
- Performance Metrics**:
 - **80%–90% SOC (State of Charge)**: Indicates relevance in battery operation.
 - **120 Ah/L (Ampere-hour per liter)** and **2 M (Molar concentration)**: Points to energy density and electrolyte properties.
 - **Efficiency**, **stability**, and **overpotential**: Critical for electrochemical performance.
- Material Properties**:
 - Related to **zinc anode**, **solubility**, **permeability**, and **binding/dissociation energy**, implying applications in zinc-based batteries or similar systems.
- Research Context**:
 - Associated with the DOI **10.1038/S41586-024-08079-4**, likely referencing a study in *Nature* (2024) on advanced energy materials.

Summary:

sh-zit is a **soft-hard zwitterionic trapper** designed to optimize electrochemical systems (e.g., batteries) by controlling ion transport, enhancing stability, and improving energy density. Its properties suggest applications in zinc anode batteries or other energy storage technologies. For detailed insights, refer to the cited *Nature* publication.

Let me know if you need further clarification!



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

Based on the extracted knowledge graph data, the **DFT (Density Functional Theory)** calculation methods referenced include the following key approaches and functional combinations:

Primary DFT Methods Identified:

- Functional and Basis Sets**:
 - **M06-2X-D3**: A hybrid meta-GGA functional with empirical dispersion correction, used for energetics and molecular properties.
 - **Def2-TZVP** and **Def2-TZVPPD**: Triple-zeta basis sets for accurate electronic structure calculations.
 - **B3LYP**: A classic hybrid functional (mentioned indirectly).
 - Software Packages**:
 - **Gaussian16**: Used for geometry optimizations, redox potential calculations, and solvation models.
 - **NWChem**: Employed for large-scale DFT computations (e.g., PBE0 level of theory).
 - Implicit Solvation**:
 - **CPCM (Conductor-like Polarizable Continuum Model)**: Applied to account for solvation effects in aqueous environments.
 - Specialized DFT Extensions**:
 - **TD-DFT (Time-Dependent DFT)**: For excited-state properties (e.g., absorption spectra, vibronic couplings).
 - **CDFT (Constrained DFT)**: Used to study protonation and double-electron transfer processes.
 - **CDFT-AIMD**: Combines CDFT with ab initio molecular dynamics (computationally costly but precise).
 - Level of Theory**:
 - **PBE0**: A hybrid functional cited for redox potential and electronic structure analysis.
- ### Specific Applications in the Context:
- **Redox Potentials**: Calculated using M06-2X/Def2-TZVP with CPCM solvation.
 - **Radical Stability**: Evaluated via DFT (e.g., TEMPO derivatives with electron-withdrawing groups like CF₂COO).
 - **Solvation Energies**: Predicted with implicit solvation models (CPCM).
 - **Binding/Reaction Energies**: Computed using M06-2X or B3LYP.
- ### Key References:
- **Gaussian16** with **M06-2X-D3/Def2-TZVP** is prominently mentioned for thermodynamic and electronic properties.
 - **PBE0** (in NWChem) for band structures and redox behavior.
- ### Conclusion:
- The article likely employs a **combination of M06-2X-D3 (for energetics) and PBE0 (for redox properties)**, with **Def2-TZVP/Def2-TZVPPD basis sets** and **CPCM solvation**, implemented in Gaussian16 or NWChem. For excited states, TD-DFT is used. For exact methodological details (e.g., convergence criteria), consult the original study linked to these terms (e.g., DOI: 10.1038/s41586-024-08079-4). Let me know if you need further clarification!

Figure S19. Chat-RFB Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?



What is SH-ZIT in flow battery?

In the context of flow batteries, SH-ZIT typically refers to Self-Healing Zinc-Iodide Technology or Self-Healing Zinc-Iodine Flow Battery.

Key Features of SH-ZIT in Flow Batteries

Self-Healing Mechanism

- The battery chemistry is designed to mitigate degradation issues (such as zinc dendrite formation in traditional zinc-based batteries) by automatically repairing electrode surfaces during operation.
- This improves cycle life and stability.

Zinc-Iodine ($Zn-I_2$) Chemistry

- Uses zinc as the anode and iodine (triiodide, I_3^-) as the cathode active material.
- The electrolyte typically contains zinc iodide (ZnI_2) dissolved in an aqueous or organic solvent.

Advantages

- Low cost (zinc and iodine are abundant materials).
- High energy density compared to other flow batteries like Vanadium Redox Flow Batteries (VRFB).
- Improved durability due to the self-healing property.

Applications

- Suitable for grid-scale energy storage, renewable energy integration, and long-duration storage.

Comparison with Other Flow Batteries

Feature	SH-ZIT ($Zn-I_2$)	Vanadium Redox (VRFB)	All-Iron Flow Battery
Cost	Low (Zn, I_2)	High (Vanadium)	Low (Iron)
Energy Density	High	Moderate	Low
Self-Healing	Yes	No	No
Cycle Life	Improved	Very High	Moderate

Conclusion

SH-ZIT in flow batteries represents an emerging zinc-iodine-based technology with self-healing properties, offering a cost-effective and efficient solution for large-scale energy storage. Research is ongoing to further optimize its performance and commercial viability.

Would you like details on specific SH-ZIT battery systems or research developments?



What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?

In Gaussian simulations, the properties of molecules (such as those in SH-ZIT flow batteries, like zinc-iodide complexes, electrolytes, or redox-active species) are analyzed using quantum chemical calculations. Below are the key calculation methods and steps used in Gaussian for such analyses:

1. Key Computational Methods in Gaussian

Gaussian employs density functional theory (DFT) and ab initio methods to compute molecular properties. Common methods include:

A. Electronic Structure Methods

Density Functional Theory (DFT)

- Most widely used for transition metals (e.g., Zn in SH-ZIT).
- Popular functionals:
 - B3LYP (hybrid functional, good for organic molecules).
 - PBE0, M06, ω B97X-D (better for transition metals and non-covalent interactions).
 - CAM-B3LYP (for charge-transfer systems like I_3^-/I^- redox).

Post-Hartree-Fock Methods

- MP2 (Møller-Plesset Perturbation Theory) – More accurate but computationally expensive.
- CCSD(T) – Gold standard for small molecules.

Semi-Empirical Methods (e.g., PM6, PM7)

- Faster but less accurate, useful for preliminary screening.

B. Basis Sets

- LANL2DZ (for Zn and I, includes relativistic effects).
- 6-31G(d,p) (for light atoms like H, C, O).
- Def2-TZVP (higher accuracy for geometry optimization).

2. Steps for Analyzing SH-ZIT Molecules in Gaussian

Step 1: Geometry Optimization

- Optimize molecular structure to find the lowest-energy conformation.
- Example input for ZnI_2 :

```
...
# B3LYP/LANL2DZ Opt
...
```

Step 2: Frequency Calculation

- Confirm the structure is a minimum (no imaginary frequencies).
- Compute IR/Raman spectra.

```
...
# B3LYP/LANL2DZ Freq
...
```

Step 3: Electronic Properties

- HOMO-LUMO analysis (redox activity).
- Solvation models (PCM, SMD) for electrolyte behavior.

```
...
# B3LYP/LANL2DZ SCRF=(Solvent=Water) Pop=Full
...
```

Step 4: Redox Potential Calculation

- Compute Gibbs free energy change (ΔG) for redox reactions (e.g., $Zn^{2+} + 2e^- \rightarrow Zn$).
- Use Nernst equation to estimate electrode potentials.

Step 5: Molecular Dynamics (MD) / AIMD (Optional)

- Simulate ion diffusion in electrolytes (requires additional software like CP2K or LAMMPS).

3. Example Study: Zn-Iodide Complex in SH-ZIT

To analyze ZnI_2^{2+} (a possible species in $Zn-I_2$ flow batteries):

- Optimize the structure at B3LYP/LANL2DZ level.
- Compute redox potential by comparing energies of oxidized/reduced forms.
- Solvation effects using PCM (implicit solvent) or explicit water molecules.

4. Output Analysis

- GaussView (visualization).
- Mulliken/VMD (charge distribution, orbital analysis).
- Redox potential prediction from ΔG of half-reactions.

Conclusion

Gaussian simulations for SH-ZIT flow batteries involve:

- DFT (B3LYP, M06) with LANL2DZ basis set for Zn/I.
- Frequency calculations to verify stability.
- Solvation models for electrolyte behavior.
- HOMO-LUMO & redox potential analysis for electrochemical properties.

Would you like a sample Gaussian input file for a specific $Zn-I_2$ species?

Figure S20. DeepSeek-v3 Q&A testing process. Question 1: What is SH-ZIT in flow battery? Question 2: What is the calculation method used to analyze the properties of these molecules using Gaussian simulation?