

Perspective on Radiolytic Charging for Redox Flow Battery Electrolytes Using the Nuclear Decay Energy of Spent Nuclear Fuel/Radionuclides

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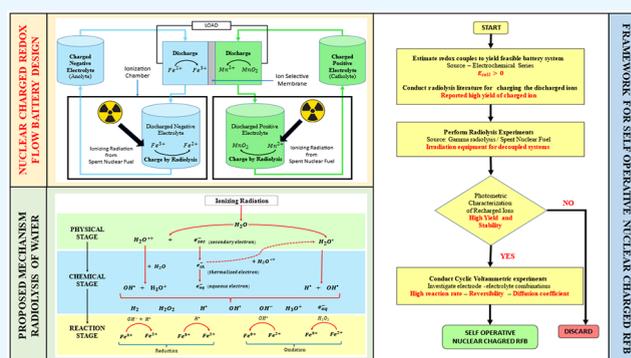
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ABSTRACT: The conversion of nuclear energy into electricity is facilitated by chemical intermediates and molecular products formed during the radiolysis of water. In this work, we hypothesize a novel radiolytic charging approach for redox flow battery electrolytes. Radiolytically produced ionic intermediates and molecular products oxidize or reduce the metal ion solutes in the electrolytes. A qualitative study for choice of redox couples based on electrochemical principles followed by a feasibility study of radiolytic conversion of active material is presented. A framework for an empirical investigation of radioactive source, equipment and dose, and product characterization techniques is discussed. The proposed method finds application in the utilization of spent nuclear fuel (specifically gamma emissions from fission products in early activity stages) as a radiolysis radiation source for electrolyte charging. We present a perspective on future investigations that are required to harness nuclear energy for charging electrolytes and developing a self-operating RFB system.



INTRODUCTION

A redox flow battery (RFB) is an electrochemical energy storage device that converts chemical energy to electrical energy using redox couples dissolved in a supporting electrolyte separated by an ion-exchange membrane. Figure 1 shows a schematic of an RFB. The system is a combination of a positive electrolyte (catholyte) and a negative electrolyte (anolyte) that undergo spontaneous reduction and oxidation

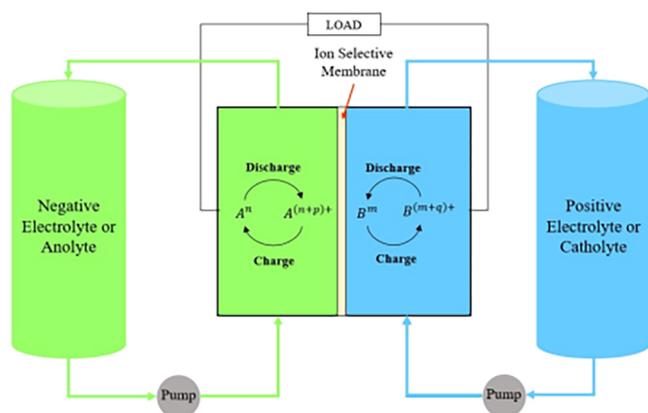


Figure 1. Schematic of a Redox flow battery.

during the discharging cycle, respectively. As these redox reactions occur at the respective electrodes, common counterions (e.g., protons) diffuse through the membrane and electron transfer takes place through the external circuit.¹ Because of the flexibility of its “decoupled” design, an RFB can be independently modified for high energy storage and increased power output. The electrodes and current collectors are housed in the cell stack, independent of the stored electrolytic solutions that are periodically pumped into the power unit for charge–discharge cycles.

Conventionally, RFBs are charged using the power available from the grid, which is generated from hydropower and fossil fuel sources. However, in order to realize a low-carbon society, renewable sources, such as solar energy, have recently found interest as alternative charging sources for RFBs. Solar energy can be employed as an auxiliary energy source for lowering the charging energy input by increasing the electrolyte temperature² or directly used for charging the electrolyte using photoelectrodes in solar flow batteries.³ Solar power faces

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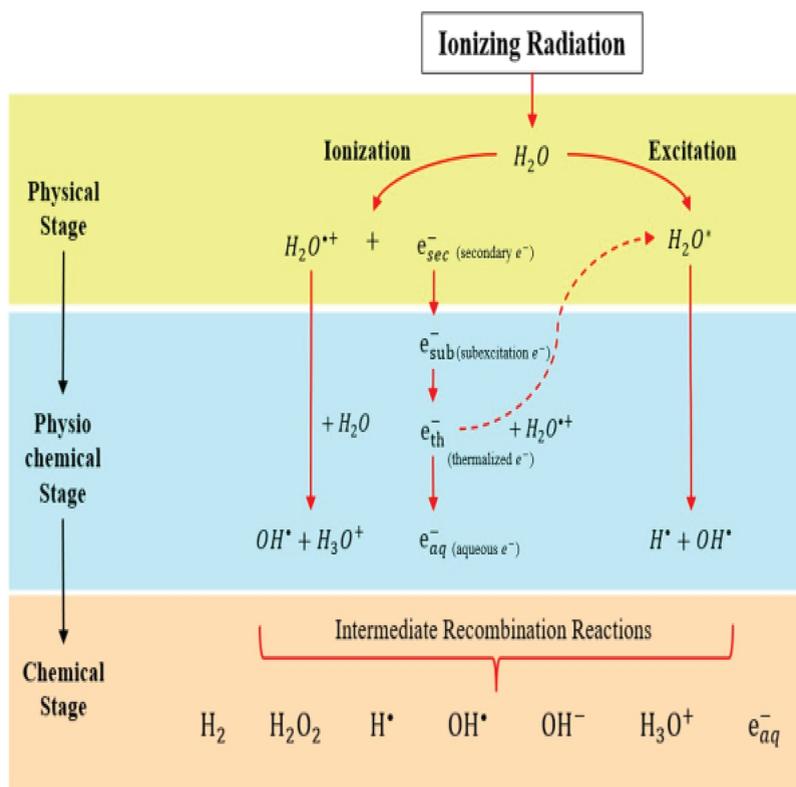
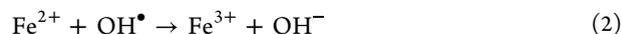
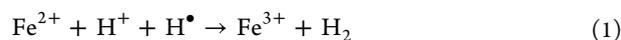


Figure 2. Mechanism of radiolysis of water.

intermittency resulting from daily and seasonal fluctuations across various geographical locations. Nuclear power can be viewed as an alternate energy source due to the long-term radioactivity of radioisotopes.

Nuclear radiation energy is emitted during the fission process and the disintegration of heavy and unstable nuclei (radionuclides). The nuclear decay of radioisotopes results in the release of ionizing radiation, which consists of charged particle radiation (alpha and beta radiation) and neutral particle radiation (neutron and gamma). As the ionizing radiation passes through a medium, nuclear energy conversion to electricity/power can be achieved by utilizing the thermal energy released or via ion production in the medium. Prelas et al.⁴ highlighted the various pathways for energy conversion of radioactive sources for the production of electric power, lasers, and chemicals based on the interaction of ionizing radiation with solids, liquids, and gases.

Nuclear to electric energy conversion through an electrochemical route can be achieved by the interaction of ionizing radiation with liquids through radiolysis. Radiolysis is the dissociation of the water molecules due to the passage of ionizing radiation through water or aqueous solutions producing intermediate products such as free radicals (hydrogen and hydroxyl radicals), solvated electrons, hydronium ions, hydrogen peroxide, and hydroperoxyl radical. Figure 2 depicts the mechanism of radiolysis of water leading to the formation of ionic and molecular intermediate products.⁵ These intermediates react with metallic ions/complexes of aqueous solutions causing the reduction or oxidation of these aqueous metallic ions. For example, the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) occurs by reaction with radiolytic species as follows.⁶



Hence, to develop a nuclear-energy-aided charging cycle for RFBs, the discharged electrolyte must undergo radiolysis using ionizing radiation from a radioactive source wherein the discharged metallic ions react with the radiolytic intermediates to generate ions characteristic of a fully charged RFB system. In this work, we propose a novel charging method for RFBs that harnesses the energy of radioisotopes to ionize the discharged electrolyte. The following text describes our proposed approach and the consequent investigation of the idea.

PROPOSED APPROACH FOR A RADIOLYTICALLY CHARGED RFB SYSTEM

An RFB uses redox-active materials such as ions and molecular species to undergo redox reactions (during discharge) at electrodes, thereby producing electric power. The choice of RFB electrolytes for the nuclear aided charging methodology is primarily based on the possibility of the regeneration of ionic species (of the charged electrolyte) by the reaction of discharged ionic species with radiolytic intermediates.

Figure 3 shows a schematic of the nuclear-radiation-based charging methodology for an RFB system. The catholyte and anolyte are pumped into tanks for temporary storage to undergo radiolysis. Exposure to ionizing radiation causes the discharged active metallic ions/complexes of the catholyte and anolyte to undergo oxidation and reduction, respectively, resulting in a charged RFB system. Post radiolysis, the charged catholyte and anolyte are pumped into the cell stack for power generation thereby providing a closed cycle charging method

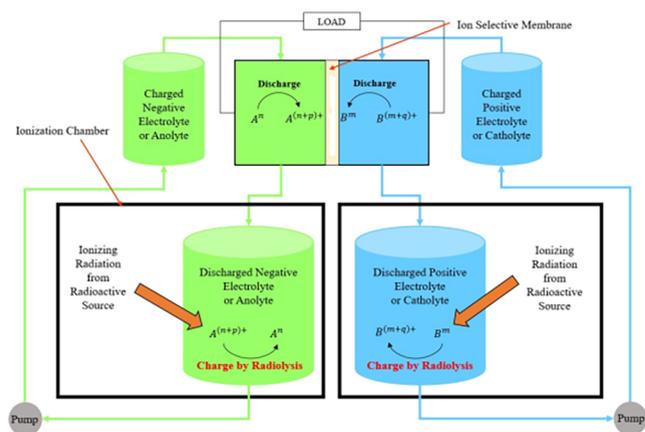


Figure 3. Ionizing radiation-based charging proposed for flow battery electrolytes.

for the RFB system. This approach necessitates the development of a charging unit (ionization chamber) to house the radioactive source and storage tanks. The charging units are decoupled from the cell stack to house the radioactive source. The discharged electrolytes should be stored in these units for sufficient periods to facilitate the charging reaction (oxidation/reduction of the redox mediator) and allow the radiolysis intermediates to achieve stability. Using this design of separate charging units leads to pumping a charged and stable electrolyte into the cell stack, which will not harm the membrane and cell components.

A potential radioactive source for the proposed charging approach is spent nuclear fuel (SNF), which is the primary waste from nuclear reactors after burnup. The high radioactivity of SNF is due to high penetrating ionizing radiation (β and γ radiation) from fission products (e.g., Cs-137 and Sr-90) and less penetrating α -decay comes from very long-lived actinides (e.g., Pu-239 and Np-237) present in it. Spent nuclear fuel is usually disposed directly into geological repository or stored in interim storage facilities (wet pools or dry storage) for reprocessing followed by disposal of high-level liquid wastes.⁷ Owing to its high radioactivity and large availability,⁸ we propose the utilization of SNF as a radiation source for the proposed RFB charging approach potentially alleviating the issue of nuclear waste management. Utilization of nuclear energy implies a prolonged energy source for charging the RFB. This enables the application of RFB systems in remote applications with limited access to continuous conventional power sources such as underwater, military, or space applications.

RESULTS AND DISCUSSION

Exploration of Redox Couples. The open cell voltage (OCV) of an RFB is characteristic of the system chemistry. Metal ion/complex systems from the electrochemical series are investigated to identify feasible RFB chemistries. The study is based on achievable cell potential and literature evidence of oxidation or reduction of the chosen metal-ion systems on radiolysis.

Electrochemical Series and Criterion for Feasible Cell Reaction. The electrochemical series is an arrangement of various elements in the decreasing order of their standard reduction potential. The standard reduction potential of an electrode system (element in contact with its ions) is measured

against a standard reference electrode (e.g., standard hydrogen electrode (SHE), calomel electrode) whose electrode potential is assigned zero by convention. The system with a negative reduction potential undergoes spontaneous oxidation and acts as an anode when connected to SHE. Similarly, that with a positive reduction potential undergoes spontaneous reduction and acts as a cathode relative to SHE. The potential difference is calculated using the equation

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 \quad (3)$$

where E_{cathode}^0 and E_{anode}^0 are the standard reduction potentials of the cathode and anode, respectively. The redox reaction is feasible for energy conversion if E_{cell}^0 is positive.

Radiolysis Literature Survey for Metal Ion Systems from the Electrochemical Series. A comprehensive study of the interaction of ionizing radiation with aqueous metal-ion solutions was performed focusing on the ability of the metal ions to undergo oxidation or reduction upon reaction with radiolysis intermediates (Figure 2). Table 1 lists possible

Table 1. Radiolysis Interaction of Metal-Ion Systems from the Electrochemical Series

| ion | reaction | E_{cell}^0 (V) | radiation | effect | references for radiolysis |
|-----|---|-------------------------|------------------|------------|---------------------------|
| Fe | $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ | 0.77 | gamma | ox | 10,11 |
| | | | gamma | red | 12,13 |
| Cr | $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ | 1.36 | gamma | red | 14 |
| | $\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$ | -0.42 | gamma | ox | 15 |
| Ce | $\text{Ce}^{4+} + \text{e}^- \rightarrow \text{Ce}^{3+}$ | 1.61 | gamma | ox | 6,16 |
| | | | | red | 17,18,19 |
| Mn | $\text{MnO}_4^{1-} + 4\text{H}^+ + \text{e}^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ | 1.7 | gamma | red | 20 |
| | $\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$ | 1.23 | gamma | ox | 20 |
| | $\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$ | -0.255 | gamma | ox | 15 |
| V | | | pulse radiolysis | ox | 21 |
| | $\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$ | 0.337 | gamma | ox | 15 |
| | $\text{VO}_2^{1+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{VO}_{2+} + \text{H}_2\text{O}$ | 1 | gamma | ox | 6 |
| Cu | $\text{Cu}^{2+} + \text{e}^- \rightarrow \text{Cu}^{1+}$ | 0.159 | gamma | red | 6,22,23 |
| Ti | $\text{TiO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{Ti}^{3+} + \text{H}_2\text{O}$ | 0.10 | gamma | ox | 6,24 |
| | $\text{Ti}^{3+} + \text{e}^- \rightarrow \text{Ti}^{2+}$ | -0.37 | gamma | red and ox | 6 |
| Sn | $\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$ | 0.154 | gamma | ox | 25 |
| Mo | $\text{Mo}^{6+} + \text{e}^- \rightarrow \text{Mo}^{5+}$ | 0.53 ²⁶ | gamma | red | 6 |

chemistries with their standard reduction potentials⁹ and the radiation response considering the type or radiation (gamma or pulse radiolysis) and effect (oxidation or reduction).

Krenz et al.¹⁰ noted the oxidation of ferrous to ferric ions in aerated ferrous ammonium sulfate solutions by gamma radiolysis. Hardwick¹¹ investigated the gamma radiolysis of ferrous ions in 0.80 N sulfuric acid and stated a G value (number of molecules consumed or formed per 100 eV of energy absorbed) of 20.8 ± 0.3 molecules of ferric ions. The G value and stability of charged ion allow us to comment on the survival of the redox mediators and the supporting electrolyte subjected to radiolysis. Hart¹² investigated the reduction of the

ferric ion Fe^{3+} to ferrous Fe^{2+} in aqueous formic acid solution and stated that the hydroxyl radical is converted to formate radical during radiolysis which reduces ferric ions. A G value of approximately 7 (i.e., 7 ions of Fe^{2+} produced per 100 eV of absorbed dose) was reported for a mixture of 0.01 N ferric sulfate and 0.01 N sulfuric acid in 0.1 M formic acid. Amphlett¹³ suggested the reduction of ferric to ferrous ions in sulfuric acid solution containing ferric ions and ferric-ferrous ions in H_2SO_4 by gamma irradiation. Irradiation of ferric ions in H_2SO_4 solution (pH 2.46) yields Fe^{2+} with a G value of 15. The author noted that difficulties in irradiation arise for ferric ion solutions above a pH of 2.5 as ferric ions tend to hydrolyze to $\text{Fe}(\text{OH})_2^+$, which leads to loss of Fe^{2+} ions from solution in the form of precipitation of $\text{Fe}(\text{OH})_3$ or colloidal solutions. Irradiation of ferrous-ferric ions in sulfuric acid was observed to cause oxidation of ferrous ions in the solution until 77% of total iron content was in the ferric state, beyond which the ferric ion reduction measurement was hindered due to the steady state achieved in the oxidation and reduction processes.

The OH radical formed during radiolysis was noted to cause the oxidation of Ce^{3+} to Ce^{4+} .⁶ Sworski¹⁷ observed that the oxidation of Ce^{3+} to Ce^{4+} by OH free radical was inhibited using thallos ions (Tl^{1+}), which upon oxidation to thallium-(II) ion (by OH radical) aided in the reduction of Ce^{4+} ions. The radiolytic reduction of Ce^{4+} to Ce^{3+} due to the presence of solvated electrons was observed in aerated nitrate solutions (0.4 M sulfuric acid + nitric acid/sodium nitrate) by Nagaiishi et al.¹⁸ The reduction of Ce^{4+} ions in 0.4 M sulfuric acid upon addition of sodium formate (formic acid) was stated by Sworski,¹⁹ wherein the reaction of OH radical and sulfuric acid gave rise to HSO_4 radical, which caused the reduction of Ce^{4+} .

Ghalei et al.²⁰ studied the oxidation of Mn^{2+} to Mn^{4+} using manganese carbonate (MnCO_3) in carbonate solution and Cs-137 as the radioactive source. Upon the fast oxidation of Mn^{2+} to Mn^{3+} , further irradiation caused the oxidation of Mn^{3+} ions to soluble Mn^{4+} ions, which precipitated as insoluble Mn^{4+} . X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) confirmed the formation of Mn^{4+} oxide precipitate.

Buxton⁶ provided a detailed account of radiation interaction of ionic systems under the effect of ionizing radiation. The reduction of Mo^{6+} to Mo^{5+} was caused by mobile electrons in gamma-irradiated sulfuric acid solution; however, no yield of the reduced Mo^{6+} was noted. The oxidation of V(IV) was suggested upon radiolysis, but no literature on yield and stability of the regenerated VO_2^+ ion was found. Radiolysis of aqueous titanium-formic acid solutions was believed to yield Ti^{2+} upon reduction of Ti^{3+} . The author noted that the Ti^{2+} is unstable and is easily oxidizable by water and no additional evidence for radiolytic reduction of titanium from Ti^{3+} to Ti^{2+} has been found during the course of this study. Furthermore, the oxidation of Ti^{3+} to Ti(IV) by hydrogen atom intermediates was also noted. Gamma radiolysis of sulfuric-acid-based Sn^{2+} solutions yielded Sn^{4+} ions.

The Cu^{2+} ions are rapidly reduced by e_{aq}^- during radiolysis and the possible reduction of Cu^{2+} to Cu^{1+} was noted using pulse radiolysis.⁶ However, owing to a high oxidation reaction rate constant for the $\text{Cu}^{1+}/\text{Cu}^{2+}$ reaction as compared to reduction, the copper ions undergo simultaneous oxidation and reduction reactions in oxygen-based systems. Using Co-60 as a radiation source, Bhattacharya et al.²² studied the degradation of uracil under the influence of Cu^{2+} ions

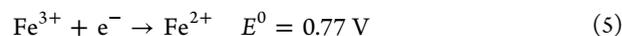
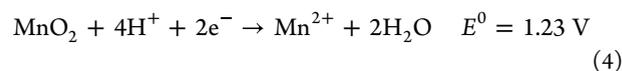
(which was reduced to Cu^{1+}) by gamma irradiation. The author investigated various reduction pathways for Cu^{2+} by uracil adducts formed by radiolysis. Baxendale et al.²⁷ stated that pulse radiolysis of Cu^{2+} solutions resulted in further oxidation of Cu ions instead of reduction.

Redox Couple Combinations for Radiolytically Charged RFB System. For the choice of radiolytically charged RFB electrolytes, first, a pair of metal-ion systems as catholyte and anolyte need to be chosen from the electrochemical series, which yields a positive cell potential (feasible cell arrangement). According to the proposed radiolytic charging cycle for RFB electrolytes, the choice of the redox couple can be validated by the radiolytic oxidation of catholyte species and the reduction of anolyte species by evidence from radiolysis literature.

The possible metal-ion systems for radiolytic charging of RFB electrolyte combinations can be explored based on three criteria considered from the radiolysis literature study performed.

- Possible generation of the metal ion (by oxidation or reduction) supported by literature based on radiolysis theory.
- Higher yield and stability of the recharged ion/compound post radiolysis in the aqueous solution.
- The recharged ion obtained during radiolysis should react with intermediates to form stable compounds or be recombined to form the discharged ion (initial ion preradiolysis stage).

Based on the redox couple combinations listed in Table 2, identified through our literature study, we concluded that the manganese–iron redox couple showed overall feasibility for a radiation-based charging cycle. The RFB conceptualized from the Mn–Fe couple employs $\text{MnO}_2/\text{Mn}^{2+}$ as the catholyte and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ as the anolyte. The standard reduction potentials for the $\text{MnO}_2/\text{Mn}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ systems are shown in eqs 4 and 5, respectively, resulting in an overall cell potential of 0.46 V.



During discharge, Fe^{2+} will undergo oxidation to give Fe^{3+} and Mn^{4+} will undergo reduction as positive electrolyte to give Mn^{2+} .

To conceptualize the radiation-based charging for the Mn–Fe RFB, we obtained radiolysis evidence of reported yield and stability for the reduction of ferric (Fe^{3+}) ions to ferrous (Fe^{2+}) ions and oxidation of Mn^{2+} ions to MnO_2 . The radiolytic oxidation of Mn^{2+} to Mn^{4+} precipitate²⁰ and the radiolytic reduction of Fe^{3+} to Fe^{2+} ions,^{12,13} were noted as charging cycle reactions for the proposed approach. Thus, from the confirmed recharged ion yield and stability metric, the Mn–Fe couple was noted as a feasible RFB system for charging by ionizing radiation.

Required Empirical Studies. In the following section, we outline the necessary empirical studies to validate the radiation-based charging approach. Radiolysis experiments are proposed to account for higher yield and stability of regenerated/recharged ions, while electrochemical characterization techniques are required to identify a suitable electrode–electrolyte combination. Figure 4 describes an

Table 2. Possible Combinations for the Proposed Radiation Charged RFB System

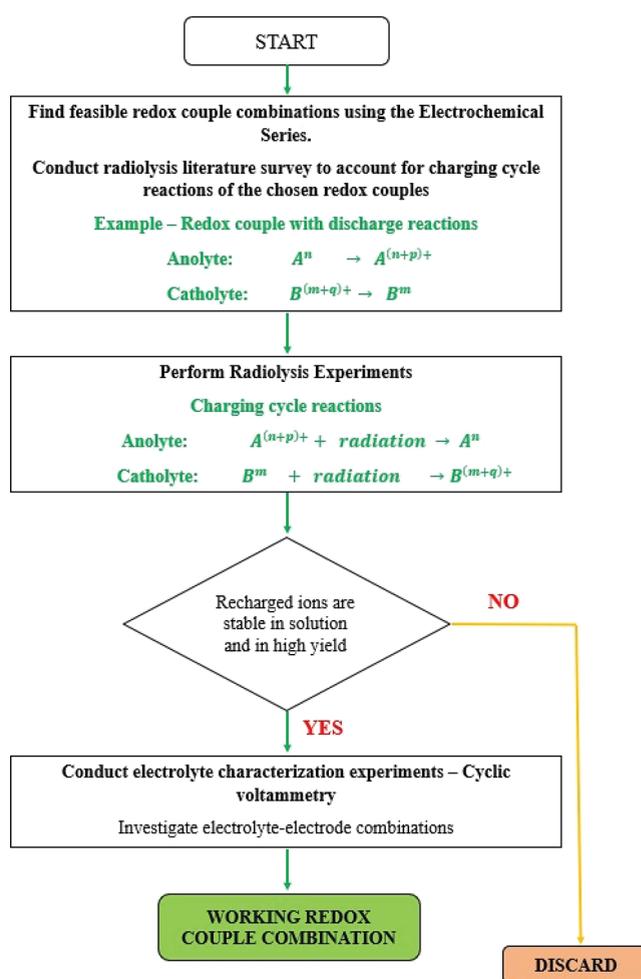
| redox couple | catholyte | anolyte | E_{cell}^0 (V) | radiolysis literature reported | desired ion stability/yield reported |
|----------------------|--|------------------------------------|-------------------------|--------------------------------|--------------------------------------|
| manganese-iron | MnO ₂ /Mn ²⁺ | Fe ³⁺ /Fe ²⁺ | 0.46 | ✓ | ✓ |
| manganese-copper | MnO ₂ /Mn ²⁺ | Cu ²⁺ /Cu ¹⁺ | 1.071 | ✓ | × |
| manganese-titanium | MnO ₂ /Mn ²⁺ | Ti ³⁺ /Ti ²⁺ | 1.6 | ✓ | × |
| manganese-molybdenum | MnO ₂ /Mn ²⁺ | Mo ⁶⁺ /Mo ⁵⁺ | 0.7 | ✓ | × |
| cerium-iron | Ce ⁴⁺ /Ce ³⁺ | Fe ³⁺ /Fe ²⁺ | 0.84 | ✓ | × |
| cerium-copper | Ce ⁴⁺ /Ce ³⁺ | Cu ²⁺ /Cu ¹⁺ | 1.451 | ✓ | × |
| cerium-molybdenum | Ce ⁴⁺ /Ce ³⁺ | Mo ⁶⁺ /Mo ⁵⁺ | 1.08 | ✓ | × |
| cerium-titanium | Ce ⁴⁺ /Ce ³⁺ | Ti ³⁺ /Ti ²⁺ | 1.98 | ✓ | × |
| vanadium-iron | VO21+/VO2+ | Fe ³⁺ /Fe ²⁺ | 0.23 | ✓ | × |
| vanadium-copper | VO21+/VO2+ | Cu ²⁺ /Cu ¹⁺ | 0.841 | ✓ | × |
| vanadium-titanium | VO21+/VO2+ | Ti ³⁺ /Ti ²⁺ | 1.37 | ✓ | × |
| vanadium-molybdenum | VO21+/VO2+ | Mo ⁶⁺ /Mo ⁵⁺ | 0.47 | ✓ | × |
| iron-copper | Fe ³⁺ /Fe ²⁺ | Cu ²⁺ /Cu ¹⁺ | 0.611 | ✓ | × |
| iron-titanium | Fe ³⁺ /Fe ²⁺ | Ti ³⁺ /Ti ²⁺ | 1.14 | ✓ | × |
| iron-molybdenum | Fe ³⁺ /Fe ²⁺ | Mo ⁶⁺ /Mo ⁵⁺ | 0.24 | ✓ | × |
| tin-titanium | Sn ⁴⁺ /Sn ²⁺ | Ti ³⁺ /Ti ²⁺ | 0.524 | ✓ | × |
| all titanium | TiO ₂ ²⁺ /Ti ³⁺ | Ti ³⁺ /Ti ²⁺ | 0.47 | ✓ | × |

approach for the exploration of radiolytically charged RFB chemistries.

Empirical Requirements for Radiolysis. The radiolysis of the aqueous metallic solutions of the respective redox couples could be conducted to determine the yield of charged ions. The yield or *G* value (number of ions produced per 100 eV of energy absorbed) of the radiolytic product can be estimated to ensure the feasibility of radiation-based charging. Furthermore, the regenerated ion must be the dominant ionic/deposited product and remain stable in the electrolytic solution after radiolysis.

The radiolysis experimental investigation depends on the type, equipment, radiation dosage measurement, and electrolytic solution. Gamma radiolysis with Co-60 or Cs-137 as radioactive sources or pulse radiolysis may be used. Previously employed equipment for gamma radiolysis (Co-60) involves the Foss Therapy model-812 self-contained cobalt-60 irradiator²⁸ and two-section lead shield for radioactive source housing and irradiation of samples.²⁹ Examples of pulsed radiation sources include Van de Graff generators,³⁰ and electron linear accelerators.^{27,31,32}

The dosage or amount of energy absorbed per unit mass by the medium or sample solution during radiolysis is measured using a dosimeter. Chemical dosimeters produce a change in chemical composition when exposed to ionizing radiation.³³ For instance, the Fricke dosimeter depends on the oxidation of ferrous ions (Fe²⁺) to ferric ions (Fe³⁺) by ionizing

**Figure 4.** Algorithm for proposed radiation charged RFB approach and experimental investigation.

radiation.^{34,35} The electrolytic solution must be modified using chemical additives to generate charged ionic species via radiolysis. These additives can generate ions and intermediates that aid in preferential oxidation/reduction of the desired ion (discharged form RFB active ion) in the electrolytic solution during radiolysis. For example, formic acid or methanol may be added to the aqueous solutions for the reduction of metallic ions.⁶ The oxidation of metallic ions occurs in aerated solutions due to the formation of hydroperoxyl radical (HO₂).¹⁰

The radiolysis of water and aqueous metal salt solutions produces oxidized/reduced metal ions, hydrogen gas (H₂), hydrogen peroxide (H₂O₂), and carbon dioxide (CO₂). Yield quantification of the ionic and molecular products is crucial to establish the stability of desired products. Spectrophotometry is used for calculating the concentration or yield of the desired ion from the irradiated solution.^{6,28} The molecular products namely hydrogen peroxide (H₂O₂), hydrogen gas (H₂), and carbon dioxide (CO₂) may be characterized using the Ghormley tri-iodide method,³⁶ gas chromatography,²⁸ and the Van Slyke method,^{37,38} respectively.

Electrolyte Characterization Technique. Cyclic voltammetry (CV) is an electrochemical technique where the current response of an electrolyte-electrode combination is measured by varying voltage.³⁹ It enables the estimation of kinetic parameters such as the rate of electron transfer, diffusion

coefficients of electroactive species, and the reversibility of the reaction. As the Mn–Fe redox couple was established feasible for radiation-based charging, CV literature survey for the $\text{MnO}_2/\text{Mn}^{2+}$ system was performed. Nijjer et al.⁴⁰ investigated the oxidation of Mn^{2+} to MnO_2 and the reduction of MnO_2 on a platinum electrode in sulfuric acid as a function of Mn^{2+} concentration, acid concentration, scan rate, temperature, and convection. The authors concluded that high temperature and convection improved the oxidation rate of Mn^{2+} to MnO_2 , whereas the reduction of MnO_2 was dependent on the acid concentration and the presence of Mn^{2+} ions in the electrolyte.

By proposing the radiolysis and electrolyte characterization experiments, we necessitate the experimental investigation of suitable electrolyte (metal salt dissolved in supporting electrolyte–solvent mixture) for radiolysis. The radiolysis experiments would help us establish the yield and stability metric for the irradiated electrolyte, whereas the cyclic voltammetric experiments will help us establish a suitable electrode system for high reaction kinetics and reversibility.

CONCLUSIONS

In this work, we propose a novel method for charging of RFB using the nuclear decay energy of radioisotopes or spent nuclear fuel. The conversion of nuclear energy to electrical energy is facilitated by the chemical intermediates formed during radiolysis of RFB electrolytes. Metal ions in aqueous solutions are oxidized or reduced upon reaction with radiolysis ionic intermediates and molecular products.

The RFB catholyte and anolyte redox couples were chosen based on the electrochemical series. Gamma and pulse radiolysis literature survey of the chosen metal-ion systems accounted for the feasibility of ion regeneration based on the G value and stability of the recharged ion. From our analysis of literature, manganese ($\text{MnO}_2/\text{Mn}^{2+}$) and iron ($\text{Fe}^{3+}/\text{Fe}^{2+}$) RFB shows promising yield and stability of recharged ion by radiolysis and was concluded as a feasible redox couple for the radiation charged RFB approach.

A stepwise guide for choosing the metal-based redox couples and empirical protocols for radiolysis and electrolyte characterization experiments are outlined. Cyclic voltammetry can be used to characterize the RFB electrolytes. Conventionally used radioactive sources (Co-60 and Cs-137) and equipment were proposed for laboratory-based radiolysis investigations. Factors such as source for radiolysis, equipment, dosimetry, optimizing electrolytic solution, and product characterization techniques were also highlighted. This study also proposed the utilization of spent nuclear fuel for the radiolytic charging cycle because of its high radioactivity and availability.

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Notes

The authors declare no competing financial interest.

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