

Article

Redox Flow Batteries: A Glance at Safety and Regulation Issues

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Abstract: Redox flow batteries (RFB) are considered one of the most promising electrochemical energy storage technologies for stationary storage applications, especially for long duration energy storage services. RFBs are electrochemical energy converters that use flowing media as or with active materials, where the electrochemical reactions can be reversed. Knowledge of technical standards and other regulations lay the foundations for successful and safe commercialization of products through uniform instructions and generally applicable rules. A small number of papers on safety and regulatory issues of RFBs are reported in the literature, mainly for two reasons. First, because this technology is considered safe; and second, because most of the publications have been limited to short-term characterization studies of materials in chemistry. This paper aims to help fill this gap, providing researchers and students with introductory knowledge on the safety and regulatory aspects of RFBs, mainly from an electrical and hydraulic point of view. The reader is referred to specific regulations for deeper studies and analyses.

Keywords: stationary storage applications; redox flow battery; standards for flow batteries; safety issues



Citation: Trovò, A.; Marini, G.; Zamboni, W.; Sessa, S.D. Redox Flow Batteries: A Glance at Safety and Regulation Issues. *Electronics* **2023**, *12*, 1844. <https://doi.org/10.3390/electronics12081844>

Academic Editors: Luis M. Fernández-Ramírez, Ahmed Abu-Siada, Jean-Christophe Crebier, Zhiwei Gao, Kai Fu and Eladio Durán Aranda

Received: 1 March 2023

Revised: 28 March 2023

Accepted: 7 April 2023

Published: 13 April 2023



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1. Introduction

Energy storage is an essential enabler of the energy transition [1]. In the past decades, several countries have shifted from an energy system dominated by centralized fossil fuel generation, which can be dispatched to match energy consumption at all times, to a system with more and more renewables. Since the most common renewable sources, i.e., wind and solar radiation, are intermittent, energy storage is required to deal with power demand of the grid and power availability from these sources [2]. Industrial consumers can install storage to reduce consumption peaks and to provide back-up power if there is a black-out. In addition, storage at any level can offer system services, safeguarding the secure and efficient operation of the electricity system. They provide flexibility at different time-scales—seconds/minutes, hours, weeks, and even months. Different energy storage systems—centralized and decentralized—consider different technological possibilities, which can be organized in five energy storage classes: chemical, electrochemical, electrical, mechanical and thermal. Electrochemical energy storage (EES), covering all types of secondary batteries, is the most important technology proposing environment-friendly and sustainable solutions for stationary storage applications. Redox flow batteries (RFBs, or simply FBs) appear as one of the most promising EES technologies, carrying two advantages compared to others: independent sizing of energy and power, and long cycling life [3]. Among the different chemistries, the most successful is the all-vanadium RFB (VRFB), which has reached a commercial fruition state. Many companies today are able to sell commercial VRFBs, and several plants have been installed globally [4]. One interesting feature of a VRFB (in common with other types of RFBs) is its intrinsic safety compared to

other EES technologies [5], granting a competitive advantage. Indeed, the more diffused Li-ion battery suffers from critical safety issues, and improper use can cause a fire [6]. Very few papers about safety aspects of RFBs have been published so far, mainly because this technology is already considered safe. In reference [7], a VRFB is tested under short-circuit conditions, and it is found that this kind of battery is much safer than others in this extreme fault state, thanks to its structure. However, some risks are associated with RFB operation, and considerable differences can exist between the various RFB types under development. The risks related to the presence of toxic gases have a different impact among various RFBs: for example, a VRFB has less problems than a hydrogen bromine (H₂-Br) RFB. This matter is faced by the battery manufacturer, but standardization of RFBs is a necessary step towards safe and widespread RFB commercialization. Technical committee 21 of the International Electrotechnical Commission (IEC) includes RFBs in its standards related to secondary batteries for energy storage [8]. A joint working group (JWG7) has developed a suite of standards published from IEC [9]. Of course, only some of them focus on guidelines on safety requirements of these systems.

Hazards related to RFB operation can be grouped mainly in three types: electrical hazards; hazards associated with corrosive and conductive fluids; and hazards associated with gases that may be toxic or explosive. In this paper, such hazards are summarized, based on their nature and level of risk. Moreover, the safety measurements and good practices for each type of commercial RFB are presented. In particular, the paper summarizes the approaches based on the main international standards and regulations that would increase the plant safety. Finally, this paper is aimed to provide researchers and students with introductory knowledge on the safety issue of RFBs, while addressing them to specific regulations for deeper studies and analyses.

2. Electrical Hazards

An electrochemical energy storage system (EESS) mainly consists of four parts: the battery system, the management, communication and protection system, the auxiliary system, and the power conversion system. The first is the battery itself. The second includes the battery management system (BMS), which controls and monitors the battery for proper operating conditions and takes appropriate action if a dangerous condition is detected. The BMS then usually communicates battery status information to devices that allow remote supervision of the system. The auxiliary system includes all additional devices required to operate the battery, such as the thermal management system (TMS) and pumping system in the case of RFBs. The power conversion system consists of static power converters and connects the battery system to the grid via the primary point of connection (POC), Figure 1. According to this generic scheme, the main electrical hazards in RFBs can be listed as:

- Direct and indirect contact with live parts of the system (danger of electric shock);
- Short-circuit of the terminals;
- Leakage currents;
- External over-voltage.

If the battery voltage at the point of connection (POC in Figure 1) is below 1 kV AC, or 1.5 kV DC, the indications reported in IEC 60364 or IEC 61936-1 series must be respected [10,11]. The main ones from the IEC 60364 are summarized in the following [11].

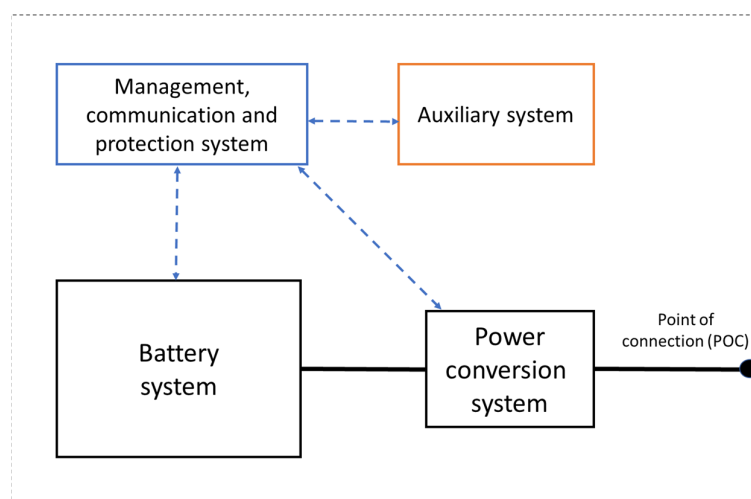


Figure 1. Scheme of an electrochemical energy storage system (EESS) and its main parts: battery system, management, communication and protection system, auxiliary system, and power conversion system. The position of the primary point of connection (POC) to the grid is highlighted [10].

2.1. Protection against Direct and Indirect Contact

The exposed conductive parts must be connected to the protective conductor under the specific conditions of the grounding system, such as a TN, TT, and IT system [12].

The main protective measures are listed below:

- Disconnection of the power supply within on time in case of a fault;
- Protection by use of Class II equipment or by equivalent insulation;
- Protection by non-conducting location;
- Protection by ground-free potential bonding;
- Protection by electrical separation;
- Protection by extra-low voltage.

Some of them deserve some explanation.

2.1.1. Disconnection of the Power Supply

In this context, it is necessary to avoid undesired tripping of the residual current breakers (RCB), especially for TT grounding systems. For such a system, the protection against direct and indirect contacts by means of such devices is compulsory, according to the IEC 60364 standard. In fact, the presence of capacitive paths between the active parts of a storage system and its grounded metallic enclosure could cause the circulation of leakage ground currents, especially during transient operations of the battery. Although the magnitude of such capacitive currents is typically very small, it is added to other capacitive currents present in the circuit. For example, they can be due to the presence of filters or power conversion devices. Hence, if the total amount of leakage current is comparable with the current threshold of the RCB, tripping could happen, even if there is not a real fault. In this regard, the IEC 61140 standard reports the leakage ground current limits for electrical equipment of Class I and II. Obviously, this issue could be even more serious in the presence of resistive ground paths for the leakage currents. In particular, if continuous current components are flowing in the ground circuit, they could saturate the magnetic core of the RCB by determining the so called “blinding effect”. This effect could lead to the malfunction of the RCB even in case of the circulation of ground currents, leading to danger for people. In such a case, it is necessary to install Type B RCB to ensure safety for people.

Hence, the magnitude of the leakage ground currents due to the normal operation of batteries and flowing in the grounding circuit should be known in advance to guarantee an effective coordination of the electric protection devices.

In VRFBs, the energy is stored in corrosive acid electrolytes, so every part of the battery in direct contact with the electrolyte must be made of materials not susceptible to corrosion,

such as plastic materials. For this reason, the battery, except for the terminals, is made of non-conductive materials, and therefore there is no need for grounding of any metal part normally in contact with the electrolyte.

For a TN or a TT system, the negative terminal can be bound to the ground. So, all battery metal parts must be connected to the grounding system by a protective conductor. An additional grounding of this protective conductor may be required to ensure the lowest deviation of its potential from the ground.

Information on the appropriate protection scheme for battery installation to the electric grid can be found in [13]. Figure 2 in [13] shows the possible faults (pole to ground, or pole to pole) to evaluate their effects and to find a good protection scheme. This helps with installing the appropriate protective devices.

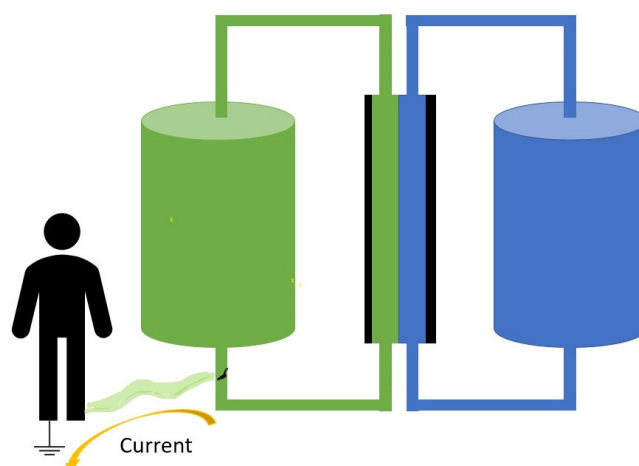


Figure 2. Electrocution is a risk in case a person accesses the fluid if a leakage of liquids from piping happens.

2.1.2. Electrical Separation

Fault protection is provided by separation of the faulted circuits from other circuits, as well as from the ground. This protective measure is provided by one current-using item supplied by an ungrounded source with simple separation. To guarantee fault protection, the live parts of the separated circuit shall not be connected at any point to another circuit nor to the ground. Basic insulation must be achieved between circuits: exposed and conductive parts of the separated circuit shall not be connected to the protective conductor or to other exposed conductive parts belonging to other circuits or to the ground.

2.1.3. Safety Extra-Low Voltage and Protective Extra-Low Voltage

The extra low-voltage protection is a protective measure consisting of two different subsystems: protective extra-low voltage (PELV), and safety extra-low voltage (SELV). Such systems require voltage limitation in the system to 50 V AC and 120 V DC, and protective isolation between the SELV or PELV system. For SELV only, basic insulation to the ground is required.

An RFB is used as a stationary battery connected to the electric grid. Therefore, if the battery voltage is less than 120 V DC, and the power electronics interfacing them to the mains provides a safety degree equivalent to the protection of a safety isolating transformer, the installation should be considered safe. This system requires basic insulation and basic enclosure, as stated in [11], Clauses A1 and A2. In addition, PELV requires the exposed conductive parts of its circuit be connected to the protective conductor of the source.

2.2. Protection against Short-Circuits at the Terminals

All battery connections must be designed to avoid short-circuits under any possible conditions [14,15]. Since the energy released during a short-circuit in an RFB depends

on the available charged species inside the stack, an RFB system can mitigate the short-circuit by stopping the pumps. Every stack should have its own fuse. Moreover, intrinsic safety of the stack under short-circuit conditions shall be verified according to Annex B of the standard [16].

The behavior of an RFB under fault conditions is analyzed in [7] by considering a VRFB system manufactured by CellCube Inc (Denver, CO, USA). The following four conditions were considered.

- Shorting with a fuse between two stacks;
- Full short with no pumping. This is the case of decommissioning a not completely discharged battery;
- Short-circuit with pumping, where the terminals of the same stack are in short-circuit;
- Internal short-circuit, caused by membrane breaking.

According to the results, nominal fault current is 50% higher than the nominal one, but even in these conditions, there is no dangerous temperature rise of the electrolyte. In addition, the temperature evolution over time is slow, thanks to the thermal inertia of the electrolyte [17]. Therefore, the control devices can react in a timely manner, avoiding problems.

If the fault occurs when the battery and pumps are operating, the rise of the electrolyte temperature in the stack is mitigated by the fresh electrolyte flowing in the stack [18]. In Reference [18], the main hazard aspect was the rise of the temperature, and therefore the electric safety is easily guaranteed by an appropriate choice of fuses.

2.3. Protection against Leakage Currents

Considering that RFB is usually composed of non-conductive materials, any leakage currents flowing toward the ground should not be present. They can arise when the electrolyte itself spills out. This may happen during maintenance. Such a problem can occur, but in the case of programmed maintenance, it is worth completely discharging the battery before undertaking any action.

Moreover, a leakage current through liquid conductive electrolyte (to the ground) may happen under faults, which should be considered a fault in the hydraulic system, as shown in Figure 2.

A good practice to face such events is to bind every metallic object located in the room where the battery is installed to the ground. This is to avoid any contact with a charged surface. Every grounding conductor of those parts can be connected to the same point of contact.

In order to prevent possible dangers for people working on the battery, protective clothes are also required. As already mentioned before, clothes must also prevent accidental direct contact with the electrolyte that can spill out of the battery. In addition, electric safety clothes preventing electrostatic discharge must be used.

Only cotton-based clothes moistened with water shall be used for battery cleaning [15].

3. Gas Hazards

3.1. Gaseous Emission

Depending on the battery chemistry, design, and operating conditions, different gases could be produced. They can be explosive (e.g., hydrogen), toxic (e.g., bromine), or corrosive. Usually, they are produced inside stacks and stored in the system. In RFBs, gases are often found in the upper volume of tanks. For example, in a VRFB, hydrogen production becomes important when the battery is charged over the rated maximum state of charge [19]. Table 1 describes the different risks associated with these gases and a possible protection for each of them.

Table 1. Different risks associated with gases and a possible protective measure for RFBs.

	HAZARDS	PROTECTION
EXPLOSIVE GAS	Generation and accumulation of combustible gases	Reduction in the generation of combustible gases
	Mixture of gas and oxygen	Dilution of combustible gases
		Prevention of diffusion of gases outside the volume where they are generated
	Presence of ignition sources	Elimination of ignition sources
Prevention of external oxygen ingress		
TOXIC GAS	Generation and accumulation of toxic gases	Elimination of toxic gases
		Dilution of toxic gases
	Human access to proximity of toxic gases	Collection of toxic gases
		Limitation to human access
CORROSIVE GAS	Generation and accumulation of corrosive gases	Construction of the system with corrosion-resistance materials
		Elimination of corrosive gases
	Human access to vicinity of corrosive gases	Dilution of corrosive gases
		Collection of corrosive gases
Gases Affecting the Respiratory System (GARS)	Generation and accumulation of GARS	Limitation to human access
		Elimination of GARS
	Human access to the proximity of GARS	Dilution of GARS
		Collection of GARS
		Limitation to human access

3.2. Protection against Explosion

In case of battery overcharging, hydrogen and oxygen gases may be produced. These gases may be stored in the upper part of the tanks and periodically (or continuously) released directly outside the battery. If hydrogen concentration rises to 4%vol or above, a potential explosive mixture can be achieved [14].

According to Faraday's law, when a cell is fully charged, electrolysis may occur. Under standard conditions of 0 °C and 1013 hPa, 1 Ah decomposes 0.336 g of pure water (H₂O) into 0.42 L hydrogen (H₂) and 0.21 L oxygen (O₂). Therefore, 26.8 Ah decompose 9 g of water into 1 g of hydrogen and 8 g of oxygen.

3.3. Ventilation Requirements

To avoid creating an explosive mixture, an appropriate ventilation system could be necessary to dilute the toxic gases into the surroundings. Ventilation requirements must be specified by the manufacturer of the RFBs. Ventilation is needed to ensure that no combustible or harmful gases reach a critical concentration level. The ventilation can either be natural or forced.

In the case of natural ventilation, the containment room or enclosure requires an air inlet and outlet with a minimum total clear opening area that meets ventilation requirements. The air inlet and outlet should be placed in the best position to create the most appropriate airflow. If they are installed on the same wall, they must be 2 m away from each other.

Conversely, in the case of forced ventilation, a continuous airflow is required. To do this, a control device must put the RFB into a standby condition when the ventilation system fails or malfunctions.

According to the IEC standard for stationary storage batteries, if the dilution requirements cannot be guaranteed in the proximity of the battery, a barrier or signs indicating the beginning of the dangerous area must be provided.

4. European Regulation about the Presence of Hazardous Substances

The directive 96/82/CE, also known as “Seveso II”, and the directive of the European Parliament 2012/18/UE, also known as “Seveso III”, are the most important European regulations to apply for stationary application of EES systems. Both of them concern the major accident hazards related to the presence of hazardous substances. The prescriptions of these regulations imply safety requirements that become very stringent in the presence of a large amount of hazardous substances. Hence, to evaluate the Seveso II and III implications, quantities of each chemical substance present in the energy storage installation (or which could be present) must accurately be determined. For instance, this holds during charge and discharge operations, short-circuit occurrence or moisture penetration. In this way, on the basis of the installed power, the safety requirements of the EES plant can be determined.

5. Liquid Hazards

Risks related to liquids in an RFB are related to their toxicity, corrosiveness, environmental impact, and flammability.

An electrolyte leak could go unstopped if the leak detection system is not suitable. To limit the associated risk, some basic protections can be implemented, as listed below.

- Ensure the sealing performance of the hydraulic system;
- Use corrosion-resistant materials for parts in contact with the electrolyte;
- Detect leaks and prepare protective devices (use a leak detector);
- Prevent leakage into the surrounding environment;
- Provide fluid-related information and markings.

The RFB must be placed in a containment tank, whose volume is at least equal to the size of the largest tank. The containment tank must be made of corrosion-resistant material.

As different RFB chemistries are currently under development, the battery manufacturer should inform users about the specific hazards of the product. The manufacturer shall provide primary emergency information for direct contact and contamination of people, as well as for contamination of the environment.

The so-called safety data sheet (SDS) should also be provided, indicating the characteristics of suitable protective clothing for battery operation, such as resistance to corrosion, non-flammability, heat resistance, and electrical insulation.

If a battery operates with different fluids, both pipes must clearly be identified with the name of the positive or negative liquid electrolyte.

The resistance of the materials to temperature and pressure must also be considered. It is also worth considering that the chemically aggressive RFB fluids could cause an accelerated loss of the initial properties of the material.

6. Housing Requirements

Batteries must be housed in protected accommodations, preventing several hazards: external hazard (e.g., fire, water, shock, vibration, vermin); hazard caused by the battery itself; access by unauthorized personnel; and extreme environmental influences (e.g., temperature, humidity, airborne contamination). If the battery is in a room enclosed inside a building, it may not be possible to connect the ventilation system of the enclosure outside the building. In this case, the room must be provided with a ventilation system fulfilling all safety requirements.

Warning labels must be placed in the housing room or outside the cabinet, if external. These labels must represent the appropriate symbol from the following list [20]:

- Green square: safe conditions;
- Red square: fire protection;
- Blue circle: mandatory;
- Yellow triangle: warning hazard.

To consent to emergency evacuation, a free escape path must be kept available any time with a minimum width of 600 mm.

7. RFB Types and Associated Necessary Safety Precautions

The protection actions and good practices discussed in the previous sections apply to every kind of RFB. In order to increase the plant safety of each specific kind of RFB with valuable market penetration, this section introduces specific instructions in terms of safety precautions and additional good practices. Three main types of RFBs are considered: VRFBs, hydrogen–bromine H₂–Br, and zinc–bromine Zn–Br. The improved good practices are summarized in Table 2. The last column of the table reports some examples of good safety practices implemented in the design stage of industrial-scale installations by the main world manufacturers for each specific type of RFB.

Table 2. Safety features, good practices, and examples of industrial-scale installations of VRFBs, H₂–Br, Zn–Br RFBs.

RFB Type	Safety Features	Good Practices	Industrial-Scale Installations
VRFBs	<ul style="list-style-type: none"> • Zero risk of thermal runaway • No chlorine off-gas • No risk of thermal event caused by short-circuit • No concrete bunding needed 	<ul style="list-style-type: none"> • True power off ⁽¹⁾ • Safe by design principles ⁽²⁾ 	<ul style="list-style-type: none"> • Worldwide diffusion of VRFB plants [21] and main world-class manufacturers [22]
H ₂ –Br	<ul style="list-style-type: none"> • Zero risk of thermal runaway • No chlorine off-gas • Hydrogen safety issues ⁽³⁾ • Bromine safety issues ⁽⁴⁾ 	<ul style="list-style-type: none"> • The use of specially designed double-walled reservoirs must provide maximum protection in case of mechanical shock • The use of a chemical neutralizing agent, in which the electrolyte reservoirs are submerged • Addition of Bromine Complexing Agent (BCA) to prevent the bromine from fuming, in the unlikely case that bromine would come in direct contact with open air [23] 	<ul style="list-style-type: none"> • Few examples of an industrial-scale, mainly by Elestor [24]
Zn–Br	<ul style="list-style-type: none"> • Zero risk of thermal runaway • No chlorine off-gas • Bromine safety issues ⁽⁴⁾ 	<ul style="list-style-type: none"> • Sequestering/complexing agents needed to avoid toxic bromine vapor emissions [25] 	<ul style="list-style-type: none"> • Few examples of an industrial-scale, mainly by Redflow [26]

⁽¹⁾ There is minimum power left in the stacks when the system is shut down, dramatically decreasing the risk of shock to maintenance crews and first responders. ⁽²⁾ Redundant safety systems in VRFB modular units include electrolyte tanks that never pressurize and built-in secondary containment that could hold the entire liquid volume if the tanks ever ruptured. ⁽³⁾ Flammability and wide explosive/ignition mix range with air. This is, however, mitigated by the fact that hydrogen, due to its low atomic weight, rapidly rises and disperses before ignition. Unless accumulated in an enclosed unventilated area, hydrogen is very unlikely to entail serious risks. ⁽⁴⁾ Elemental bromine is a red–brown liquid at room temperature. It is corrosive and toxic, with properties between those of chlorine and iodine.

8. Conclusions

Redox flow batteries (RFBs) are gaining more and more popularity due to their advantages in stationary applications, especially in sizes of several kW or even MW, and with long discharge times.

A small number of papers about safety aspects of RFBs have been published, mainly because this technology is considered intrinsically safe. In order to partially fill this gap, this study has discussed the safety aspects and regulations of RFBs, mainly dealing with the hazards due to electric issues, gases, and harmful liquids, and related protection strategies. Such aspects have paramount importance in the design and the operation of large electrochemical energy storage (EES) systems.

The topic has been discussed with particular focus to the most commercialized RFB: the all-vanadium RFB (VRFB), which is considered among the safest EES technologies on the market at present.

Criteria and rules for unambiguous evaluation and comparison of installation aspects of RFBs were presented. The main international regulations for RFB are summarized, with the aim of providing an overview of the latest advances in this field. Finally, the essential safety issues and some proposal to improve well-established good practices for a RFB-based ESS system were presented, with specific reference to the three most commercialized types of RFB, i.e., VRFBs, zinc–bromine, and hydrogen–bromine RFBs and to some industrial-scale installations.

Author Contributions: Conceptualization, A.T.; methodology, G.M., W.Z. and S.D.S.; formal analysis, A.T., S.D.S. and W.Z.; investigation, G.M.; data curation, A.T. and G.M.; writing—original draft preparation, A.T. and G.M.; writing—review and editing, W.Z. and S.D.S.; project administration, A.T. and S.D.S.; funding acquisition, W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by “Holistic approach to EneRgy-efficient smart nanOGRIDS—HEROGRIDS” grant number [PRIN 2017 2017WA5ZT3] within the Italian MUR 2017 PRIN program and by University of Salerno FARB funds.

Data Availability Statement: No new data were created in this work.

Conflicts of Interest: The authors declare no conflict of interest.

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