

Performance goals in RFC development for low earth orbit space missions

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Abstract

By comparing alkaline regenerative fuel cells (RFCs) with advanced battery systems, the RFCs show better performance in regard to the overall system mass for a widest range of space applications; however this does not embrace the low earth orbit (LEO) missions, which are most practical. For LEO applications of RFCs, their storage efficiency must be increased significantly. In the present work, different RFC technologies and system designs are discussed in order to minimize the required effort in fundamental electrocatalytic research. The performance goals of the electrochemical properties of RFCs applied in low earth orbits are defined.

Introduction

An essential problem for RFCs operation in the low earth orbit (LEO) is their deficient overall efficiency compared with the storage efficiency of advanced battery systems, e.g., NiH₂-batteries. Since the excess fuel-transport capacity caused by the aerodynamic drag in LEO exceeds the system mass of the energy storage in long-term missions, the decision whether the RFC or the battery is the most attractive depends on the storage efficiency of the considered concept.

Recently it has been shown [1], that alkaline fuel cells (AFCs) showing today's performance would not be competitive in orbits less than 500 km. To achieve competitiveness of alkaline RFCs, a significant improvement in their overall efficiency is required. However, improvements in efficiency due to changed stack designs are limited by the open-loop cell voltages using today's catalysts. Assuming open-loop voltages of $u^*_{\text{el}} = 1.4$ V and $u^*_{\text{fc}} = 0.96$ V for the electrolyzer and the fuel cell, respectively, the overall efficiency will not exceed $\eta = 0.685$. Thus, fundamental research in catalyst technology is required to reduce the overpotential on the electrode surfaces.

If the preparation of electrocatalysts showing sufficient low overpotentials will succeed high efficient energy storage based on fuel cell technology can be operated in LEO space missions. The appropriate current densities must be optimized regarding the minimization of the entire transport capacity required during the mission. On the other hand, the maximum allowable current density for RFC operation depends on the overpotentials at the electrode surfaces. Beyond this fundamental dependence, the relation between the limiting overpotential and the maximum current density is influenced by the design of the RFC storage.

In the past, the integrated and the dedicated RFC design have been discussed [2]. Whereas the dedicated RFC is an external interconnection of separate fuel cell

and electrolyzer stacks, fuel-cell elements and electrolyzer cells are stacked alternately in the integrated RFC. Thus, the current densities during charging and discharging the dedicated RFC can be optimized independently. However, they are correlated by the operating periods of the electrolyzer and fuel-cell mode, applying integrated systems.

For this reason both designs were considered to define the performance goals regarding the overpotentials on the electrode surfaces. In addition, the influence of a thermal interconnection of the electrochemical components is considered.

RFCs and batteries: a theoretical comparison

To achieve competitiveness of RFC systems with batteries for LEO space missions, the overall RFC efficiency must be higher than the storage efficiency of the battery. Since the efficiency of the electrochemical cells depends on their characteristics, a simplified description of fuel cell and electrolyzer characteristics is applied to obtain an analytical expression of the RFC efficiency depending on the overpotentials and internal resistances of the cells.

In a first approach the u versus i characteristics of the cells are described by linear approximations:

$$\begin{aligned} u_{el} &= u^*_{el} + ir_i \\ u_{fc} &= u^*_{fc} - ir_i \end{aligned} \quad (1)$$

where the intercept and the slope are given by the open loop voltage u^* and the internal resistance r_i of the cell, respectively. Further, the open-loop voltage is described by the lower heating value of the hydrogen/oxygen reaction ΔG and the overpotentials u_{ov} at the electrodes:

$$u^* = \Delta G/zF \pm u_{ov} \quad (2)$$

where the sign of the overpotential refers to the electrolyzer (+) and fuel cell (-), respectively. This approximation does not consider any temperature dependence of the characteristics and the internal resistances of fuel cell and electrolyzer are assumed to be equal, however a comparison with experimental data shows sufficient agreement, as shown in Fig. 1. The experimental data represented by the asterisks are fitted assuming a reversible cell voltage of $\Delta G/zF = 1.18$ V corresponding to the operation temperature of alkaline cells. The overpotentials and internal resistances are set to $u_{ov} = 220$ mV and $r_i = 0.25 \Omega \text{ cm}^2$.

Since the overall efficiency of the RFC storage is given by the ratio of the voltages of fuel cell and electrolyzer, the performance requirements to the electrochemical properties of the catalysts are expressed by:

$$\frac{\Delta G/(zF) - u_{ov} - ir_i}{\Delta G/(zF) + u_{ov} + ir_i} > \eta_{bat} \quad (3)$$

where η_{bat} denotes the efficiency of the reference battery. From eqn. (3) it is obvious, that decreasing current densities will increase the efficiency of the RFC. However, a lower limit of the current density is determined by the increase of the geometric electrode area. From recent works [5] we know, that the system mass increases by 35% when the cells are operating at 100 mA/cm^2 . Thus from eqn. (3) the upper limit for the electrodes overpotentials can be derived for the given operating conditions.

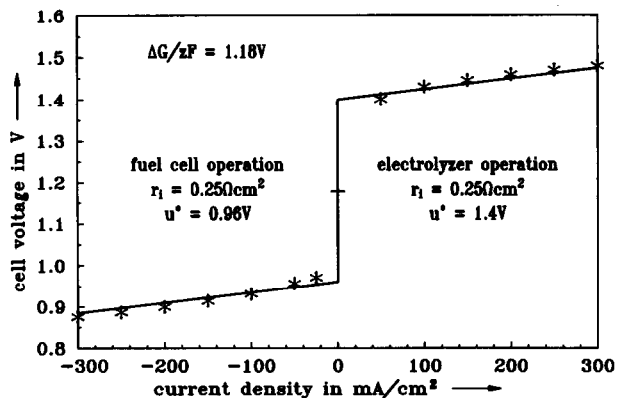


Fig. 1. Linear approximation to the u vs. i characteristics of fuel cells and electrolyzer. The experimental data were taken from the electrolyzer of Asea Brown Boveri (ABB, AG, Zurich, Switzerland) and the fuel cell of United Technology Corporation (UTC, Hawford, CT, USA) [3, 4].

Non-interconnected dedicated RFC

The first storage system considered is a dedicated RFC neglecting the thermal interconnection of electrolyzer and fuel cell. Then the substitution of thermal energy for electricity is not possible unless an external thermal source is available. If the whole primary energy must be supplied as electricity, the lower limit of the electrolyzer voltage is determined by the enthalpy of the hydrogen/oxygen reaction: $\mu_{el} \geq \Delta H/zF$ and the appropriate electrolyzer current density has to be adjusted. Then, only the fuel cell current density is an independent variable and from eqn. (3) follows:

$$\frac{\Delta G}{\Delta H} - \frac{(u_{ov} + ir_i)zF}{\Delta H} > \eta_{bat} \quad (4)$$

and the upper limit for the electrodes overpotential is given by:

$$u_{ov} < \frac{\Delta G}{zF} - \eta_{bat} \frac{\Delta H}{zF} - ir_i \quad (5)$$

Since the storage efficiency of batteries is in the order of $\eta_{bat}(Wh) \geq 0.75$ [6], the maximum allowable overpotential is less than: $u_{ov} < 68.5$ mV, if the described RFC storage should receive competitiveness in regard to batteries for LEO applications. A more detailed evaluation of eqn. (5) depending on the current density limit and the internal resistance leads to overpotentials $u_{ov} < 40$ mV for reasonable system parameters.

Assuming an overpotential of $u_{ov} = 220$ mV of today's catalysts, the required performance goal for future catalysts is an overpotential reduced by at least 82%. To reduce the performance goals for the electrocatalytic properties, the fundamental research should be accompanied by introducing a thermal storage into the RFC system.

Interconnected dedicated RFC

Realizing a thermal interconnection of fuel cell and electrolyzer, the substitution of thermal energy for electricity becomes possible. The waste heat generated during discharging operation due to the entropy changes of the fuel-cell reaction can be recycled during charging the RFC.

For the dedicated RFC design we assumed equal current-density limits for fuel-cell and electrolyzer operation. Again, the upper limit of the overpotential can be derived from eqn. (3):

$$u_{ov} < \frac{1 - \eta_{bat}}{1 + \eta_{bat}} \frac{\Delta G}{zF} - ir_i \quad (6)$$

Equation (6) shows a linear expression whose intercept is determined by the battery's efficiency and the free energy of the fuel-cell reaction. From the intercept the theoretical maximum overpotential must be less than 14.3% of the reversible cell voltage ($u_{ov} < 168$ mV). For practical applications this limiting value is decreased by a finite current density. A complete evaluation of eqn. (6) is shown in Fig. 2. For reasonable current densities and internal resistances ($i = 100$ mA/cm²; $r_i = 0.25$ Ω cm²), the overpotential is limited to $u_{ov} < 143$ mV for both, fuel-cell and electrolyzer operation.

This operating mode of the electrolyzer would require a thermal flow of $\dot{Q}_{el} = 13.2$ mW/cm² as substitution for electricity, on the other hand, the fuel cell produces a waste-heat flow of $\dot{Q}_{fc} = 46.8$ mW/cm². Due to the limiting conditions ($i_{fc} = i_{el}$), the ratio of the thermal flows is equal to the ratio of the required and produced heat, thus the thermal efficiency of the system must exceed 28.2% including all losses in coolant feeds.

Integrated RFC

If for any reasons different but constant current densities of electrolyzer and fuel cell operation are desired, eqn. (6) has to be modified. Since the ratio of the current densities is constant (i.e., $i_{fc} \propto i_{el}$), a constant $c_1 \geq 1$ must be introduced into eqn. (3). This will lead to a modified slope of the linear expression in eqn. (6):

$$u_{ov} < \frac{1 - \eta_{bat}}{1 + \eta_{bat}} \frac{\Delta G}{zF} - c_2 r_i i \quad (7)$$

where i denotes the lower current density of either i_{el} and i_{fc} and $c_2 = (c_1 + \eta_{bat}) / (1 + \eta_{bat})$ or $c_2 = (1 + c_1 \eta_{bat}) / (1 + \eta_{bat})$ depending on whether i refers to the electrolyzer's or fuel cell's current density, respectively. Since from this definition $c_2 \geq 1$, the slope in eqn. (7) will receive its minimum when the current densities of fuel-cell and electrolyzer operation become equal. However, the integrated RFC design as well as

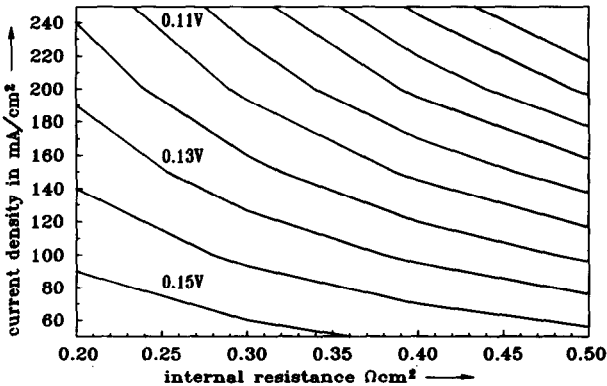


Fig. 2. The maximum allowable overpotential on the electrodes depending on current density and internal resistance. The data are calculated for a dedicated RFC system.

the reversible fuel cell will require different current densities, since here the total electrode areas are of equal size. Then c_1 can be expressed in terms of operating periods, since the total charge transition during both charge and discharge operation must be equal.

For space applications, the operating periods can be expressed in terms of orbit altitude, thus the performance goal for the electrocatalysts depends on the space mission under consideration. Figure 3 shows the allowable overpotential versus the current density of the electrolyzer for different orbit altitudes.

An additional requirement to reduce the overpotentials is due to the integrated RFC design or by the reversible fuel cell. Depending on orbit altitude and the low current density limit, the performance of their electrocatalysts must be increased by 2–22% with respect to the dedicated system. Assuming reasonable current densities and internal resistances ($i = 100 \text{ mA/cm}^2$; $r_i = 0.25 \Omega \text{ cm}^2$), the overpotentials should not exceed 135 mV for the 450 km orbit.

Solid oxide electrolyzer/solid oxide fuel cell (SOE/SOFC) systems

Striking the thermal balance for an integrated RFC system in a 450 km orbit, it is found, that $\dot{Q}_{el} = 16.5 \text{ mW/cm}^2$ thermal energy is required during electrolyzer operation with $i_{el} = 100 \text{ mA/cm}^2$, and $\dot{Q}_{fc} = 69.8 \text{ mW/cm}^2$ waste heat is produced during fuel-cell operation. Considering the different operating periods of these components, the efficiency of the thermal storage should exceed 37.9% including all losses in thermal feeds.

Finally, the solid oxide fuel cell (SOFC) is considered as an energy storage device. Recently it was shown, that this electrochemical device can be operated reversibly [7, 8]. Due to the high operating temperature ($T = 1000 \text{ }^\circ\text{C}$), kinetic losses do not play a prominent role, thus the u versus i characteristics of those cells show no overpotential. On the other hand, the internal resistance of SOFCs is usually larger than in alkaline or solid polymer cells and the reversible cell voltage $\Delta G/zF$ is lower due to the high operating temperature. Both effects will contribute to the current density limit in SOFCs.

Since the left side in eqn. (7) becomes zero, the current-density limit can be expressed directly in terms of the internal resistance and the efficiency of the reference system, e.g., the Ni/H₂ battery:

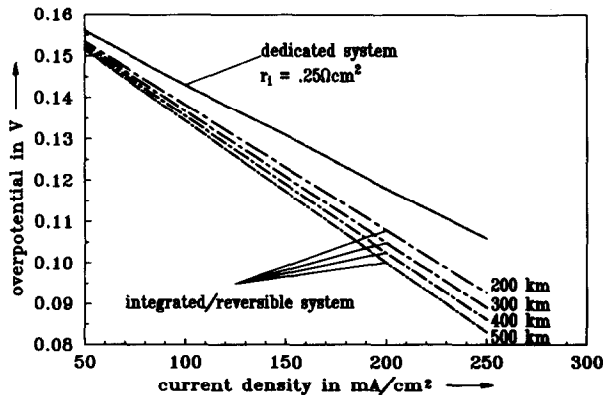


Fig. 3. The maximum allowable overpotential on the electrodes vs. current density. The data are calculated for integrated RFC systems assuming different orbit altitudes.

$$i < \frac{\Delta G}{r_1 z F} \frac{1 - \eta_{\text{bat}}}{c_1 + \eta_{\text{bat}}} \tag{8}$$

The evaluation of the i versus r_1 dependence is shown in Fig. 4 for orbit altitudes in the range from 200 to 500 km. For comparison, the current-density limit of a dedicated low temperature RFC system is given assuming an overpotential of $u_{\text{ov}} = 120$ mV. The internal resistance of today's SOE/SOFC does not fall below $r_1 = 0.48 \Omega \text{ cm}^2$ [7, 8]. Thus, the allowable current density of the solid oxide RFC is below $i = 203 \text{ mA/cm}^2$, corresponding to a high-temperature heat requirement of $\dot{Q}_{\text{el}} = 54.4 \text{ mW/cm}^2$ in the electrolyzer mode and a waste-heat production rate of $\dot{Q}_{\text{fc}} = 170.7 \text{ mW/cm}^2$ in the fuel-cell mode. Considering different operating periods, 51.1% of the fuel cell waste heat must be fed into the electrolyzer.

Conclusions

The comparison of the current density limits of both, low temperature cells and solid oxide cells (SOCs) shows, that the SOC is not the superior technique, their performance being limited by their insufficient internal conductivity. However the SOC technique of today's performance may compete with the battery storage, if their technical problems can be solved. Thus, no performance goals for electrocatalytic research are defined for the SOC.

On the other hand, the alkaline and solid polymer technique require elevated effort in fundamental research to reduce the overpotentials on the electrode surfaces. The performance goals for the electrocatalytic properties of future electrodes as shown in Fig. 5 depend on the RFC technique desired. The dedicated RFC system shows the lowest performance requirements. Note that the data in Fig. 3 refer to the current density of the electrolyzer, that operates at lower current densities than the fuel cell in integrated RFCs. If the x -axis would refer to the fuel-cell current density, the integrated RFC would require apparent lower development effort, however this scaling would compare the integrated system with a dedicated RFC operating at elevated current densities. Evaluating the performance goals of the RFC, i.e., the allowable

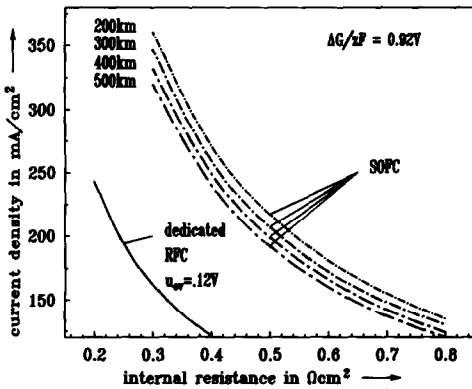


Fig. 4. Current-density limits for SOFC application in LEO. The allowable current density vs. the internal resistance of the cells assuming orbit altitudes between 200 and 500 km is shown. The current-density limit of a dedicated low temperature cell is given for comparison.

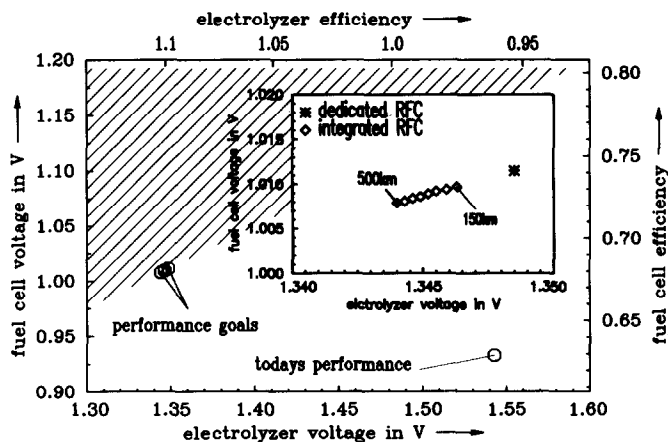


Fig. 5. Performance goals of regenerative fuel cells for LEO application. The operating points of both dedicated and integrated RFC stacks are shown in the two-dimensional voltage plane. Note that these operating points are independent of the current densities, since the requirements of the electrocatalytic performance increase with increasing current density. The hatched area indicates those operating points of the RFC leading to overall efficiencies $> 75\%$.

cell voltages during fuel-cell and electrolyzer operation, it is easy to see, that the integrated stack design will require greater technological effort in catalytic research. The data shown in Fig. 5 are independent of the absolute values of the current densities, however the data for the RFCs in integrated stack design depend on the current density ratio i_{el}/i_{fc} during charging and discharging periods.

From the presented results we conclude:

- The reduction of the overpotentials on the electrodes is the most important development goal even when receiving high current densities in order that the RFC should succeed in their space energy supply
- The thermal interconnection of fuel cell and electrolyzer is of essential importance to decrease the electrochemical development requirements regarding the overpotentials on the fuel-cell electrodes. Secondly, the allothermal SOE operation will require a thermal energy source, which may be the fuel cell producing waste heat
- Alkaline or solid polymer RFCs may become competitive if the reduction of the overpotential will succeed: (i) here the dedicated RFC is more attractive, since it requires less reduction of the overpotentials than the integrated stack design. To achieve competitiveness regarding the Ni/H₂ battery, the overpotentials must be reduced by 35% assuming current densities of $i = 100 \text{ mA/cm}^2$, and (ii) if the overpotentials can be reduced by 45% then the alkaline or solid polymer RFCs may compete with current densities in SOCs
- The SOE/SOFC may become competitive if their technical problems can be solved. Electrocatalytic research is not required
- Since today's solid oxide electrolyte cells show distinct lower conductivity per unit area than advanced low temperature cells, the dedicated alkaline or solid polymer RFC will still be in competition, if the reduction of the electrodes overpotentials will succeed

Note that the electrocatalytic properties of the electrodes defined in this work are performance goals, no evidence is given, whether these goals are achievable.

List of symbols

F	Faradays constant, As/mol
i	current density, A/cm ²
i_{el}	current density of the electrolyzer, A/cm ²
i_{fc}	current density of the fuel cell, A/cm ²
\dot{Q}_{el}	heat flow into the electrolyzer, W/cm ²
\dot{Q}_{fc}	heat flow from the fuel cell, W/cm ²
r_i	internal resistance of the cells, Ω cm ²
u_{el}	operating voltage of the electrolyzer, V
u_{fc}	operating voltage of the fuel cell, V
u_{el}^*	open-loop voltage of the electrolyzer, V
u_{fc}^*	open-loop voltage of the fuel cell, V
u_{ov}	overpotential at the electrode surface, V
z	electron transfer in the H ₂ /O ₂ reaction
ΔG	free energy of the H ₂ /O ₂ reaction kJ/mol
ΔH	enthalpy of the H ₂ /O ₂ reaction, kJ/mol
η	efficiency
η_{bat}	current efficiency of battery

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