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Electrical Characterization and Modeling of an Innovative Acid/Base Flow Battery

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ABSTRACT This article presents an experimental validation of modeling approaches for the AB-FB battery, an innovative technology with significant potential for large-scale energy storage applications. The results demonstrate, through experimental analyses that a simplified zero-order equivalent circuit model (ECM) provides adequate accuracy in predicting the electrical behavior of AB-FB cells, particularly in scenarios requiring constant current. In comparison, the more complex electrochemical model, while offering detailed insights into material and electrolyte interactions, is excessively intricate for the sole purpose of describing electrical behavior. Additionally, the study confirms that the discharge characteristics of the AB-FB align with those of established battery technologies, indicating familiarity with its operational principles, mitigating technical risks associated with large-scale deployment. The main contribution is therefore the assessment of the potential use of this technology and the possibility of modeling it with already established approaches.

INDEX TERMS Acid/Base Flow Battery (AB-FB), electrical characterization, AB-FB modeling, energy storage, equivalent circuit model, electrochemical model.

I. INTRODUCTION

THE growing production of electrical energy from renewable sources and the consequent need for facing the uncertainty of such sources are leading to the development of high performance energy storage systems, based on eco-friendly design and operation to reduce the environmental footprint of each spreading technology.

Lithium-ion batteries are currently widespread and used for different applications, such as automotive, portable devices and also large-scale energy storage [1], [2]. It is due to their high energy and power density, compared to other electrochemical storage technologies [3], [4]. However, such batteries present issues related to the raw material extraction, such as lithium and others critical minerals [5] and operational safety, since phenomena as thermal runaway require can require the implementation of complex thermal management strategies [6], [7]. Besides, battery disposal [8] and life cycle assessment are key aspects of this technology [9]. In order to address these issues, research is moving towards new materials and technologies. In particular, this work examines the innovative, cutting-edge Acid Base-Flow Battery (AB-FB) to ensure intrinsically safe

operations and sustainable materials [10]. The main advantages of this technology are related safety, materials and design. In particular, dangerous storage mediums and pollutants for the operation of AB-FBs are not used and the raw materials for their production are widely available since only not dangerous water solutions and bipolar membranes are needed. Besides, the low self-discharge rate and the flexible design, due to modularity allow AB-FB to be a good trade-off between of energy density and cost, in competition with the leading technology for large-scale energy storage, as fully demonstrated in [11] and [12].

Based on the main characteristics of the AB-FB technology, the following applications have been recently individuated in literature: energy storage systems for light-commercial applications such as office buildings, providing for instance the integration of a rooftop PV system; distribution network decongestion and voltage management, by improving the grid flexibility and stability and finally bulk energy storage to support generation with large-scale installation at the power grid generation points as reported in [13] and [14]. In particular it is stated that AB-FBs are a viable

solution to face the issue of the renewable energy intermittent nature. Besides, it is also remarked that AB-FB technology is not suitable for power grid services requesting extremely fast actuation time such as the primary frequency control and for applications where a space saving is required such as in electrical vehicles (EV) on-board applications. This stems from the main drawbacks of AB-FBs, that are the slow dynamic, due to hydrodynamic phenomena occurring inside the battery and the space required for the installation. The latter is due to the AB-FB energy density which is currently significantly lower than that of Li-ion batteries [15]. Most of the studies in the literature are conducted on AB-FBs that are properly designed and developed to optimize the electrical energy production through the reverse electro dialysis with bipolar membranes. However, it is possible to use EDBM (Electrodialysis with Bipolar Membranes) devices, which are typically employed for generating chemicals, in their reverse operation, effectively operating as AB-FBs. In this way, a bidirectional operation of the device is possible, the charging phase is represented by the chemicals generation (acid and base) through electrical energy, whereas, in the discharging phase, the chemicals are used to generate electrical energy. Specifically, the electrical modeling of an EDBM device in its reverse operation as an AB-FB is only addressed theoretically and poorly investigated in the literature, without practical or experimental quantification of the process. Generally, the development of new electrochemical energy storage systems requires their adequate modeling. The main goal is to investigate the electrical behavior of these systems in order to verify their potential development and to optimize energy management, including the possibility for integration with diverse energy sources. Besides, modeling allows indubitably for large-scale proper design.

From the scientific literature, different approaches can be used for a proper battery modeling [16], [17], [18]. Basically, they can be divided into three main categories: electrochemical models, analytical models and equivalent circuit models (ECMs) [19], [20], although hybrid battery modeling approaches are often used to combine the advantages of different methodologies [21]. Electrochemical (or physical-chemistry) models can be considered as the basis for the other models. They are extremely accurate, but also present high complexity, since thermodynamic and kinetic phenomena occurring within the cell are considered, by correlating geometric, electrical, and chemical parameters, as in [11] and [22]. Analytical models can be categorized into two main areas: stochastic and empirical/semi-empirical models. The firsts offer high accuracy while maintaining reasonable complexity [23]. They often leverage discrete-time Markov chains for simulations. Empirical/semi-empirical models prioritize simplicity and real-time parameterization. They achieve this by simplifying complex electrochemical models with suitable mathematical equations [24]. ECMs represent batteries as electrical circuits. These circuits use basic components like resistors, capacitors, and voltage sources to model the battery electrochemical and physical behavior, including its

ability to respond to load changes (dynamic characteristics). Depending on the specific application, different levels of complexity can be chosen. These models are categorized by order from the simplest zero-order model to complex n-order approach [25]. Zero-order models treat the battery as an ideal voltage source in series with a single resistor representing the internal resistance [26]. It is suitable for basic applications but lacks accuracy for dynamic behavior. To capture the battery dynamic response more accurately, multiple resistor-capacitor (RC) branches with varying time constants can be connected in series within the model [27], [28]. ECMs offer a balance between complexity and accuracy. However, models with orders higher than zero require experimental testing to determine their specific parameters. In this work, the electrical modeling of an AB-FB is carried out through a zero-order model, also known as Rint model, since higher-order ECMs require rather lengthy experimental tests, which cannot be considered standard since the presented AB-FB is a prototype and no parameter can be identified as nominal. The Rint model is then compared to an electrochemical model to highlight the limitations and advantages of each model, investigating the possibility of use of a zero-order ECM to overcome the complexity of an electrochemical approach to predict the external electrical behavior of the cell. In general, the main contribution of this work can be summarized as follows.

- An innovative AB-FB is electrically characterized to assess its suitability for implementation in stationary applications, on the basis of the limited existing research on AB-FB batteries. In particular, a bipolar membrane structure, typically employed for the production of chemicals through electrical energy via the electro dialysis process, is investigated to evaluate its performances in reverse operation as an AB-FB. The key objective is to investigate this innovative technology with the aim to assess its potentialities to be an enabling solution, compared to traditional batteries, in providing grid support to the energy demand within the realm of stationary energy storage.
- Cell modeling is performed using a zero-order ECM, focusing on evaluating the cell performance under steady-state and slow-dynamic operating conditions. The key objective is to assess the effectiveness of this model in delivering reliable preliminary results, serving as a valid tool for rapid emulation of the system electrical behavior in steady-state conditions. In particular, the analysis of using a zero-order ECM, never been conducted for the characterization of this type of AB-FB, aims to understand whether it is possible to model cell internal phenomena such as dissipations, side effects of the membranes, concentration gradients variation, with a simple equivalent circuit, without significantly affecting accuracy. This approach aims to bypass the complexity of previously developed electrochemical model in [29], offering a useful tool for designers facing with complex

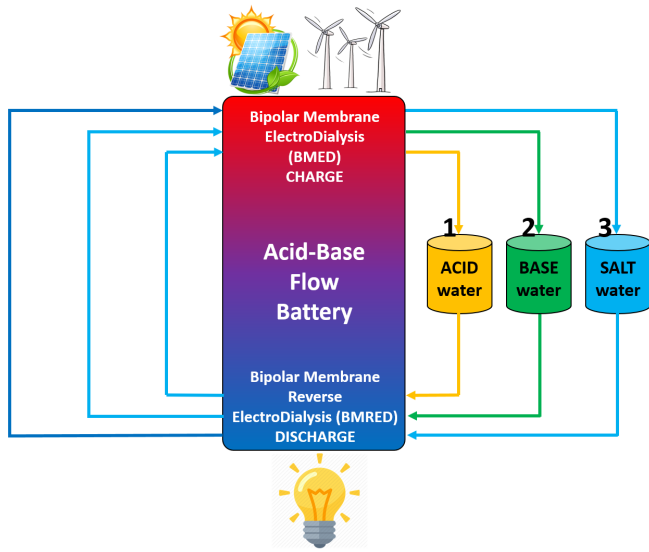


FIGURE 1: Schematic drawing of an AB-FB system.

electrical system of which the AB-FB is included as a component.

The article is structured as follows. Section II delves into the fundamental principles governing the operation of AB-FB batteries. It provides a comprehensive understanding of the underlying mechanisms that enable these batteries to store and release electrical energy. In section III the authors delve into the formulation of both the electrochemical model and the zero-order ECM. Section IV focuses on the process of model parametrization and the methodology employed to extract the necessary parameters from experimental data is outlined. Section V presents the experimental findings obtained from testing of the AB-FB, providing insights into the performance characteristics of these batteries under various operating conditions. Finally, in Section VI, the key contributions of the work are summarized.

II. INNOVATIVE ACID-BASE FLOW BATTERY: WORKING PRINCIPLE

In recent works [11], [12], the authors presented the AB-FB technology, accurately describing and illustrating its operation principle and highlighting the related state-of-the-art. Fig. 1 shows a schematic drawing of an AB-FB system, useful for illustrating its basic operating principle. Essentially, this operation is based on two membrane processes: the Electro-dialysis with Bipolar Membranes (EDBM) during the charge phase and its opposite process, the Reverse Electro-dialysis with Bipolar Membranes (REDBM), during the discharge phase. Energy storage occurs in the form of salinity and pH gradients, with fresh water and saltwater streams as inputs. The stored energy can be supplied to an electrical load during the discharge phase when a controlled neutralization through the REDBM process occurs. During this process, acid and base solution streams are reconverted into saltwater and fresh water. This operation requires separate tanks (with adequate

capacity based on the total energy capacity desired for the specific application) where the different solutions involved in the battery operation are stored. Specifically, an AB-FB system includes three containers holding the three different electrolyte solutions, as shown in Figure 1. Container 1 stores the acidic solution, container 2 holds the alkaline solution, and container 3 contains the saline solution. Initially, when the battery is discharged, containers 1 and 2 are filled with fresh water, while container 3 holds a concentrated saltwater solution. During the charging process, water is dissociated into H^+ and OH^- ions by the bipolar membrane (BPM), causing the solutions in containers 1 and 2 to become acidic and alkaline, respectively, while the saline solution in container 3 reduces its salt concentration. Particularly, Cl^- and Na^+ ions from the salt migrate to the acidic and alkaline channels through the anionic exchange membrane (AEM) and cationic exchange membrane (CEM), respectively. During the discharge process, the acidic and alkaline solutions in the AB-FB are neutralized in a controlled manner, thus producing fresh water again, while the salt solution in container 3 increases its salt concentration. This operation mode, involving three containers, is called batch configuration. The advantage of the batch configuration, used in this work, lies in the need for only three containers, which, for large-scale cell applications, results in a significant reduction in required volume, compared to an open-loop operation mode, for which six containers are needed (three as input and three as output). As remarked in [13], it is noteworthy that the AB-FB, belonging to the category of flow batteries, presents the following relevant characteristic: there is a decoupling between the battery's energy capacity (which depends on the volumes of the water tanks) and its rated power (which depends on the size of the membranes chosen during the battery design stage). This characteristic ensures flexibility and a certain degree of freedom in battery design, making the battery adaptable to the specific application.

III. BATTERY MODELING

To model the AB-FB, two main battery models are considered: the electrochemical model, previously developed and described in detail in [29] and the well-known Rint model [26]. In this section, the general formulation of both models is provided, by remarking the main peculiarities.

A. ELECTROCHEMICAL MODEL

The electrochemical model of ABFB has been initially formulated in [11] and subsequently refined in [30] and [31]. It features a multi-scale (four scales) and multi-level structure and is semi-empirical, requiring membrane properties as parameters. This modelling strategy allows to limit computational burden while maintaining a high level of accuracy. With its various scales and levels, the model predicts ionic transport across the membranes and accounts for significant non-ideal phenomena occurring during ABFB operation, such as parasitic currents via manifolds, concentration polarization, and

pressure losses. A schematic of the electrochemical model is shown in Fig. 2.

The model can also predict key electrical variables, including the electrical potential of the triplet, the Nernst potential associated with the membranes, and the electrical resistance.

Specifically, the electrical resistance (R) of the triplet is given by

$$R = \sum_{sol} R_{sol} + \sum_m R_m, \quad (1)$$

where R_{sol} is the electric resistance of the generic electrolytic solution (*i.e.*, acid, base or salt), and R_m is the electric resistance of the generic IEM (*i.e.*, CEM, AEM or BPM). The Nernst potential is calculated using Tanak approach [32], extended to the three IEMs that constitute the triplet.

$$E = \sum_{IEMs} \left(-\frac{R_g T}{F} \int_{left,IEM}^{right,IEM} \sum_{ions} \frac{t_{i,m}}{z_i} d \ln(a_{int,i}) \right), \quad (2)$$

in which R_g is the gas constant, T is the temperature, $a_{int,i}$ is the ion activity calculated at the solution-membrane interface, solution side. The stack scale includes two levels: the parasitic currents (shunt currents) model via manifolds and the hydraulic model of the stack. The parasitic currents model calculates the distribution of electrical current and potential in the equivalent electrical circuit of the unit. Specifically, the parasitic currents model includes Ohm's equations for the branches (3) and Kirchoff's equations for the nodes (4) of the equivalent electrical circuit of the EDBM unit.

$$\Delta V_k = R_k I_k, \quad (3)$$

$$\sum_k I_k = 0. \quad (4)$$

ΔV_k and R_k are the generic branch ohmic voltage drop and electric resistance and I_k is the electric current intensity flowing to or from a generic node of the equivalent electric circuit. The hydraulic model calculates the distribution of the solutions volumetric flow rates in the channels and the pressure drops both distributed and concentrated, in each branch of the equivalent hydraulic circuit. Lastly, the external circuit calculates the pressure drops in the external hydraulic circuit and includes dynamic mass balances for each of the three external tanks, namely the acid, base, and salt compartments. The system of equations is implemented in the *gPROMS Model Builder*® simulation platform. The described electrochemical model involves parameters such as ion diffusivity (*i.e.*, Na^+ , H^+ , Cl^- , OH^-), fixed charge density, membrane resistance, geometric characteristics (*i.e.*, spacer flow attack angle, spacer pitch-to-height ratio, number of triplet), and process conditions (*i.e.*, reagent flow velocity, solution volumes, blank resistance). To identify these parameters, several analyses are necessary, such as two-compartment cell diffusion experiments to obtain diffusivity or Electrochemical Impedance Spectroscopy (EIS) for the internal resistance of the membrane. The model is primarily used for

the identification of the ion concentrations in the solution and membrane phase, the ion ohmic and diffusive flux, the boundary layer voltage drop and the mass balances. However, it is also possible to model the electrical behaviour of the AB-FB by deriving the electrical characteristics Q-V. A summary is provided in Table 1.

B. ZERO-ORDER EC MODEL

The zero-order ECM (Rint) basically consists of an ideal DC voltage generator used for modeling the battery open circuit voltage (OCV) connected in series with a resistor, modeling the battery internal resistance due to the electrodes, as shown in Fig. 3.

According to this model, the battery terminal voltage $V(SoC)$, State-of-Charge (SoC) dependant, is simply expressed through the following equation:

$$V(SoC) = E(SoC) - R_i(SoC) \cdot I, \quad (5)$$

in which $E(SoC)$ is the voltage of the ideal DC voltage generator, $R_i(SoC)$ is the internal resistance and I is the current delivered by the cell.

As denoted from the governing equation, the main advantage of the Rint model is related to its oversimplicity. Besides, if it is employed for modeling a commercial cell, there is no need for experimental tests, since the model parameters can be retrieved only using the discharge curves within the manufacturer datasheet, ensuring an adequate accuracy, as demonstrated in [4] for a Li-ion cell. In the case of a prototype, experimental tests for the parameters identification are needed, because manufacturer data is unavailable, but they consists solely of discharging the cell in CC mode for different current values. This aspect, along with the intrinsic simplicity of the model, is one of the main reasons for choosing this model for the AB-FB. In fact, unlike the zero-order ECM, the first-order one requires a Pulse Discharge Test (PDT) [33], whereas second-order ECMs require a more complex Hybrid Pulse Power Test (HPPT) [27]. The PDT test consists of repeating constant current discharge intervals for fixed percentages of SoC, followed by rest intervals allowing the cell reaches its internal equilibrium. It is performed from a set initial SoC (typically a fully charged cell), until the cut-off voltage is reached. In the specific case of the work, the PDT would be valid only for AB-FB working in batch configuration and not for open-loop operation (see Section II). For the latter case, since the SoC depends on the quantity of reagents, while their concentration would not change, the cell OCV would be always the same during each rest interval. It makes the parameters identification procedure not standardly defined. As for the HPPT, it involves alternating charge and discharge phases, leading to a more complex experimental set-up and to a dynamic operation of the cell. The latter has never been electrically characterized and it is considered reasonable for this initial experimental phase not to stress the membranes. Besides, during the experimental tests different reagents sample collections are required in order to get an

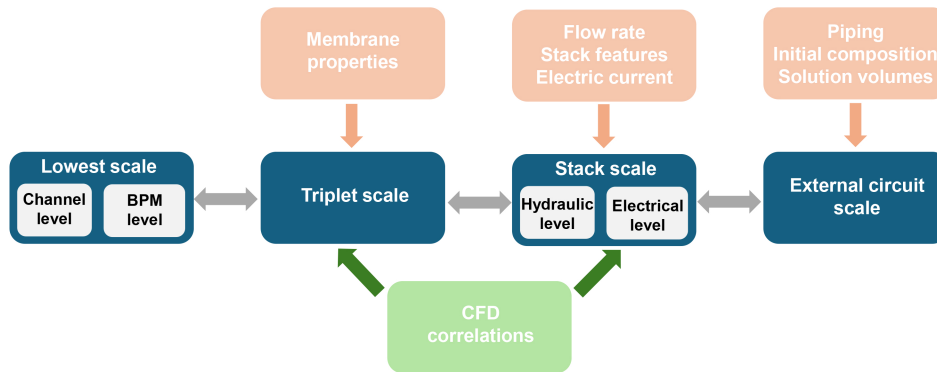


FIGURE 2: Schematics of the multi scale model with levels and inputs. The cyan boxes represent the four dimensional scales of the model. The light blue boxes indicate the levels included in each model scale. The orange boxes display the main input parameters. Correlations for flow and mass transfer characteristics derived from Computational Fluid Dynamics (CFD) simulations are used as inputs for the triplet scale and the hydraulic level of the stack scale.

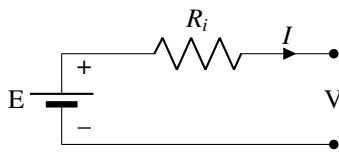


FIGURE 3: Schematic representation of the Rint equivalent circuit model.

indication of the reagents concentration, to be referenced and reported to the electrochemical model for the comparison. In both PDT and HPPT, a higher number of reagent sample extractions would be required, compared to a CC discharge test. This could alter the quantities of the reagents between the beginning and the end of the test, since the system involve a small-scale prototype using relatively small amounts of reagents.

IV. METHODOLOGY

In this section, the experimental set-up is described, by specifying the main characteristics of the tested lab-scale AB-FB unit, the methodology used for the Rint model parametrization is provided and, finally, the dataset processing method is highlighted.

A. EXPERIMENTAL SETUP

1) Test bench

For the electrical characterization of the lab-scale AB-FB unit, a CC discharge test is performed for different discharge current values. A single test consists in a complete discharge of the device under test (DUT) and the acquisition of the voltage across the DUT terminals and the current delivered by the cell. A full description of the test is provided in the next paragraph. To perform the experimentation, a test bench is set up, as shown in Fig. 4. The green-outlined element is the DUT, the blue-outlined elements are auxiliary equipments for the DUT operation, and the red-outlined elements represent

the measurement system. In particular, the test bench consists of:

- 1) lab-scale AB-FB unit which characteristics are reported in Table 2,
- 2) electrode rinse solution (ERS),
- 3) electrolyte solutions,
- 4) volumetric Lead Fluid Technology (LFT) pumps BT601S,
- 5) current clamp probe YOKOGAWA 700937,
- 6) voltage probe YOKOGAWA 700988,
- 7) data acquisition module NI 9215,
- 8) DC electronic load BK PRECISION 8540 150W,
- 9) PC.

The automatic measurement system (AMS), composed of the equipment from 5) to 9) and depicted schematically in Fig. 5 works as follows. The electronic load is used to discharge the DUT in CC mode. The voltage across the DUT terminal and the delivered current are measured through the voltage probe and the current probe respectively, then acquired through the acquisition board and stored in the PC.

2) Test description

The test consists in a complete discharge of the DUT with a superimposed CC through the electronic load. The complete procedure involves preliminary operations consisting of verifying the absence of leaks and checking the initial conditions. The test is then conducted, followed by the final steps to restore the setup. The phases of the procedure are explained in more detail below:

- 1) **Leakage check:** before performing the discharge tests, a leakage test is performed. It consists in the inlet of demineralized water trough the membrane, and a successive check of the precipitates. The ABFB unit sealing is verified if the quantity of precipitates, thus the leakage between the battery compartments is negligible.

TABLE 1: Comparison between electrochemical model and equivalent circuit model.

	Electrochemical model	Zero-order equivalent circuit model
Model parameters	ion diffusivity fixed charge density geometrical features process conditions	open circuit voltage internal resistance
Experimental test needed	Electrochemical Impedance Spectroscopy (EIS) membrane calibration two-compartment cell diffusion experiments	CC discharge
Model output	Ion ohmic/diffusive flux water neutralization rate ion concentration in membrane/solution phase boundary layer voltage drop Q-V characteristics	Q-V characteristics

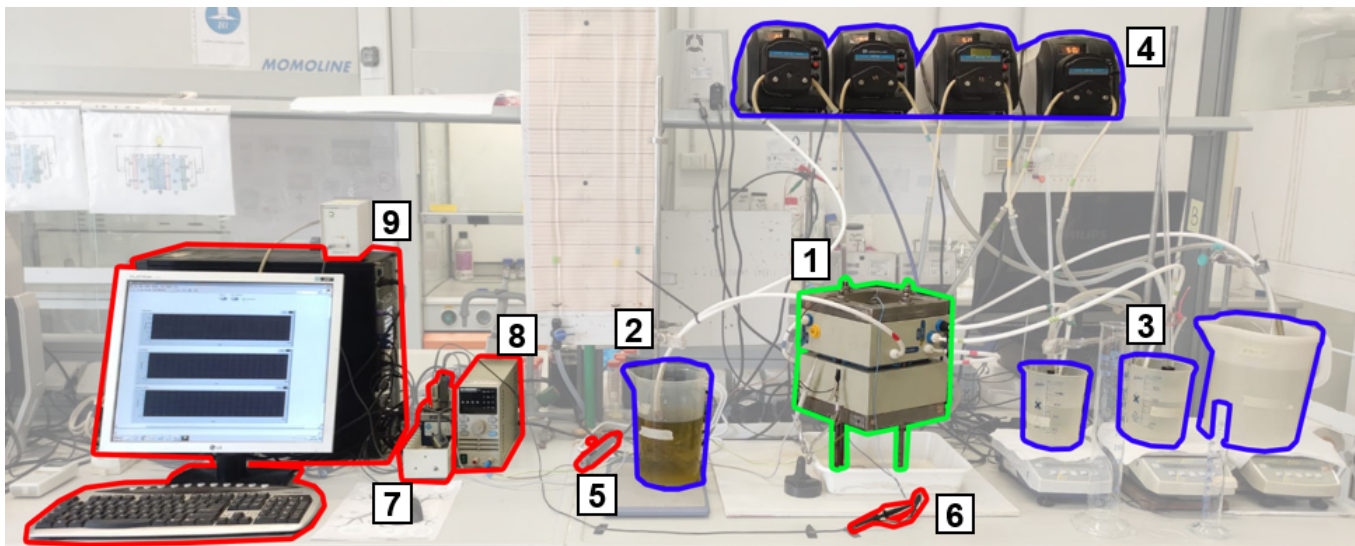


FIGURE 4: Test bench setup: 1) AB-FB unit, 2) Electrode Rinse Solution, 3) Electrolyte solutions, 4) Volumetric pumps, 5) current probe, 6) voltage probe, 7) acquisition board, 8) electronic load, 9) PC.

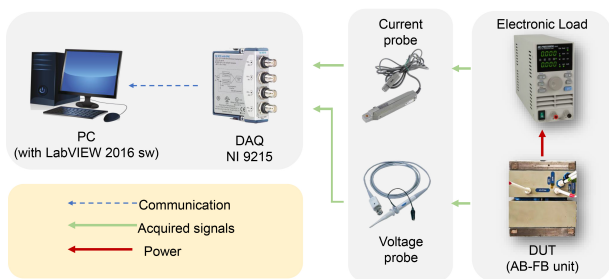


FIGURE 5: Block diagram of the automatic measurement setup for the DUT characterization.

TABLE 2: AB-FB unit characteristics.

	Value
Model	FT-ED-100
Manufacturer	Fumatech BWT GMBH
Anionic membrane	FAB-PK-130
Cationic membrane	FBK-PK-130
Bipolar membrane	FBM
N. of units	5
Active area	100 cm ²
Spacer material	PVC/ECTFE
Spacer tickness	480 μm

2) **Initial condition check:** once the absence of leakage is verified, the initial conditions chosen for the experimental tests are checked. They are reported in Table 3. The electrolyte solutions used for the experimental tests is prepared with NaCl with 99.7% purity (ChemSolute), HCl at 37% by weight (Merck), and NaOH in pellets with 98-100% purity (Honeywell Fluka). The Electrode Rinse Solution (ERS) is prepared with 0.5M

$FeCl_2/FeCl_3$ with a purity of 99% (ChemSolute), and 0.6M HCl is added to prevent the precipitation of iron oxy-hydroxides. The HCl, NaOH and NaCl concentrations are obtained through acid-base titrations, the solution volumes are set using graduated containers and their consistency is monitored throughout the entire test, as the containers (labeled as numbers 2 and 3 in Fig. 4) are placed on scales to ensure that there are no solution losses. The current density range is defined by the currents imposed for the experimental tests, within a range that prevents delamination of the bipolar

TABLE 3: Initial operating conditions for the conducted discharge tests.

	Unit	Value
HCl concentration in the Acid comp.	mol/l	1.0
Acid solution volume	ml	600
NaOH concentration in the Base comp.	mol/l	1.0
Base solution volume	ml	600
NaCl concentration in the Salt comp.	mol/l	0.25
Salt solution volume	l	3.6
Current density	A/m ²	52-76

membrane.

3) Discharge phase

- a) *chemical-hydraulic level*: the electrolyte solutions are circulated through the hydraulic circuit using the volumetric pumps. The average flow rate in the acid, base, and salt channels is 75 ml/min, while the flow rate in the ERS compartment is set 3–4 times higher to avoid potential mass transfer issues at the electrode surfaces. The test is conducted in a batch configuration as depicted in Fig. 1.
- b) *electrical level*: the electronic load is set in CC mode, the voltage and current probes are enabled, then a Virtual Instrument (VI), built-up in *Lab-View* stores the acquired signals. The sampling frequency is set to 2 Hz. The number of samples is set to $N_s = 2$.

- 4) **Discharge finished**: once the discharge is completed, the electronic load is disabled and demineralized water is used to clean the membranes through the the volumetric pumps.

The test is repeated for the following current values: $I = 0.52A, 0.61A, 0.68A, 0.76A$. For each current value, the test is repeated three times to ensure measurement repeatability and new reagent solutions are prepared and used.

B. RINT MODEL PARAMETRIZATION

For the Rint model parametrization, the procedure reported in [4] is used. The output of the procedure are the internal resistance and the OCV as function of the SoC $R_i(SoC)$, $E(SoC)$ respectively, and the Peukert capacity as calculated in [34] to take into the account the dependence between the discharge current and the delivered cell capacity. The parameter identification procedure is developed in *MATLab*.

C. DATASET PROCESSING METHOD

To compare both electrochemical model and Rint model, to assess the viability of the latter as a useful tool for the AB-FB modeling, the percentual error $e_I(SoC)$ and the Route Mean Square Error $RMSE_I$, for each I discharge current, are evaluated as follow:

$$e_I(SoC) = \frac{V_{exp}(SoC) - V_{model}(SoC)}{V_{exp}(SoC)} \cdot 100, \quad (6)$$

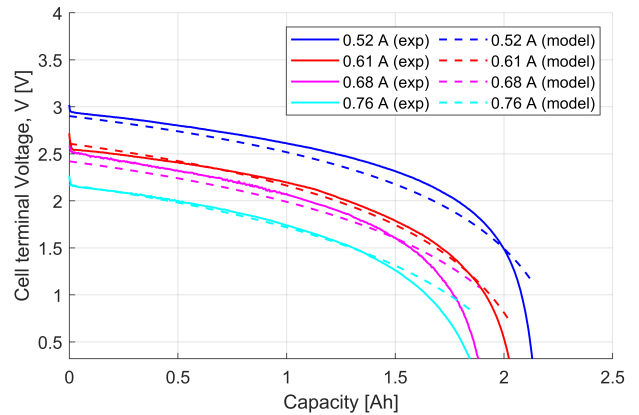


FIGURE 6: Comparison between electrochemical model (dashed lines) and experimental results (continuous lines).

$$RMSE_I = \sqrt{\frac{\sum_{i=1}^K [V_{exp}(SoC) - V_{model}(SoC)]^2}{K}}, \quad (7)$$

in which $V_{exp}(SoC)$ and $V_{model}(SoC)$ are the acquired voltage and the model obtained voltage trends, respectively and K is the number of acquired samples.

V. RESULTS AND DISCUSSION

In this section, the electrochemical and Rint model output are presented, then compared and discussed together with the experimental results.

A. OBTAINED RESULTS

The experimental uncertainty in terms of DUT terminal voltage, derived from re-tests at a given discharge current value, is ± 20 mV. Such a value is considered acceptable since it is less than 5% of the lowest measured value. The comparison between the electrochemical model presented in Subsection III-A and the experimental results obtained from the tests described in paragraph IV-A2 is shown in Fig. 6. It can be noted that the model adequately predict the external behavior of the cell, even if, for low values of the SoC, the model starts to diverge and is unable to match the experimental voltage trend. It can be also observed from the error trends reported in Fig. 7. In particular, for a discharge current equal to 0.52 A (Fig. 7 (a)), the error is within the $\pm 5\%$ bandwidth for a SoC range equal to 60%. Better results can be observed for greater discharge current values ((Fig. 7 (b), (c) and (d)) for which the error is limited within the $\pm 5\%$ for a SoC range greater than 80%. The RMSE values are reported in the second column of Table 4.

Figs. 8 and 9 show the internal resistance and the OCV as function of the SoC, obtained by following the parameter identification procedure described in Subsection IV-B. In Fig. 10, the comparison between the Rint model output and the experimental voltage trends is depicted. As depicted in Fig. 11, the error trend is lower than the one reported by the

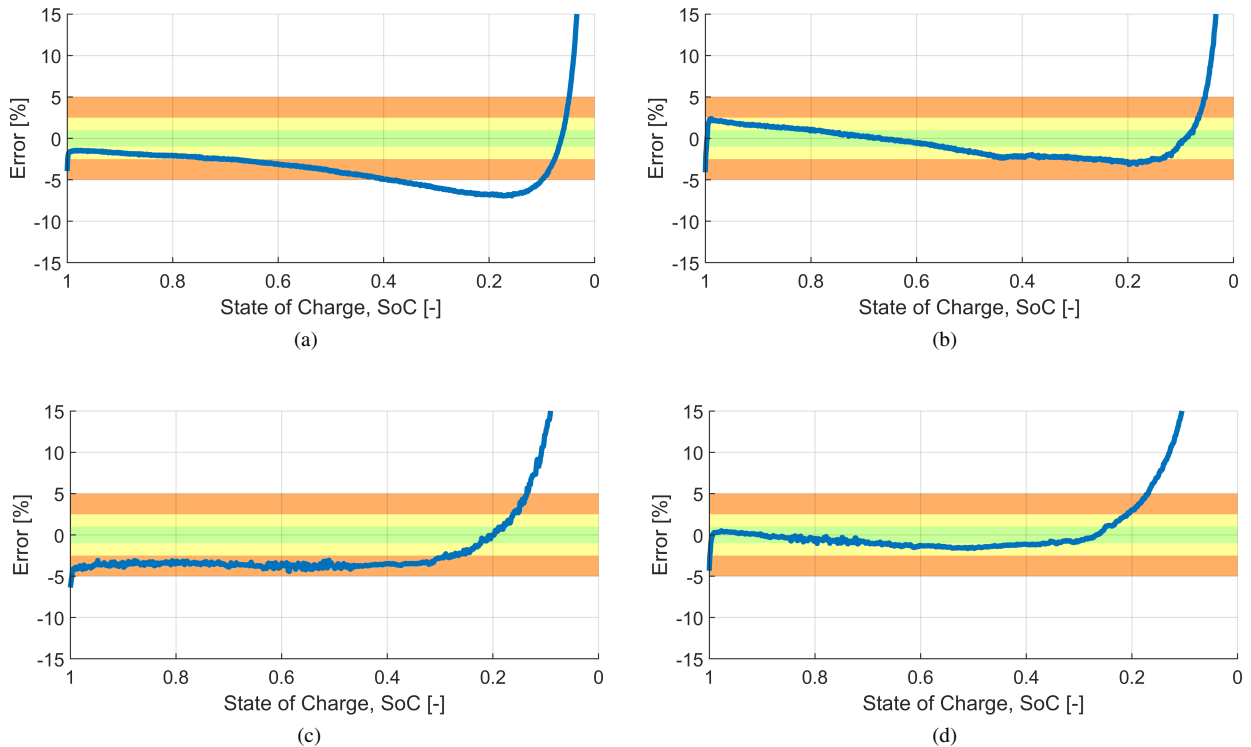


FIGURE 7: Electrochemical model error trends for different discharge current values: (a) 0.52 A, (b) 0.61 A, (c) 0.68 A, (d) 0.76 A.

TABLE 4: Initial operating conditions for the conducted discharge tests.

Current [A]	RMSE [V]	
	Electrochem. model	Rint model
0.52	0.134	0.050
0.61	0.060	0.091
0.68	0.152	0.055
0.76	0.108	0.017

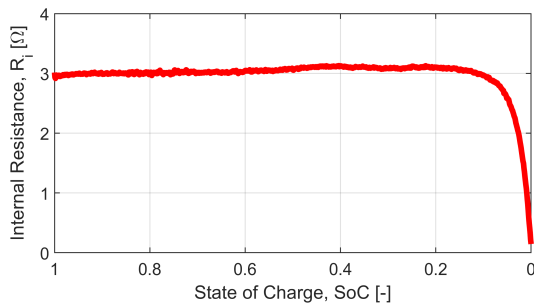


FIGURE 8: Internal resistance as function of the State of Charge.

electrochemical model. In particular, for a current equal to 0.76 A, the error is limited to the $\pm 1\%$ for a SoC range greater than 80%, as confirmed by the extremely low RMSE value, reported in the third column of Table 4.

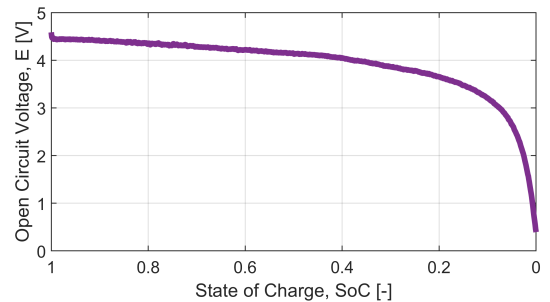


FIGURE 9: Open circuit voltage as function of the State of Charge.

B. DISCUSSION

A first relevant element to be remarked concerns the AB-FB electrical behavior, as it results from the set of experimental discharge curves. In particular, two relevant aspects of this behavior appear evident: the battery output voltage and its maximum capacity decrease with the increasing of the discharge current. Such a behavior is consistent with other battery types (*e.g.* lithium-ion battery [35]). This confirms, albeit a preliminary analysis, that AB-FB is a possible solution for large-scale energy storage applications, as its electrical behavior can be traced back to the already known literature. One aspect in which AB-FB differs from lithium cells is related to the high internal resistance values. The internal resistance

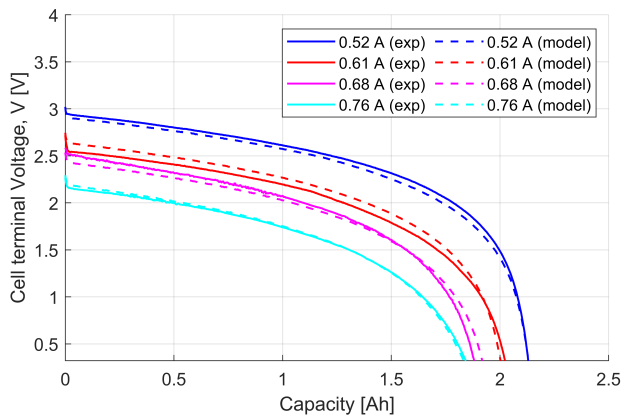


FIGURE 10: Comparison between Rint model (dashed lines) and experimental results (continuous lines).

of the AB-FB primarily depends on the composition and concentration of ionic species within the acid, alkaline, and saline channels, as well as, on the water transport phenomena, such as osmosis and electro-osmosis. Moreover, the wear of the membranes of the prototype used for testing cannot be neglected. Furthermore, considering that this cell is applicable for stationary technologies for which high performances and rapid power transients are not required, a high internal resistance value could be considered acceptable.

As the electrochemical model is concerned, the AB-FB electrical behavior is well predicted for high SoC values, whereas, for high Depth of Discharge (DoD=1-SoC), the voltage across the cell terminals obtained by the model is always greater than the experimental one. The significant discrepancy between the model and the experimental data is due to an underestimation of the cell resistance at low acid and base concentrations. In fact, SoC is intrinsically linked to the concentration of both acidic and alkaline solutions, which depend on the ionic fluxes that are influenced by non-ideal phenomena. The analysis of the AB-FB reveals that a simple modeling approach can be quite effective. By comparing experimental data with a basic Rint model, a high degree of accuracy can be observed. This suggests that for the AB-FB, more complex models might be unnecessary.

There are two key reasons for this finding. Firstly, the Rint model achieved good results, with a maximum RMSE of 90 mV. This low error indicates a close match between the model predictions and the battery actual behavior and it is reasonably of the same order of the ones in the literature.

Secondly, the inherent characteristics of the AB-FB itself favor a simpler modeling approach. Due to the large size of the tanks required for its electrolyte solutions, this battery is not practical for mobile applications. Mobile applications (*e.g.* automotive) typically require frequent and rapid changes in power output. Conversely, the AB-FB excels in scenarios with constant current demands. Since the battery operates primarily in a stable state, a complex model to capture rapid fluctuations becomes unnecessary. Furthermore, when com-

pared to the electrochemical model, the Rint model not only yields lower errors but also reaffirms its validity as a tool for modeling these cells. While the electrochemical model remains essential for membrane design, material studies, and solution investigations, its complexity proves excessive for solely describing electrical behavior. In fact it requires parameters such as ionic diffusion coefficients, ionic concentration in the membrane phase and so on. In contrast, the Rint model necessitates solving only a few algebraic equations. Moreover, the model two parameters can be readily obtained through a CC discharge test.

VI. CONCLUSION

In conclusion, the analysis demonstrates that for the AB-FB, with its focus on constant current applications, a simple Rint model is sufficient to emulate the cell external electrical characteristics due to its accuracy and the battery inherent characteristics. This finding highlights the importance of considering both the model performance and the specific battery application when choosing a modeling approach. The Rint model demonstrates lower errors in predicting the electrical behavior of AB-FB cells. This translates to more reliable simulations for practical applications focused on slow-dynamic characteristics. The strength of the electrochemical model lies in its ability to delve into intricate details relevant to material properties, membrane design, and electrolyte behavior. This level of detail is invaluable for researchers investigating these aspects to improve future cell performance. However, for situations requiring solely an accurate representation of the cell electrical response, this depth of information becomes unnecessary complexity. The Rint model, focusing solely on electrical behavior, provides a simpler and faster approach. Besides, the ease of parameter identification further underscores the practicality of the Rint model for real-world applications. In essence, the Rint model offers a valuable trade-off between accuracy and complexity, particularly with respect to the procedure for the model parameters identification, making it a compelling choice for modeling the electrical behavior of AB-FB cells, particularly when detailed electrochemical understanding is not the primary focus. The electrochemical model remains a powerful tool for in-depth research and development, but for applications focused on electrical performance prediction, the Rint model emerges as a more practical and efficient choice. This tool is particularly useful for rapidly simulating battery behavior within the context of a larger electrical system design, when the AB-FB is included as a component. Besides, discharge characteristics of the AB-FB prototype align with what observed in established battery technologies like lithium-ion. This consistency suggests that AB-FB operates on similar fundamental principles, it implies a level of predictability in the AB-FB performance that engineers already understand and can model effectively. Existing knowledge and experience gained from established battery technologies can be leveraged when designing and implementing large-scale AB-FB storage systems. This reduces the technical risk associated with deploying this new technology

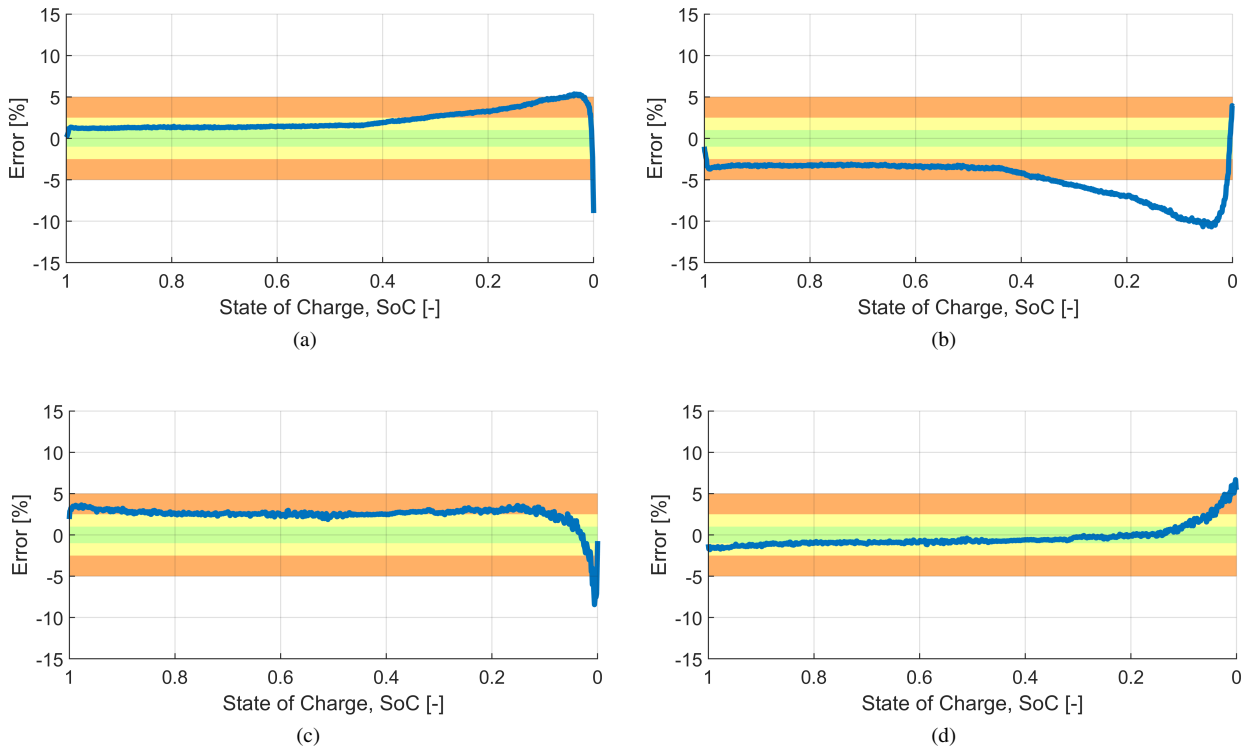


FIGURE 11: Rint model error trends for different discharge current values: (a) 0.52 A, (b) 0.61 A, (c) 0.68 A, (d) 0.76 A.

at scale. Further investigation is necessary to optimize the membrane design and reduce internal resistance. This optimization could lead to significant efficiency gains and bring the AB-FB performance closer to its ideal potential.

VII. FUTURE DEVELOPMENT

Once assessed the potentials of the technology, scaling up AB-FB technology to achieve higher power outputs requires key modifications and presents a series of technical challenges. In particular, it is necessary to enlarge the membrane active area, as the power generated is proportional to the active surface. It leads to issues related to membrane structural integrity and specific materials to ensure uniformity and durability over time. Besides, in order to reach efficiency values comparable to the actual storage solutions, lower internal resistance values are needed. Moreover, at a larger scale, higher volumes of alkaline, acidic, and saline solutions are required. It results in the need for efficient volumetric or variable-speed pumps capable of maintaining a steady flow with large electrolyte volumes and complexity in controlling concentration, mixing, and preventing leaks. However, with advancements in materials technology and control systems, AB-FB could become a viable solution for large-scale energy storage.

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VIII. BIOGRAPHY SECTION



FABIO RICCO GALLUZZO received the master degree in electrical engineering from the University of Palermo, Italy, in 2014 and the Ph.D. degree in Materials Science and Nanotechnology from the University of Catania, Italy, in 2020. In 2023, he joined the Sustainable Development and Energy Saving Laboratory, at the Engineering Department of the University of Palermo, Italy, focusing his research activities on the development and interfacing of innovative electrochemical Energy Storage

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