Proceedings of EFC2019
European Fuel Cell Technology & Applications Conference - Piero Lunghi Conference
December 9-11, 2019, Naples, Italy

EFC19085

EXPERIMENTAL AND NUMERICAL STUDY OF PERFORMANCE HETEROGENEITIES IN A VANADIUM REDOX FLOW BATTERY

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***Abstract* – An experimental investigation of global and local polarization curves and impedance spectra of a 25 cm^2 segmented vanadium redox flow battery is carried out, in order to have an insight on electrode-distributor interplay and on operation heterogeneity and the causes thereof.**

From the analysis of local polarization curves and impedance spectra of the positive electrode, it is found that the serpentine suffers of mass transport issues in the area near the outlet, while the interdigitated shows those issues in the central area of the electrode. Instead, the negative electrode shows a higher homogeneity of operation, since it is characterized by a kinetic dominated regime and poorly influenced by mass transport.

The experimental campaign is supported by a 3D numerical model that couples fluid dynamics and electrochemistry, fitted on experimental data and then validated extensively, also locally, in different operative conditions, with different flow fields and different electrolytes configurations.

***Index Terms* – heterogeneity, impedance spectroscopy, segmented cell, VRFB.**

I. NOMENCLATURE

EIS: electrochemical impedance spectroscopy;
SOC: state of charge;
VRFB: vanadium redox flow battery.

II. INTRODUCTION

With the growth of the electric production from renewable sources, the need of an efficient and durable on-grid and off-grid energy storage technology raised in the last years. Very promising candidates are vanadium redox flow batteries (VRFB) thanks to the possibility of decoupling power and stored energy, their high efficiency and high charge/discharge cycle life.

One of the key factors hindering the performance of vanadium redox flow batteries is the electrolyte distribution over the porous electrode, which is the result of a complex interaction among flow field geometry, electrode morphology and electrolyte properties. In the present work an experimental analysis is carried out with the aid of an innovative segmented cell hardware which allows a local resolution of polarization curves and impedance spectra, in order to have an insight on operation heterogeneity and the causes thereof. The experimental characterization is supported by the development of a 3D numerical model, that couples fluid dynamics and electrochemistry, fitted on experimental data and then validated extensively, also locally, in different operative conditions, with different flow fields and different electrolytes configurations.

III. EXPERIMENTAL

An innovative 10 segments macro-segmented cell has been used for the characterization of the battery, in order to obtain a local resolution of performance and impedance. Not only all-vanadium configuration, but also positive symmetric and negative symmetric configurations have been investigated in order to study separately each side of the battery, at a SOC of 50% and 1M electrolyte concentration. Polarization curves have been performed at different flow rates, in potentiostatic mode inside a voltage range chosen to avoid undesired side reactions; EIS have been performed, only in the symmetric configuration to assure a constant SOC, in the same operative conditions of polarization curves at current values of 0.05 and 0.1 A cm^{-2}, with an oscillation semi-amplitude of 5 and 10 mA cm^{-2} respectively. The frequency range has been selected between 10 kHz and 0.01 Hz, in order to catch both the kinetics-related and mass transport-related phenomena.

IV. EXPERIMENTAL RESULTS

The comparison of local polarization curves recorded for positive (a,b) and negative (c,d) electrolytes with serpentine (a,c) and interdigitated (b,d) flow fields is reported in Figure 1. It can be noticed how the positive electrolyte has a typical mass transport dominated behavior, while the negative one is characterized by a kinetic limited regime, which hinders the performance of this configuration. Moreover the serpentine outperforms the interdigitated distributor.

The local performance of the serpentine follows the depletion of reactants from the inlet to the outlet, while the interdigitated distributor shows a reduction of performance in the middle area of the electrode. In order to study the heterogeneities, a heterogeneity index (ξ) is defined as the coefficient of variation of the local currents corresponding to a selected value of global current. This index reveals greater heterogeneities for the positive electrolyte if compared with the negative one, due to the highly kinetics-limited behavior of the latter, which reduces the influence of mass transport and reactants consumption along the channel; moreover, an higher inhomogeneity is obtained for the interdigitated flow field with respect to the serpentine, because

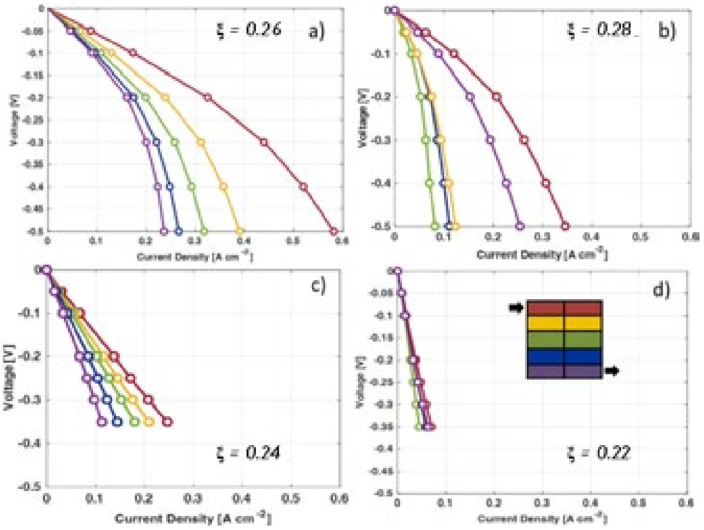

Figure 1: Local polarization curves for positive (a,b) and negative (c,d) electrolytes with serpentine (a,c) and interdigitated (b,d) flow fields. Heterogeneity index is evaluated at 0.05 A cm^{-2}.

of the reduced velocity of the flow in the porous electrode in the middle zone of the electrode, responsible for less intense and inhomogeneous under-the-rib fluxes. It is worth saying that, if the comparison is carried out at a fixed pressure drop, the interdigitated results less heterogenous than the serpentine.

Also the investigation of the local impedance is carried out to enlighten the local phenomena determining the performance: it can be observed that the positive electrolyte shows a large feature related to mass transport which overlaps the feature related to kinetics, that is not the limiting factor for performance with this electrolyte. Instead, the negative electrolyte, which is characterized by a kinetics limited regime and reduced mass transport issues, reveals clearly distinguished features and higher impedance values.

The spatial distribution of local spectra is consistent with the one observed for polarization curves, with growing impedance along the channel path for the serpentine, and a higher impedance of the middle segments for the interdigitated geometry.

V. Model Fitting and Validation

The 3D model has three fitting parameters: electrode active area, electrode permeability and negative electrolyte kinetic constant.

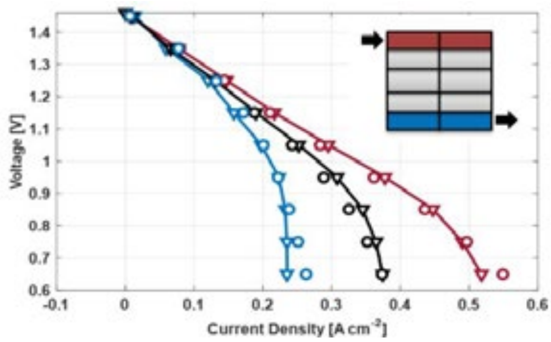

Figure 2: Results of fitting procedure on discharge of the all-vanadium configuration with serpentine flow field.

These parameters are fitted on global and local experimental data of positive and negative symmetric configuration at a flow rate of 20 ml min^{-1}, with both serpentine and interdigitated distributors. The obtained set of parameters is than validated at different flow rates and SOC values, showing a good agreement with experimental results (Figure 2).

VI. Model Results

Analyzing the profile of velocity magnitude inside the electrode in three location and the contour of the reaction rate, it is visible a lower value of velocity in the middle zone of the interdigitated distributor, responsible for the lower reaction rate and then the lower performance of the middle segments observed during the experimental campaign, since the mass transport resistance in the proximity of the carbon fibers of the electrode is determined by a convective mechanism [1].

The model helps also to explain the overperformance of the serpentine with respect to the interdigitated distributor at fixed flow rate: the mean value of velocity inside the porous electrode for the former geometry is nearly 20 times higher than the latter.

The capability of the model to correlate the velocity field and the reactants distribution determined by the flow field pattern, with the global and local performance, allows not only to interpret and analyze the experimental data, but also to design optimized geometries of the distributor with the aim to achieve a better performance and reduced heterogeneity, topic that is investigated in a currently undergoing work.

VII. Conclusion

The main conclusions of the work are:

- The serpentine outperforms the interdigitated with both electrolytes. The reason of this behavior is found in the greater value of velocity of the electrolyte in the electrode, which enhances the reaction rate in serpentine;
- The local distribution of current density follows the pattern of reactants depletion along the channels, but performance shows a reduction in the middle zone of the interdigitated. The reason is found in the lower local value of the electrolyte velocity in the porous electrode;
- The positive electrode, characterized by a mass transport limited behavior, shows generally higher heterogeneity if compared with the negative one, characterized instead by a kinetic limited regime;
- The serpentine reveals lower heterogeneities than the interdigitated when coupled with the positive electrolyte, but its heterogeneity overcomes the interdigitated when the negative electrolyte is considered.

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