

Abstract

The energy transition toward a decarbonized civilization has to be driven by renewable energy sources (RESs). Their installed capacity is anticipated to expand significantly to solve the issues of the depletion of fossil fuels and the mitigation of greenhouse gas emissions. However, the fluctuating behaviour of variable RESs makes it difficult to integrate them into electrical networks. Electrical energy storage hence becomes essential to address the RES-related difficulties. H₂ is becoming one of the most prominent choices for energy storage. Consequently, green H₂ production using water electrolysis has become the subject of many recent researches. Studies are mainly focused on cost reduction via performance improvement and degradation limitation.

In the current work an experimental test rig was built at Environmental Park of Turin. It aims at the characterization of electrochemical devices for the production of hydrogen. This electrochemical test station is designed to enable testing of low temperature electrolytic devices (up to 150°C and 30 bar) both with anionic and cationic electrolyte cells and from individual electrolytic cells to small-assembled cells called stacks.

To be able to deeply study the degradation phenomena starting from the technology level in each P2P system component, accelerated experimental degradation tests were designed and series of tests have been arranged on low-T PEM cells. In order to have all the necessary information about the cells, commercial MEA with acidic chemistry were chosen and assembled in the laboratory using the separated anode and cathode side. Industry standard Nafion membranes (Nafion 115 and 117) and gas diffusion layers were used. The 5X5cm single cells were put under test inside a housing connected to the electrochemical test bench which can control the relevant test variables such as temperatures, mass flow rates and pressures. Cells were characterized by the resultant voltage-current polarization curves and electrochemical impedance spectroscopy (EIS).

A 0D MATLAB model has also been developed that fits the voltage-current curves very well and it can predict the behaviour of the cell in different conditions as well as giving the possibility to study the effect of various electrochemical and physical variables -such as T, P, current densities at anode and cathode i.e. $I_{0,anode}$, $I_{0,cathode}$, etc- on the cell performance. At the same time the hydrogen production rate was also investigated, and the experimental production rate was found to be within 99.5% of theoretical production.

Furthermore, using the COMSOL Multiphysics® environment 2-D and 3D Multi-Phase Multiphysics Model (Bubbly Flow, $k-\omega$) of the PEM electrolytic cell was developed to simulate the main involved physics with special consideration on biphasic anodic mixture interactions within the system. The effect of different variables such as temperature gradient

at anode and cathode, bubbles overpotential and oxygen and hydrogen concentration at electrode interface on the system were modelled.

Since the designed electrochemical test bench has the possibility to send liquid to both anode and cathode electrodes, an array of open versus closed cathode experiments were done to compare the difference between the performance in these cases. The improvements in the performance in open vs closed cathode case can be related to the more homogeneous temperature distribution inside the housing and better hydration of the MEA and gas removal from the reaction sites. Besides, EIS tests have also been performed in these experiments to investigate the trend of changes in each cell characteristics such as ohmic resistance (R_{ohm}) or charge transfer resistance (R_{ct}) of the cell. To study these results in depth, they are modelled with equivalent electrical circuits (EEC) in which each element represents an electrical contribution related to a physical phenomenon. A comparison of the results in open vs closed cathode experiment presents the approximately constant ohmic resistance and a decreasing trend of the charge transfer resistance while increasing temperature.

Lastly a series of accelerated degradation tests have been performed on the cells. These tests give insights on the comparison of constant current working with respect to profiles with frequent variations and shutdowns. Meanwhile during the experiments, the circuit water (demineralized water) was analysed for its thermal conductivity continuously and for fluoride ion quantities by sampling at specific time steps. After the degradation tests on the mentioned cells, they undergo post-mortem analysis using SEM, and XRD methods too.