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Review Article

Frequency response diagnostics of electrochemical energy devices

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Abstract

The development, fabrication, and operation of electrochemical energy devices like fuel cells, batteries, or electrolyzers require powerful diagnostic techniques. Frequency response analysis methods deconvolute and quantify reaction and transport processes based on their dynamics, extract properties such as conductivity, diffusivity, permeability, and electrocatalytic activity, and assess the state-of-health, state-of-charge of a battery, mass activity of an electrocatalytic layer, or the presence of faults. Taking nonlinear information into account improves process identifiability, while using different input or output signals increases the sensitivity towards specific processes. Sensitivity analyses and design of experiments techniques are valuable tools to evaluate different frequency response techniques and help building optimized test protocols.

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Introduction

Electrochemical energy devices like fuel cells, batteries, and electrolyzers play a key role in the transition towards a sustainable and climate-friendly energy system. The success of these devices hinges on the development, production, integration, and optimal operation of advanced materials, components, cells, and systems. Powerful diagnostic techniques are required throughout the development, fabrication, and operation stages.

In development, diagnostic characterization tools quantify properties such as conductivity, diffusivity, permeability, and electrocatalytic activity, as well as rates of reaction, transport, and degradation processes of relevant materials and interfaces. This helps to identify bottlenecks and limitations and optimize the trade-off between performance and lifetime at the device level.

In the fabrication process, diagnostic techniques ensure quality control, especially in postproduction factory acceptance testing. In fabrication, diagnostic techniques are subject to different requirements than those at the development stage. For example, in the automotive fuel cell sector, so-called 10 Hz manufacturing is envisaged, i.e., producing 10 cells per second, in order to fully transform the industry towards a hydrogen economy. This production speed requires diagnostic techniques to be fast while still maintaining reliability and sufficient accuracy.

During operation, diagnostic methods and tools are essential to assessing the state of the device. The state encompasses state variables like voltage, current, temperature, or concentration that are used by control systems to operate the device. Furthermore, the state-of-health, the state-of-charge of a battery, the mass activity of an electrocatalytic layer, or the presence of faults can be evaluated, which are essential pieces of information for the management of the device.

For these diagnostic purposes, frequency response analysis (FRA) methods form a powerful class of techniques. In FRA, the system under investigation is perturbed harmonically, i.e., an input signal of a single frequency is applied, and the response in an output signal (or multiple signals) is analyzed. Scanning through a range of input frequencies successively perturbs processes with different time constants, which allows us to deconvolute and quantify them.

The frequency response principle allows the application of different analysis techniques that we want to discuss in this perspective article. Linear response methods like electrochemical impedance spectroscopy (EIS) allow for a simplified mathematical treatment in the analysis and are valid as long as the input amplitude is sufficiently small. If larger input amplitudes are used, the output signal contains distortions in the form of higher harmonics, which are caused by the nonlinearities of the analyzed system. While taking the nonlinearities into account complicates the analysis, it can enable the deconvolution of processes with similar time constants that cannot be distinguished in the linear approximation.

For FRA, electrical perturbation signals, i.e., current and voltage are often used. They are easily accessible (even in situ or in operando) and have high accuracy in both application and measurement. However, it is possible to use other input or output signals, like pressure, concentration, humidity, or temperature. This opens up avenues for developing new diagnostic methods, especially when modeling is combined with expertise in experiments and instrumentation.

Electrochemical impedance spectroscopy and the distribution of relaxation times

Electrochemical impedance spectroscopy is a mature linear FRA method [1,2], in which a small-amplitude input signal (current or voltage) results in a linear, harmonic output signal. Exploiting this linearity simplifies modeling and analysis [3]. EIS allows for easy parameter extraction through direct fitting or graphical methods [4], as well as deconvolution and quantification of processes and even electrode structures [5,6]. There are seized analysis methods for interpreting measured EIS spectra: equivalent circuit models are descriptive and intuitive, but unreliable without an underlying physical understanding. Physical models offer direct interpretation of the results, often with analytical solutions that simplify computation [4,6].

An emerging technique for EIS spectra analysis is the distribution of relaxation times (DRT), which enables the analysis and deconvolution of physical processes without a priori knowledge or assumptions [7–9]. However, the conversion of EIS spectra into the DRT is a mathematically ill-posed problem that requires developing new theoretical [10] or data-driven [11] methods. Equipped with these tools, DRT is already widely used in the analysis of solid oxide cells [12,7] and recently for the more complex analysis of oxygen transport in low-Pt-loading polymer electrolyte fuel cells (PEFC) [13], as well as stack-level analyses [14].

Nonlinear frequency response

When the amplitude of the input signal is increased beyond the linear range, the output signal contains nonlinear distortions in the form of higher harmonics, i.e., frequency components that are multiples of the input frequency. These higher harmonics contain information about the nonlinearities of the system that can be used to identify processes that are “masked” in the linear EIS spectra, e.g., processes that have similar time constants [15,16]. Examples of such processes include losses due to water management problems and carbon monoxide poisoning in PEFC, which result in similar features of EIS spectra but leave unique “fingerprints” in the higher harmonics [17]. For lithium ion batteries, it has been found that while EIS is not sufficient to diagnose the safety-critical aging process of lithium plating, nonlinear frequency response analysis (NFRA) and especially the third harmonic are very sensitive to plated lithium [18].

For analyzing experimental data, a simple way is to evaluate the total harmonic distortion (THD), i.e., the sum of all higher harmonics, as developed for direct methanol fuel cells [19,20] and the oxygen reduction reaction (ORR) in PEFC [21]. Recently, a similar technique has been used to fundamentally analyze the capabilities of NFRA for the analysis of electrochemical cells [22]. A more complex analysis theory based on Volterra series expansion uses the Volterra kernels or higher-order frequency response functions (HFRF) as input signal-independent descriptors of the nonlinear dynamic behavior of the cell [23,17,24]. A similar but more straightforward approach to directly analyzing higher harmonics in the output signal was recently applied to lithium ion batteries [25–28], which gave valuable insights for process identification [29,30] and state-of-health diagnostics [30–32].

Input/output signals

Another way of advancing frequency response diagnostics towards higher accuracy and the ability to deconvolute ambiguous contributions is through the use of alternative, nonelectric input or output signals. Recently, frequency response methodologies based on nonelectrical quantities have been reviewed [33]. The first nonelectrical perturbation used for PEFC frequency response diagnostics has been the cathode back pressure [34]. This so-called electrochemical pressure impedance spectroscopy (EPIS) is especially sensitive to diagnosing the liquid water accumulation in the cathode catalyst and gas diffusion layer. Model-based analyses [35,36] and experimental works [37] followed and helped furnish the suitability of the method. A recent current opinion paper summarizes and discusses the state-of-the-art in EPIS [38], while a model-based analysis remarks critically that measured EPIS spectra might not be unique [39]. Another problem with EPIS is the effect of the humidifier volume on the applied pressure perturbation, which makes measured spectra dependent on the fuel cell system setup.

A further complication of EPIS is that a perturbation of the pressure also perturbs the partial pressures of oxygen and water vapor. This weakness was circumvented by keeping the overall pressure constant but perturbing the oxygen partial pressure or concentration [40,41]. This so-called concentration frequency response analysis (cFRA) does not mechanically perturb the pressure-dependent liquid water distribution, thus leading to a high sensitivity towards oxygen transport. One way of achieving concentration perturbation is by switching between dry and humidified oxygen, thus simultaneously perturbing both oxygen and water vapor concentrations. In combined modeling and experimental work, it has been shown that this simultaneous perturbation can be used to decouple the oxygen and water transport dynamics [42]. Easy parameter extraction was enabled by deriving analytical solutions for cFRA spectra [36,43].

Apart from perturbing different input signals, it is also possible to measure and analyze different output signals. Direct electrochemical mass spectrometry (DEMS) has been used to measure the reaction product concentration during an EIS experiment [44]. This so-called species frequency response analysis (sFRA) was demonstrated in a combination of experimental and modeling work on electrochemical methanol oxidation. It was found that sFRA can decouple the interplay of mass transport and electrochemical reaction kinetics and is sensitive to transport parameters that are not accessible by EIS. A similar method, termed concentration admittance spectroscopy (CAS), was recently suggested, in which the measurement of the oxygen concentration at the outlet of a PEFC during an EIS measurement can be used to extract oxygen transport parameters more accurately [45].

Sensitivity analysis

As diagnostic models become increasingly complex, the problem of parameter identification becomes increasingly significant. The process of parameter identification encompasses three aspects: Firstly, how accurate are the determined parameter values, i.e., how large are the parameter uncertainties? Secondly, how strongly does the model prediction depend on the parameter values, i.e., how large are the parameter sensitivities? Thirdly, how strongly are parameters correlated, or stated differently, how independent and thus identifiable are they? Despite the central and increasingly important role of parameter identification, this topic is still not sufficiently considered in the fuel cell community, and the literature on the topic is sparse. However, recently, parameter identifiability and sensitivity analyses, as well as design of experiment methods, were introduced for model parameterization [46,47], cell performance optimization [48], modeling, and diagnostics [33].

In order to find the best FRA method or combination of methods, or to explore the potential of new methods model-based analyses of controllability, observability, and sensitivity are suitable tools. A framework based on linear system theory was developed, which is suitable to compare different input and output signal combinations [33]. In this way, the strengths and weaknesses of different methods can be evaluated before investing in experimental instrumentation. In order to evaluate the strength of a given method, relative sensitivities were introduced as a measure and used for the evaluation of EPIS [35], while others analyzed sFRA [44] and CAS [45]. By analyzing the relative sensitivity as a function of the input frequency, the optimal frequency band to extract a certain parameter can be determined. This helps optimize the measured frequency range and can be used to combine different methods. Further, design of experiment methods can be used to optimize the distribution of the input frequency to achieve desired diagnostic tools, e.g., maximize accuracy for a given measurement time or to minimize measurement time while maintaining a desired accuracy [49].

Overall, frequency response analysis methods are a versatile class of diagnostic tools for energy devices. Enhancing the renown electrochemical impedance spectroscopy into the nonlinear regime, as well as taking into account different input and output signals, allows to tailor the diagnostic capabilities towards the specific requirements during the development, fabrication, implementation, and operation of energy devices. Optimizing the sensitivity of different methods and their combinations allows for the building of advanced tools and test protocols.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Data availability

No data was used for the research described in the article.

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