Harmonic Ratio Analysis (HRA) for Online Monitoring of Electrolyzers and Fuel Cell Systems - A Nonlinear Diagnostic Method Complementing Electrochemical Impedance Spectroscopy (EIS)

Hannes Benecke[1]*, Robert Benecke[1]
[1] SIVONIC GmbH, Magdeburg-Barleben, Germany
* ORCID: https://orcid.org/0009-0000-1794-6650

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Abstract

Reliable operation and long-term stability of electrolyzers and fuel cells require diagnostic methods that can be applied under realistic operating conditions without interrupting system operation. Electrochemical impedance spectroscopy (EIS) provides detailed information on linear processes [1-3], but its small-signal requirement and multi-frequency sweeps often limit its use for rapid online monitoring under load. Harmonic Ratio Analysis (HRA) is a fast, model-light nonlinear diagnostic method that deliberately excites mild nonlinearities by periodically modulating the operating point in the low-frequency range (typically two or more selected modulation frequencies) and evaluates the harmonic content of the voltage response. From short time records (typically on the order of seconds, depending on f_0 and the number of periods N), Fourier analysis yields harmonic amplitudes H_1, H_2, H_3 …, which are converted into ratio metrics. For each modulation frequency, the ratios $|H_2|/|H_1|$ and $|H_3|/|H_1|$ are computed, together with additional higher-order ratios to increase selectivity. Even-order ratio metrics (in particular $|H_2|/|H_1|$) are associated with asymmetric effects such as transport limitations, gas accumulation, disturbances in water management, or crossover [8,10-12], whereas odd-order ratios ($|H_3|/|H_1|$, $|H_5|/|H_1|$) typically indicate symmetric kinetic nonlinearities [4,5,11]. HRA is evaluated trend-wise relative to a baseline (reference "healthy" state), which increases robustness against manufacturing variation and slow drift. This technical note defines practical diagnostic indices, provides a reproducible measurement protocol and quality criteria (including SNR gating/persistence across multiple frequencies), and supports implementation in test stands and stack controllers.

Keywords

Harmonic Ratio Analysis (HRA); electrochemical impedance spectroscopy (EIS); nonlinear electrochemical diagnostics; online diagnostics; condition monitoring; electrolyzer; water electrolysis; fuel cell; stack diagnostics; stack monitoring; frequency response analysis (FRA); harmonic analysis; nonlinear frequency response; multi-frequency modulation; industrial process monitoring

1. Introduction

Electrochemical hydrogen systems are increasingly operated under dynamic load profiles and are expected to maintain high efficiency, availability and reliability over long operating periods [13]. In addition to performance characterization, online-capable diagnostic methods are therefore needed for condition monitoring, degradation detection and condition-based maintenance. EIS is a standard laboratory method for resolving linear electrochemical processes such as charge transfer, diffusion and capacitive contributions [1-3]; however, the very small excitation amplitudes and long measurement times required are often difficult to reconcile with industrial operation under load. At the same time, pronounced nonlinearities occur in real operation, caused by transport phenomena (gas evolution, water management), temperature gradients, contact changes or ageing processes [4,5,9]. These nonlinearities generate harmonic distortion in the electrical response, which can be used as an additional information channel for operational diagnostics.

HRA targets exactly this information channel. In contrast to global distortion metrics such as Total Harmonic Distortion (THD), which aggregate all harmonics into a single number [6,7,10], HRA evaluates selected harmonic ratios individually. This preserves diagnostic selectivity: even and odd harmonics carry different physical signatures [4,5,11,12]. The method is designed for short measurement times (typically seconds, depending on f_0 and the number of periods N), low computational effort and trend-based monitoring.

2. Principle of Harmonic Ratio Analysis

2.1 Excitation and response under galvanostatic operation

In galvanostatic operation, HRA superimposes a sinusoidal current modulation on the DC operating point:

$$i_k(t) = I_{DC} + \Delta I \sin(2\pi f_{0,k} t), \quad k = 1 \dots K$$

where I_{DC} is the steady-state operating current, ΔI is the modulation amplitude, and $f_{0,k}$ is the k-th excitation frequency. HRA is typically performed at at least two fixed frequencies $f_{0,k}$ in the low-frequency range. Since cell voltage is a nonlinear function of current, the voltage response v(t) is generally not purely sinusoidal and contains harmonics at $n \cdot f_{0,k}$ [4,5].

2.2 Extraction of harmonics and definition of ratios

For each selected modulation frequency $f_{0,k}$ (k = 1 … K), a short time record v(t) is acquired during modulation. Fourier analysis (FFT/DFT) yields complex harmonic components at the frequencies $n \cdot f_{0,k}$. For each frequency, HRA forms a ratio vector from selected harmonics and evaluates these values trend-wise relative to a baseline; for $K \geq 2$, ratio vectors can be combined (fused) across frequencies to increase selectivity and field robustness.

$$R_n = |H_n| / |H_1|$$

where H_n denotes the amplitude of the n-th harmonic. Using ratios substantially reduces sensitivity to absolute gain and offsets of the measurement chain and facilitates comparison between cells and operating points. In practice, n = 2 … 6 is often sufficient. In the robust standard implementation, additional meta-ratios between higher-order harmonics and non-adjacent lower-order harmonics are used in addition to the ratios to the fundamental (see Section 3).

2.3 Scaling of harmonics under weak nonlinearity

For many operating states the nonlinearity is moderate; the characteristic $v = f(i)$ can be approximated locally around the operating point I_{DC} by a Taylor series. This implies qualitatively that the harmonic amplitudes contain powers of the modulation amplitude ΔI (weak nonlinearity) [4,5].

$H_1 \propto \Delta I, \quad H_2 \propto (\Delta I)^2, \quad H_3 \propto (\Delta I)^3$

Accordingly, approximately: $R_2 = |H_2|/|H_1| \propto \Delta I$ and $R_3 = |H_3|/|H_1| \propto (\Delta I)^2$. Consequence: For reliable trend diagnostics, ΔI and f_0 must be kept constant during monitoring and the evaluation (n_{max}) must be chosen consistently; otherwise R_n can change even without a change in state.

The workflow of the method is shown in Figure 1.

Figure 1. Workflow of Harmonic Ratio Analysis (HRA): operating-point modulation, distorted voltage response, Fourier analysis, and computation of harmonic ratios.

3. Diagnostic indices and interpretation

HRA distinguishes between asymmetric and symmetric nonlinearities by separately considering even- and odd-order harmonic ratios [4,5,11]. Asymmetric nonlinearities arise when the system responds differently during the positive and negative half-wave (e.g., gas bubble accumulation, local flooding, non-uniform humidification, mass-transport limitations, or crossover) [8,11,12]. These effects preferentially increase even-order harmonics. Symmetric nonlinearities affect both half-waves in a similar manner (e.g., kinetically dominated changes in curvature due to catalyst ageing) and primarily increase odd-order harmonics. A representative spectrum of harmonic ratios is shown in Figure 2.

Note: The assignment “even harmonics ↔ asymmetric effects” and “odd harmonics ↔ symmetric effects” should be understood as a robust indication, not as exclusive proof of a single mechanism. In practice, multiple effects may overlap; additionally, nonlinearities of excitation and measurement chain (current controller, power electronics, saturation) can generate harmonic components. Therefore, signal quality and the input sinusoid $i(t)$ should be checked and interpretation should be supported by baseline and validation measurements (see Section 4.5).

For practical monitoring, the following indices are useful:

$|H_2|/|H_1|$, $|H_3|/|H_1|$, and additional higher-order ratios to increase selectivity.

Meta-ratios compare higher-order harmonics with non-adjacent lower-order harmonics and increase diagnostic selectivity (e.g., separation of even/odd contributions) as well as robustness against amplitude fluctuations. In the robust implementation, the indices are evaluated at at least two modulation frequencies and considered as ratio vectors per frequency; the diagnosis can then be combined across frequencies. In all cases, interpretation must be anchored to a baseline recorded for the specific system and operating point.

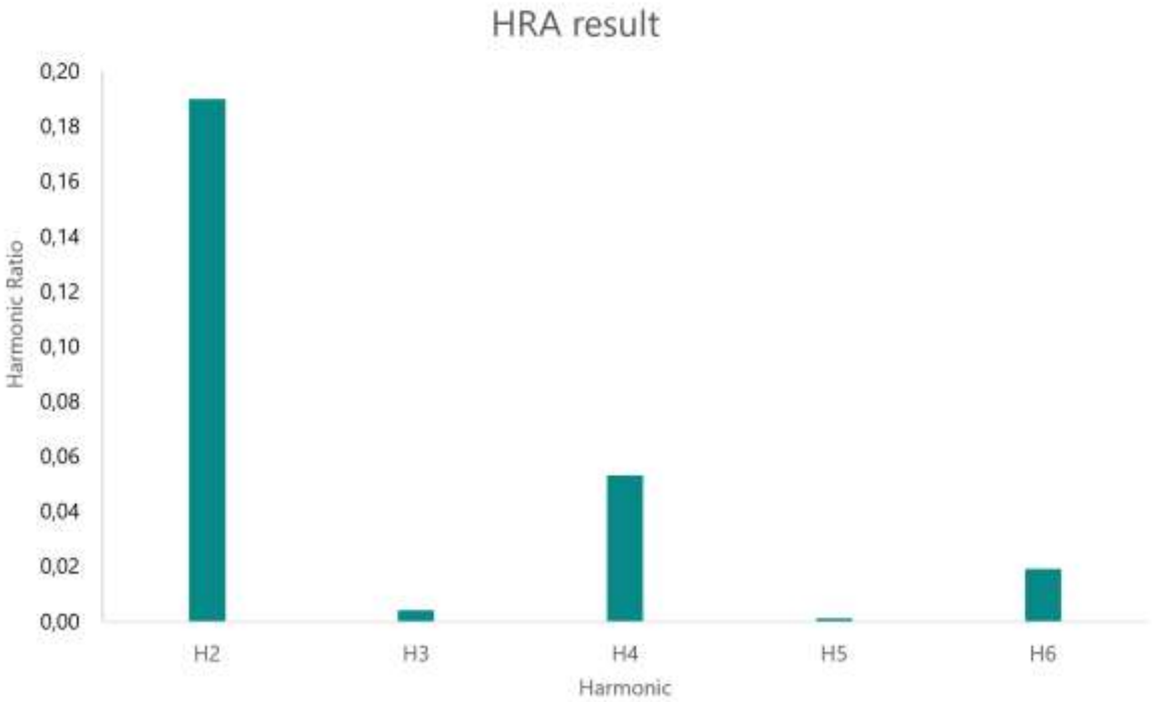

Figure 2. Example spectrum of harmonic ratios $R_n = |H_n|/|H_1|$ (n = 2-6) at a modulation frequency $f_{0,k}$. Dominance of even-order harmonics typically indicates asymmetric nonlinearities (transport/water-management related).

4. Reproducible measurement protocol and signal processing

4.1 Selection of excitation parameters

Parameter selection determines sensitivity and robustness. Typical starting values are ΔI = 5-10% of I_DC (up to ~20% for method development) and modulation frequencies $f_{0,k}$ in the range 0.1-10 Hz. Low frequencies (~0.1-1 Hz) tend to emphasize transport and water-management phenomena; mid frequencies (~1-10 Hz) can capture faster interfacial and kinetic dynamics. For online operation, at least two fixed frequencies should be used and ΔI should be kept constant so that trends in ratio and meta-ratio metrics can be interpreted unambiguously [4,8,12].

Per diagnostic snapshot, at least N = 5-20 full periods should be recorded. More periods improve repeatability and noise suppression but increase measurement time. For dynamic systems, N should be chosen such that the operating state remains approximately stationary over the acquisition interval.

The acquisition time of a diagnostic snapshot per frequency follows directly from $T = N / f_{0,k}$. Example: N = 10 at $f_{0,k}$ = 1 Hz corresponds to $T \approx 10$ s; N = 10 at $f_{0,k}$ = 0.1 Hz corresponds to $T \approx 100$ s. If K frequencies are evaluated sequentially, the total measurement time is the sum of the individual times. For online operation, $f_{0,k} \geq 1$ Hz and $N \approx$ 5-10 are therefore typically used (seconds per frequency), whereas very low $f_{0,k}$ can be sensitive to transport/water-management effects but require longer acquisition times.

4.2 Data acquisition and instrumentation

The voltage response must be sampled with sufficient temporal resolution to capture the highest relevant harmonic. As a rule of thumb, at least 100-200 samples per fundamental period are suitable, with sufficient Nyquist margin for $n_{max} \cdot f_0$. Anti-alias filtering and - if possible - sampling synchronized to the excitation (coherent sampling) should be ensured. Scaling/units should be consistent; in addition to the electrical signal, the DC operating point and key operating variables (temperature, pressure, flow rates) should be recorded.

For interpretation of voltage harmonics it is important that the impressed current i(t) itself is sufficiently sinusoidal. Where possible, i(t) should be recorded in parallel and its harmonics (e.g., $|I_2|/|I_1|$, $|I_3|/|I_1|$) should be monitored as a quality criterion. Otherwise, there is a risk that harmonic voltage components are partly driven by input distortion or controller artifacts.

4.3 FFT/DFT computation

The cleanest harmonic computation is obtained with coherent sampling: an integer number of cycles is recorded so that the DFT bins align with $n \cdot f_0$ and spectral leakage is minimized. If coherent sampling is not possible, a window function (e.g., Hann) should be applied and harmonic amplitudes corrected for the window's amplitude loss. Before the FFT, the DC component should be removed. Harmonic magnitudes are computed from the complex DFT and reported as ratios $R_n = |H_n|/|H_1|$.

For robust monitoring, estimating the noise floor (e.g., from spectral regions outside the bin frequencies) and tracking a simple signal-quality metric such as the SNR of the fundamental is recommended. Snapshots with poor signal quality or obvious transients should be discarded.

4.4 Repeatability, drift robustness and uncertainty information

Because HRA uses ratios, many multiplicative gain errors cancel; however, repeatability still depends on operating stability, excitation coherence and measurement noise. To quantify repeatability at an operating point, multiple snapshots are acquired and mean and standard deviation of R_n are computed. For trend monitoring, a baseline distribution is defined during "healthy" operation; subsequent results are reported as relative changes including confidence bands.

HRA is primarily intended for trend-based diagnostics. Absolute limits should be considered system-specific and should be validated by calibration experiments or cross-checks with complementary methods (e.g., EIS, polarization curves, or reference sensors) [1-3,8,9]. A typical trend of the harmonic ratio $|H_2|/|H_1|$ is shown in Figure 3.

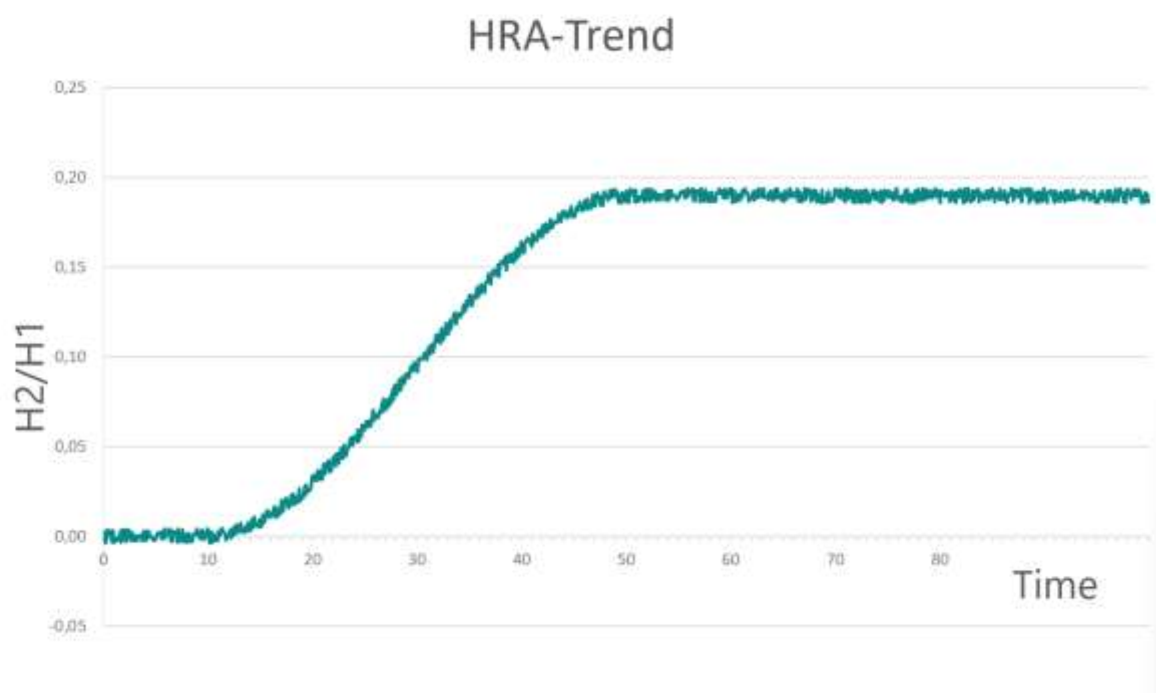

Figure 3. Trend of the harmonic ratio $|H_2|/|H_1|$ during the build-up of an asymmetric transport limitation at constant modulation parameters.

4.5 Quality control of the input signal and commissioning

To interpret harmonic voltage components reliably, excitation and measurement chain must be sufficiently stable. Simple quality control reduces false alarms due to controller/electronics artifacts and facilitates commissioning in the field.

- Input sinusoid (current): no limiting/clipping, no saturation; current harmonics (e.g., $|I_2|/|I_1|$) small compared with $|I_1|$.
- Coherence: integer number of periods in the evaluation window (coherent sampling); if not possible, windowing + amplitude correction.
- Signal quality: SNR of the fundamental sufficient (rule of thumb > 20 dB); if SNR is low, increase N or discard the snapshot.
- Persistence across frequencies: evaluate ratio and meta-ratio metrics only if the numerator harmonics (e.g., H_2, H_3, H_4, H_5, H_6) meet the QC criteria.
- Transients: no load steps/controller changes within the evaluation window; use trigger/wait time after load changes.
- EMC/ripple: consider known disturbance frequencies (e.g., rectifier/PWM ripple) in the measurement setup and filter/mask if needed.

If current harmonics are not negligible, an extension is to normalize by current (e.g., $|V_2|/|I_1|$) or to evaluate complex harmonics (magnitude + phase); this step is outside the core scope of this technical note.

5. Positioning relative to EIS and global distortion metrics

EIS, THD and HRA all rely on periodic excitation and evaluation of response signals, but differ in objective and information content. EIS provides detailed linear process resolution, but is time-consuming and assumes approximate linearity [1-3]. THD is fast but non-specific because all harmonics are aggregated [6,7,10]. HRA closes this gap by selectively evaluating individual, physically interpretable harmonic ratios [4,5,11,12], which are suitable for rapid online trend analysis.

Aspect	EIS	THD	HRA
Principle	Linear small-signal response via frequency sweep	Global metric of all harmonics	Selective ratios of individual harmonics
Signal level	Small (to enforce linearity)	Operating distortion / ripple	Moderate modulation (e.g., 5-10% of I_DC)
Information content	Process resolution (R, C, diffusion models)	Overall nonlinearity (non-specific)	Symmetry vs. asymmetry + trends
Measurement time	Minutes to hours	Seconds	Seconds
Interpretation	Model-dependent	Non-specific	Physically interpretable ratios; baseline/trend-based
Typical application	Labor characterization	Coarse screening	Online monitoring and early deviation detection

Table 1: Comparison of EIS, THD and HRA.

6. Implementation in test stands and controllers

HRA can be implemented with moderate computational resources. A typical cycle comprises: (1) apply modulation, (2) acquire voltage time series, (3) compute FFT/DFT, (4) compute ratio and meta-ratio metrics, (5) update trend metrics and alarms. This workflow is executed for each of the fixed modulation frequencies $f_{0,k}$; the resulting ratio vectors can be combined across frequencies. The method can be run periodically during normal operation if modulation amplitude and frequencies are chosen such that the process is not disturbed unacceptably. For stacks, parallel acquisition of individual cell voltages enables spatially resolved diagnostics; per-cell ratio metrics can be visualized as trends or heat maps.

6.1 Requirements for measurement hardware and data rate

Requirements for measurement hardware strongly depend on whether only total voltage, cell groups or each individual cell is evaluated. Practical guidelines for implementation:

- Sampling rate: at least 100-200 samples per fundamental period ($1/f_0$) for stable estimation of $H_1 \ldots H_n$; additionally, $n\_max \cdot f_0$ must be considered with sufficient Nyquist margin.
- Multi-channel stacks: if individual cell voltages are acquired in parallel, the data rate scales with N_channels · f_s. Alternatively, cell groups can be formed or diagnostic windows can be distributed in time (given sufficient stationarity).
- Synchronization: for coherent sampling, a defined timing relationship between excitation and sampling is helpful; if synchronization is not available, apply windowing and QC consistently.
- Resolution/noise: sufficient ADC resolution and clean referencing are important because harmonic components are often in the percent or per-mille range of H_1.

7. Limitations and good practice

HRA provides macroscopic nonlinear signatures and does not replace methods that resolve parameters of individual sub-processes. Multiple fault mechanisms may overlap and may require multi-frequency evaluation or additional sensors. Interpretation requires stable excitation conditions (ΔI, f_0) and a clearly defined baseline. Before deploying alarms, the diagnostic logic should be validated with controlled experiments (e.g., deliberately induced flooding, defined crossover conditions, variation of contact pressure) and cross-checked against independent observations.

8. Conclusion

Harmonic Ratio Analysis (HRA) is a fast, online-capable nonlinear diagnostic method that complements EIS by exploiting harmonic signatures that arise under realistic operating conditions. By selectively evaluating harmonic ratios relative to a baseline, HRA enables robust, trend-based detection of operational deviations such as transport and water-management disturbances - while requiring short measurement times and low computational effort. The protocol and signal-processing guidance provided support reproducible implementation in the laboratory and in industrial environments.

Disclosures

The authors are employed by SIVONIC GmbH. Certain aspects of the HRA method may be protected by patents and/or patent applications held by SIVONIC GmbH.

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