Note S4 | Extended robustness analysis (extra statistics and replicates) for MXene EIS fitting

Beyond the primary fit quality metrics and the baseline noise tests (**Notes S3**), we performed an extended robustness study to quantify how reliably the MXene EIS parameter vector $\theta = \{R_s, L, R_{ct}, Q_1, \alpha_1, Q_2, \alpha_2\}$ can be recovered under realistic perturbations. The objective is twofold: (i) to demonstrate that the reported solutions are not artifacts of a single initialization or a single noise realization, and (ii) to provide distribution-level statistics (not only point estimates) that support identifiability and practicality claims. These results are summarized in **Table S2** (extended distributions across noise levels) and in robustness figures showing basins of attraction and parameter clouds.

S4.1 Noise model and replicate protocol.

We adopt a frequency-dependent complex noise model consistent with typical EIS measurement variability: the clean impedance spectrum $Z_{clean}(\omega_k)$ is perturbed by complex Gaussian noise scaled by the local impedance magnitude,

$$Z_{noisy}(\omega_k) = Z_{clean}(\omega_k) + \eta|Z_{clean}(\omega_k)|\varepsilon_k, \varepsilon_k \sim \mathcal{CN}(0,1) \qquad \text{(S13)}$$

where η is the noise amplitude (reported as a fraction or percent of $|Z|$). Scaling by $|Z|$ captures the empirically observed heteroscedasticity of EIS, larger absolute deviations at low frequency where $|Z|$ is typically larger, and smaller deviations at high frequency. For each η, we generate multiple independent noise realizations and refit the spectrum using bounded decoding (**Note S3**). Importantly, we also randomize the solver initialization around the baseline (e.g., u_0 plus a small Gaussian perturbation in bounded u-space) to probe basin sensitivity and to reduce bias from a single starting point. Each replicate thus reflects a paired perturbation: one from data noise and one from initialization.

S4.2 What is recorded per replicate.

For every run we store: (i) the final decoded parameters θ, (ii) a binary "boundary hit" flag indicating whether the optimum lies near the feasibility limits (a practical sign of weak identifiability or over-regularization), (iii) the complex-domain error measured both on the noisy spectrum (SSE_{noisy}) and on the original clean spectrum (SSE_{clean}). Reporting SSE_{clean} is especially useful because it separates *overfitting to a particular noise draw* from genuine recovery of the underlying impedance structure. A robust model/solver combination should produce stable SSE_{clean} across replicates even as SSE_{noisy} inevitably increases with η.

S4.3 Summary statistics and distribution reporting (Table S2).

Rather than reporting only $mean \pm s.d.$, **Table S2** provides a fuller distributional picture per parameter and per noise level: median, inter-quantile range, and tail quantiles (P5–P95). This is essential for non-Gaussian parameter clouds, which commonly occur in EIS due to correlated parameter trade-offs and multi-modal minima. We additionally report the coefficient of variation (CV%) to allow direct cross-parameter comparison despite different physical units and scales. Alongside parameter distributions, **Table S2** includes success and boundary-hit rates. A rising boundary-hit rate with noise indicates that the objective becomes flatter in certain directions and the optimizer compensates by pushing parameters toward limits, an operational marker of poor identifiability.

S4.4 Basin-of-attraction stability.

To quantify sensitivity to initial conditions independent of measurement noise, we perform multi-start refits with controlled perturbation amplitude in u-space. For each perturbation scale σ, we compute the fraction of runs converging to a near-best solution (e.g., within 5% of the best observed SSE) and the fraction hitting bounds. This "basin map" explains why some solutions appear repeatedly: stable basins correspond to physically meaningful parameter combinations supported by the data, while unstable basins often reflect compensating trade-offs among R_{ct}, Q_1, and α_1, or between the two CPE elements at low frequency.

S4.5 Interpretation and links to identifiability.

The extended robustness results connect directly to **Table 3**. Parameters that show low CV% under noise, low boundary-hit tendency, and weak dependence on the initialization scale are classified as well-identifiable. In contrast, parameters with high CV% and strong correlations across replicates are treated as poorly identifiable under the current circuit and frequency window. Overall, the extended robustness analysis demonstrates that the reported MXene EIS solutions are supported by distribution-level evidence: the solver repeatedly finds consistent parameter regions, and the remaining variability is structured (correlated manifolds) rather than random drift, which is characteristic of realistic EIS inverse problems.