Note S5 | Residual structure and error propagation in MXene EIS analysis

This work evaluates model adequacy and parameter reliability by analyzing the *structure* of complex residuals and by propagating measurement/model errors into fitted parameter uncertainty. For each frequency point ω_k, the complex residual is defined as

$$r_k(\theta) = Z_{model}(\omega_k; \theta) - Z_{data}(\omega_k; \theta) = r_k^{\mathcal{R}} + r_k^{\Im} \tag{S14}$$

and the fitting objective used in the main text is the complex-domain sum of squares

$$SSE(\theta) = \sum_{k=1}^{N} |r_k(\theta)|^2 = \sum_{k=1}^{N} \left| \left(r_k^{\Re}\right)^2 + \left(r_k^{\Im}\right)^2 \right| \tag{S15}$$

This formulation constrains both magnitude and phase simultaneously and prevents “phase-only” or “magnitude-only” overfitting. Because EIS errors are typically heteroscedastic across frequency (large $|Z|$ at low f, small $|Z|$ at high f), we also examine *normalized residuals*:

$$\tilde{r}_k^{\Re} = \frac{r_k^{\Re}}{|Z_{data}(\omega_k)|},\ \tilde{r}_k^{\Im} = \frac{r_k^{\Im}}{|Z_{data}(\omega_k)|} \tag{S16}$$

These dimensionless quantities are used to diagnose whether the fit error is dominated by specific frequency decades (e.g., inductive region, charge-transfer arc, or low-frequency dispersive tail), and to make $\Re e/\Im m$ residuals directly comparable even when the impedance magnitude spans orders of magnitude. In practice, an acceptable model exhibits (i) residuals centered near zero, (ii) no systematic drift versus frequency, and (iii) comparable scatter in $\Re e$ and $\Im m$ components once normalized. Persistent sign patterns (e.g., $\Re e$ residuals positive across a whole decade) indicate structural mismatch rather than noise, suggesting missing physics (additional RC branch, Warburg-like diffusion, or an over-constrained dispersion exponent).

To evaluate distributional assumptions, we report residual histograms and Q–Q diagnostics separately for $\tilde{r}^{\Re}$ and $\tilde{r}^{\Im}$. If the residuals were purely i.i.d. Gaussian, the Q–Q points would align with the best-fit reference line. Deviations at the tails suggest outliers or non-Gaussian noise (common in low-frequency EIS), while curvature across the full range suggests a frequency-dependent variance or unmodeled correlation. In addition, the parity plots (fit vs data for $\Re e$ and $-\Im m$) provide a global linearity check; curvature away from the diagonal indicates systematic misfit in specific impedance regimes.

Error propagation into parameter uncertainty is treated via a local linearization of the complex residual vector. Let the stacked residual vector be

$$r(\theta) = [r_1^{\Re} \cdots r_N^{\Re}, r_1^{\Im} \cdots r_N^{\Im}]^{\top} \in \mathbb{R}^{2N} \quad \text{(S17)}$$

and define the Jacobian

$$\mathbf{J}(\theta) = \frac{\partial \boldsymbol{r}}{\partial \theta} \in \mathbb{R}^{2N \times 7} \quad \text{(S18)}$$

which can be estimated numerically by finite differences around the optimum $\hat{\theta}$. Under the standard least-squares approximation, the parameter covariance is

$$Cov(\hat{\theta}) \approx \sigma^2 (\mathbf{J}^{\top}\mathbf{W}\mathbf{J})^{-1} \quad \text{(S19)}$$

where $\mathbf{W}$ is a weighting matrix (identity for unweighted SSE; diagonal weights $\propto 1/|Z|^2$ for magnitude-normalized fitting), and σ^2 is an effective noise variance estimated from the residual energy:

$$\sigma^2 \approx \frac{\|r(\hat{\theta})\|_2^2}{2N-7} \quad \text{(S20)}$$

This covariance captures *local* identifiability: directions in parameter space with weak curvature (small eigenvalues of $\mathbf{J}^{\top}\mathbf{W}\mathbf{J}$) correspond to large uncertainties and strong parameter trade-offs. In the MXene circuit, such trade-offs commonly occur between R_{ct} and CPE_1 parameters (Q_1, α_1), or between CPE_2 and the low-frequency portion of the interfacial arc. Accordingly, we quantify dominant correlations (Pearson r) across noisy refits and label parameters as well-, moderately-, or poorly identifiable depending on their curvature proxy, CV% under noise, and correlation strength.

Finally, we assess robustness by controlled noise injection using a complex Gaussian perturbation scaled by |Z|:

$$Z_{noisy}(\omega_k) = Z_{clean}(\omega_k) + \eta \mid Z(\omega_k) \mid \varepsilon_k, \varepsilon_k \sim \mathcal{CN}(0,1) \tag{S21}$$

followed by bounded refitting. The spread of recovered θ across replicates provides an empirical uncertainty that complements the Jacobian-based estimate and directly reflects practical sensitivity to measurement noise and model degeneracy.