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3-point Measurement in Solid State Devices: (Novel) Artefacts and How to Avoid Them

Richard Schlesinger [1], Tobias M. Huber [1,2,3], Alexander Schmid [1],
Markus Kubicek [1], and J. Fleig [1]

Introduction

There are **two common methods** to measure the **impedance** response of only one electrode of a **solid-state electrochemical cell; microelectrodes or a three-terminal configuration**. In aqueous electrochemistry, three-terminal configurations are widely used, however, implementing this method in **solid-state electrochemistry** is highly non-trivial. This work summarizes, which method is most suitable for different applications. We show potential error sources and evaluate each of them quantitatively with special emphasis on their impact in **thin film electrode measurements**. Evaluation is done by means of finite elements analysis (FEA), electric circuit simulations and impedance measurements.

Three potential error sources were identified as particularly crucial factors:
(i) Asymmetric sample cells
(ii) Short circuit currents across the reference electrode (RE),
(iii) Especially for highly resistive electrodes, coupling capacitances between the three electrodes.

These error sources can result in different measurement errors such as additional high frequency semicircles, additional low frequency semicircles, inductive loops and even more critical, erroneous electrode properties without indicating of additional features in the impedance spectrum.

3-Terminal Approaches in Literature

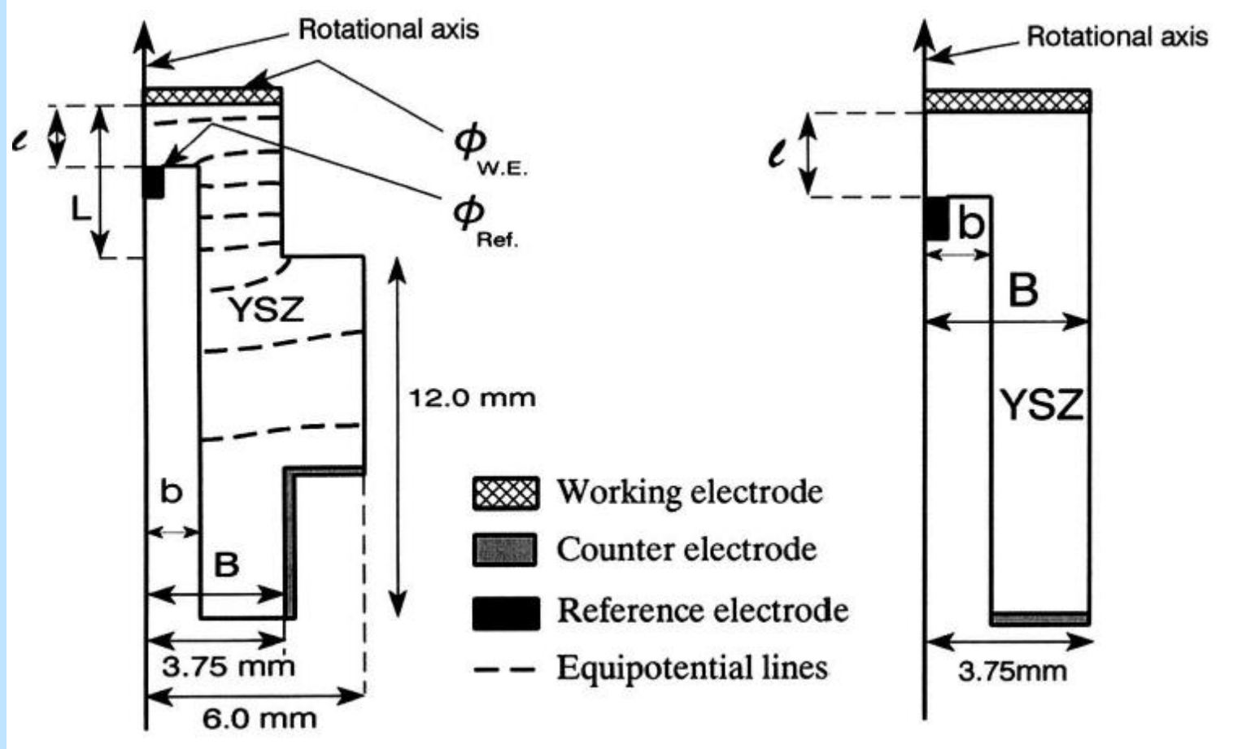


Fig. 1 Pellet like 3-terminal configuration [1]

Many attempts were already tried to minimize errors in three-terminal measurements [1-4]. Geometries as shown in Fig. 1 suffer from many shortcomings:
(i) Very complicated and expensive to fabricate
(ii) Limited to simple electrodes. E.g. hard to use different deposition methods and to change microstructures of the electrodes
(iii) Errors strongly depend on geometrical factors and thereby on manufacturing limitations such as the hole diameter and depth (l and b in Fig. 1)
(iv) Very thick electrolytes are necessary → electrodes with small resistances can not be measured

The novel "WING GEOMETRY"

We propose a novel sample geometry, the **Wing Geometry**, which was designed to minimize the measurement errors significantly, but still remains affordable and suitable for different applications.

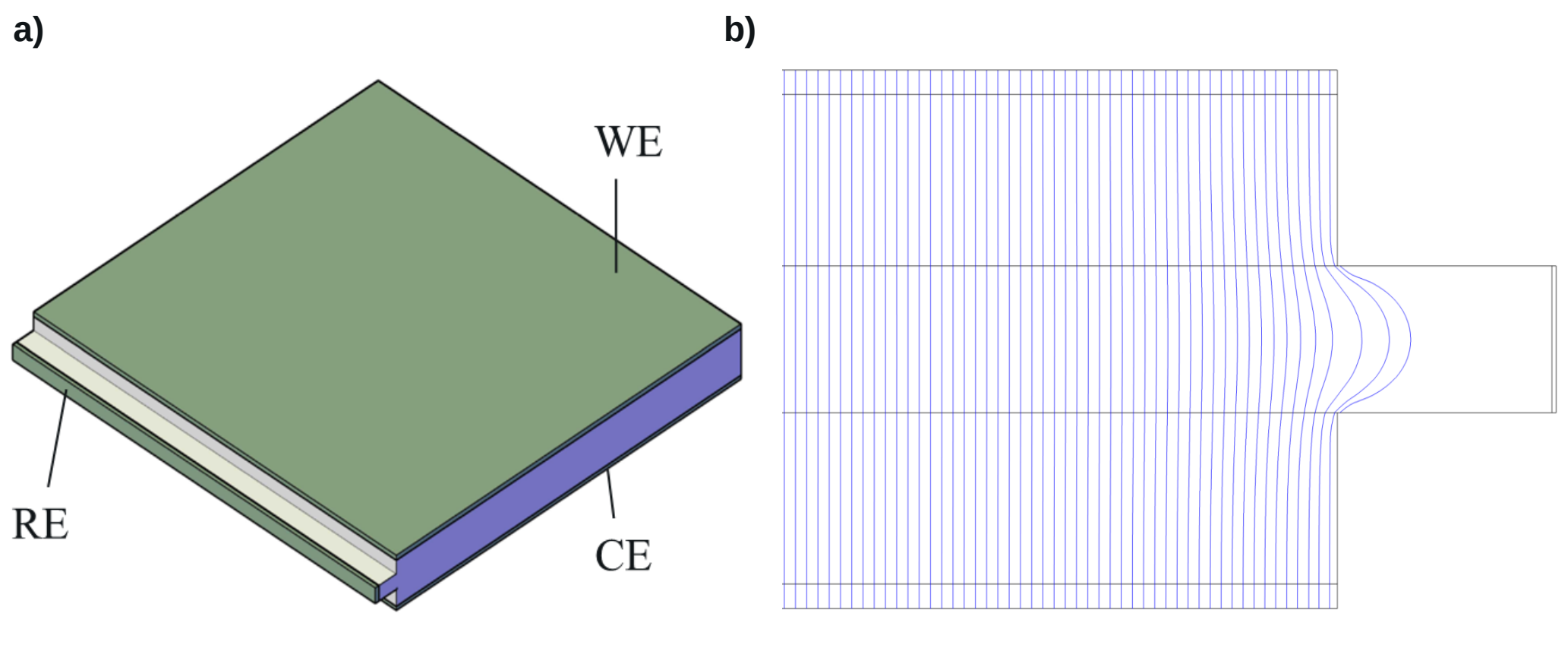


Fig. 9 a) Wing geometry with b) Current distribution (ω → ∞)

Advantages of **Wing Geometry**:
+ WE/CE alignment easy to achieve
+ short circuit effect avoided
+ no error for identical WE, CE
+ similar to produce as regular symmetrical cells

High resistive samples/ High frequencies

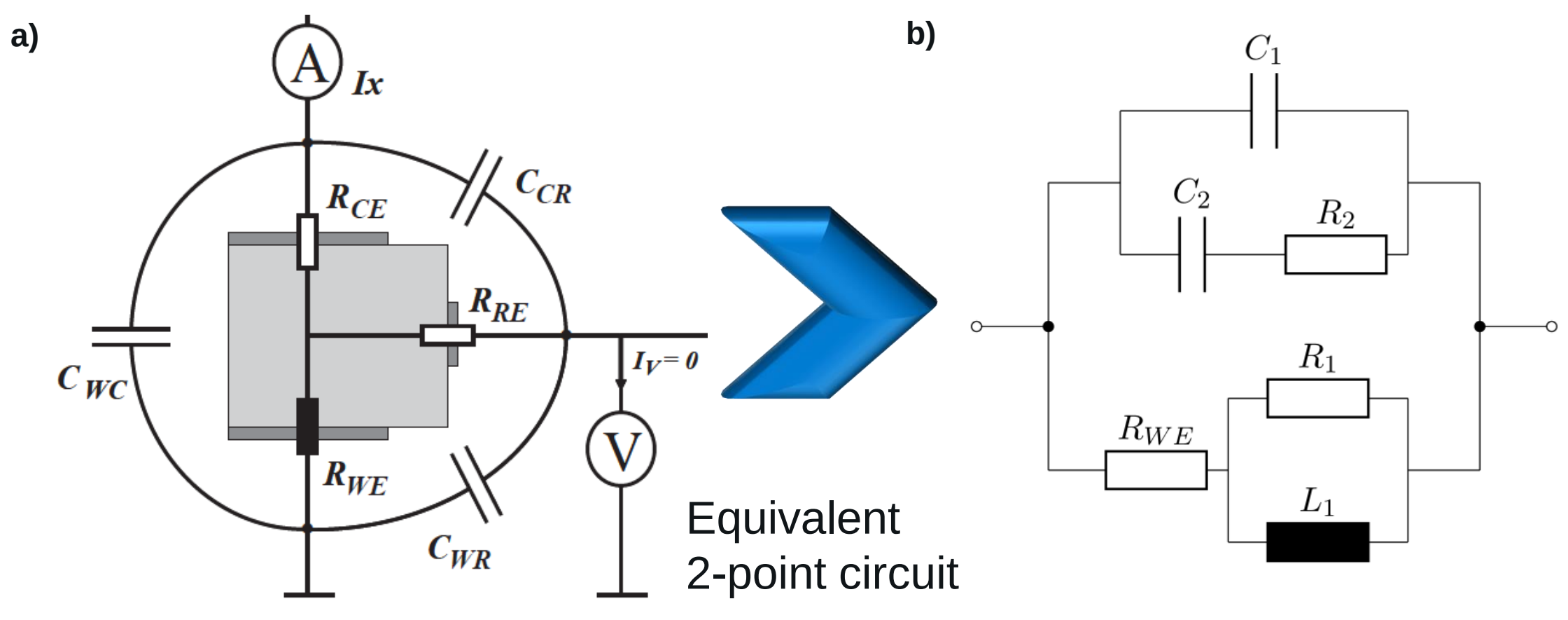


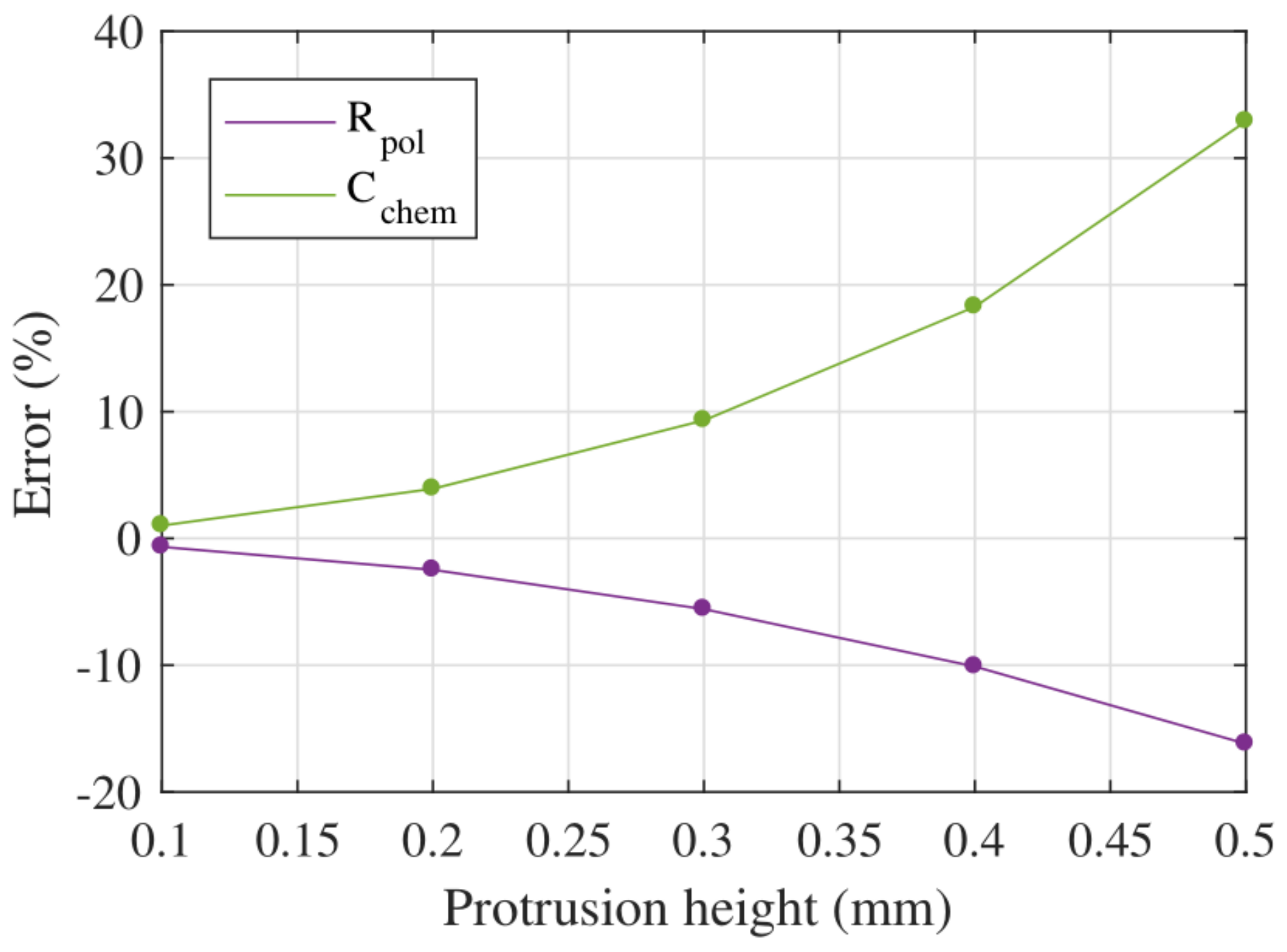
Fig. 8 a) Equivalent circuit for a sample with 3 terminal connection, b) The two-terminal equivalent network of a three-terminal electrochemical cell [5]

$$\underline{Z}(\omega)_{\text{3-point}} = \frac{\underline{V}}{\underline{I}} = \underline{Z}(\omega)_{\text{2-point, equivalent}}$$

This capacitance can be cancelled out by actively shielding the reference electrode coaxial cable. This measure forces the shield of the BNC cable on the same potential like its core, which actively eliminates the capacitance.

→ Coupling capacitances may lead to distorted measurement results!
→ Important for:
  → Frequency in GHz range
  → High resistive samples

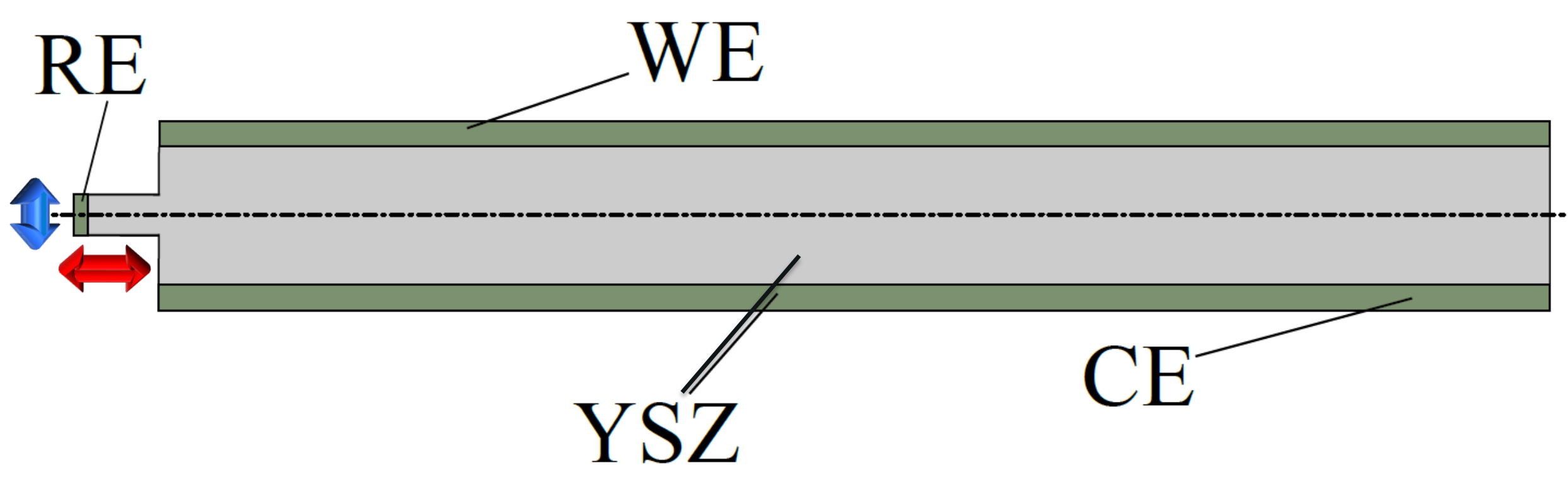
Limitations of the "WING GEOMETRY"



Error sources:
- 3-point transfer characteristic for high ohmic electrodes and high frequencies
- Reference potential shift caused by WE/CE
  - Geometrically asymmetry
  - Resistive asymmetry
  - Capacitive asymmetry
- Short circuit effect

Fig. 10 Measurement errors for worst case scenario (low-ressistive electrodes and identical relaxation times) with given geometry and changing **protrusion height (blue arrow in Fig. 11)**, **protrusion depth = 0,5 mm (red arrow in Fig. 11)**, electrolyte thickness = 1 mm.
This intrinsic error source can be minimized by minimizing a and b.

$$a = \frac{R_{electrolyte}}{R_{electrode}}$$



$$b = \frac{h_{protrusion}}{h_{electrolyte}}$$

Fig. 11 Wing geometry with indicated protrusion of the electrolyte wing, red and blue in X and Y direction respectively

Practical solutions for the "WING GEOMETRY"

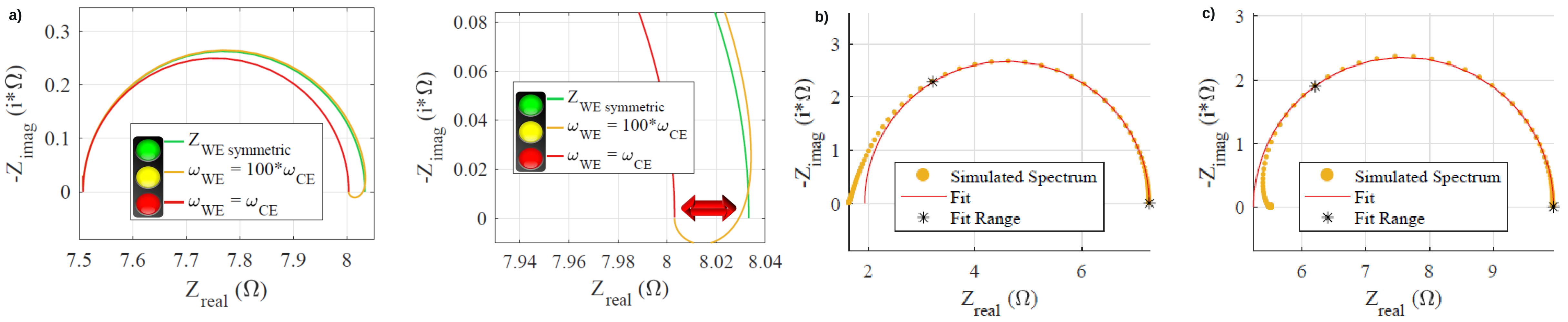


Fig. 12 a) Low frequency error. Simulated impedance spectra of three electrode arrangements on a **Wing Geometry** sample. The red arrow indicates the effect from reference potential shift as shown in Fig.3 & 5. b) & c) High frequency error. Simulated impedance spectra with $\omega_{WE} = \omega_{CE}/100$ resulting in a measurement error in the high frequency range. Fig. 12b and 12c represent spectra from WE and CE respectively.

🟥 Red $\omega_{WE} = \omega_{CE}$ (error not visible)
🟨 Orange $\omega_{WE} = 100 \times \omega_{CE}$ (low frequency error)
🟩 Green $\omega_{WE} = \omega_{CE}$ (symmetric, ideal measurement)
Fig.12b $\omega_{WE} = \omega_{CE}/100$ (high frequency error)

$$\omega = \frac{1}{RC}$$

Cross check results by measuring CE vs RE switch WE, CE at impedance spectrometer to get an idea of WE/CE asymmetry.

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Abbreviations

WE…	Working electrode
RE…	Reference electrode
CE…	Counter electrode
R_{pol}…	Polarization resistance
C_{chem}…	Chemical capacitance

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