



AC IMPEDANCE SPECTROSCOPY FOR BETTER UNDERSTANDING DYE SOLAR CELLS

**Hans Desilvestro, Michael Bertoz, Graeme Evans,
Paul Moonie, Ravi Harikisun and Paul Murray**



Outline

- **Rationale**



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- **Influence of electrolyte composition and I_2 concentration**



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- **Influence of electrolyte composition and I_2 concentration**
- **Influence of type of dye and surface modification**
- **Some EIS results from long term testing**
- **Untangling some of the counter electrode surface chemistry**



Why AC impedance spectroscopy ?

Non-intrusive method for probing resistivity contributions from:

- **Electrolyte**



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Establish a better understanding of factors influencing performance and power loss mechanisms

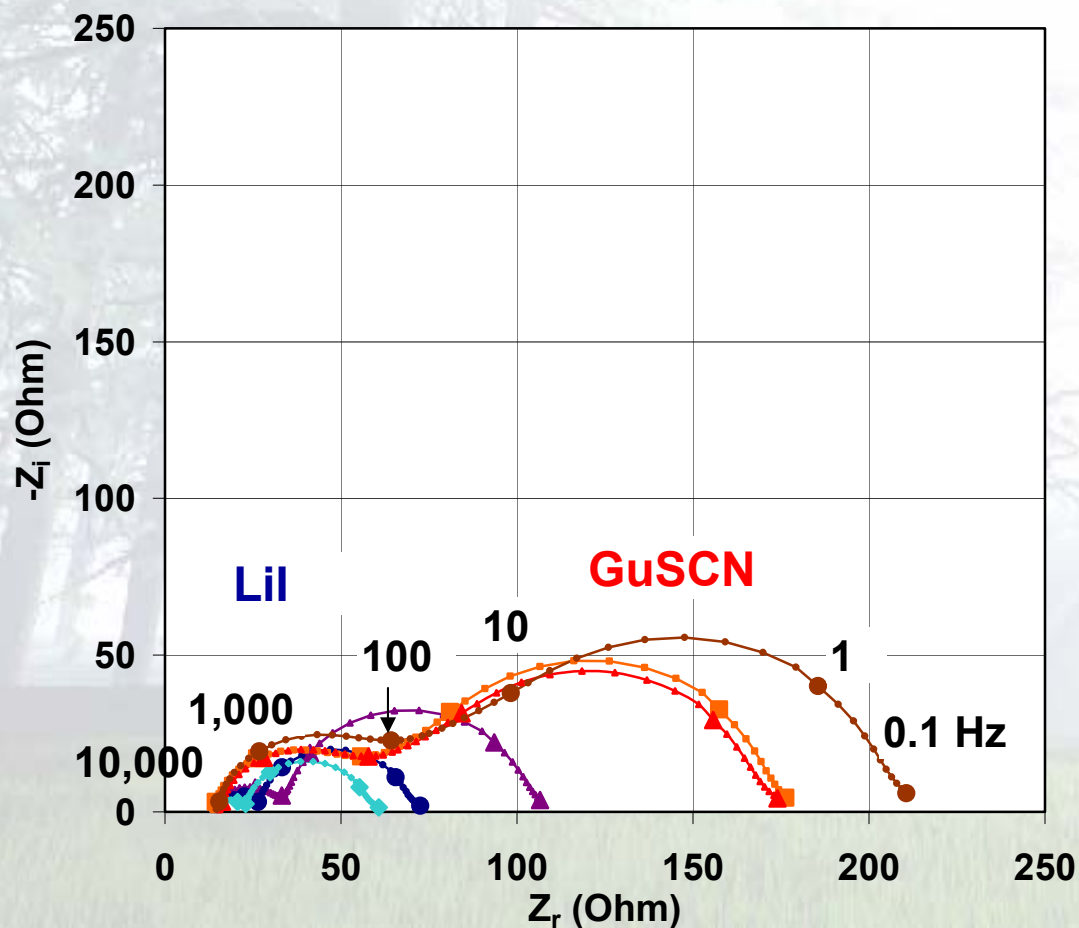


Influence of electrolyte composition (GBL-based)



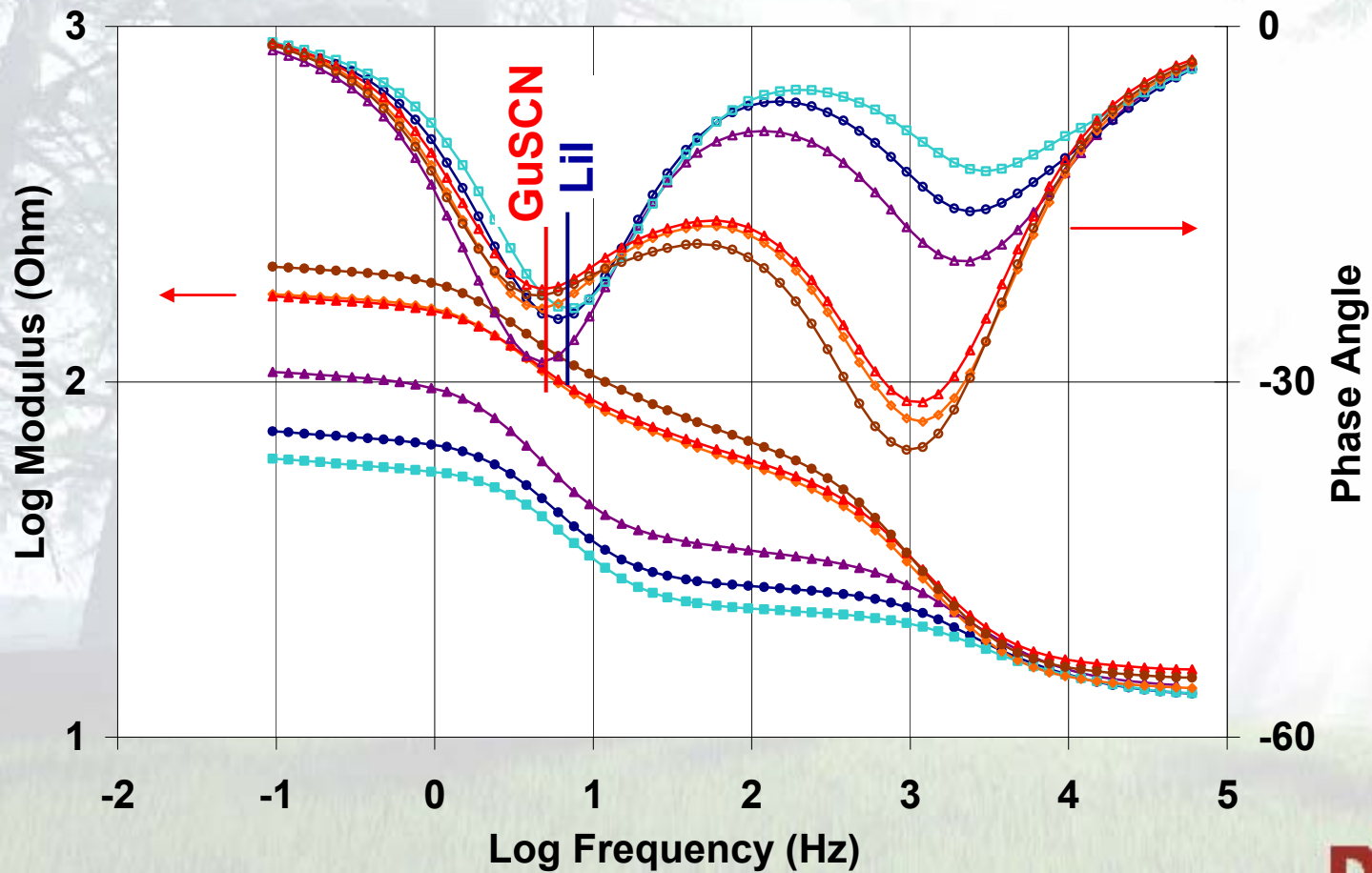
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Nyquist plots of test cells
-0.68V, dark, Lil vs GuSCN



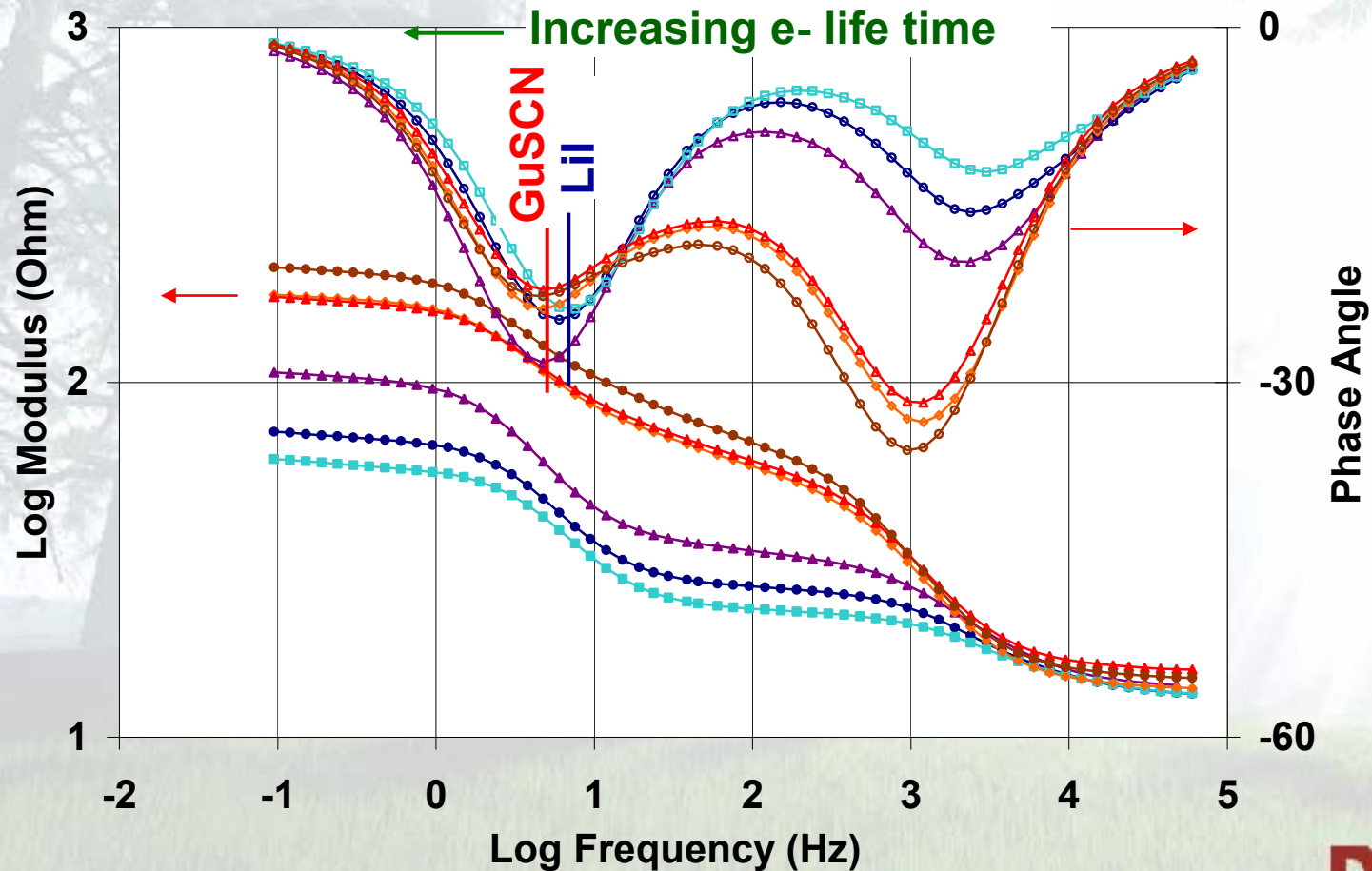
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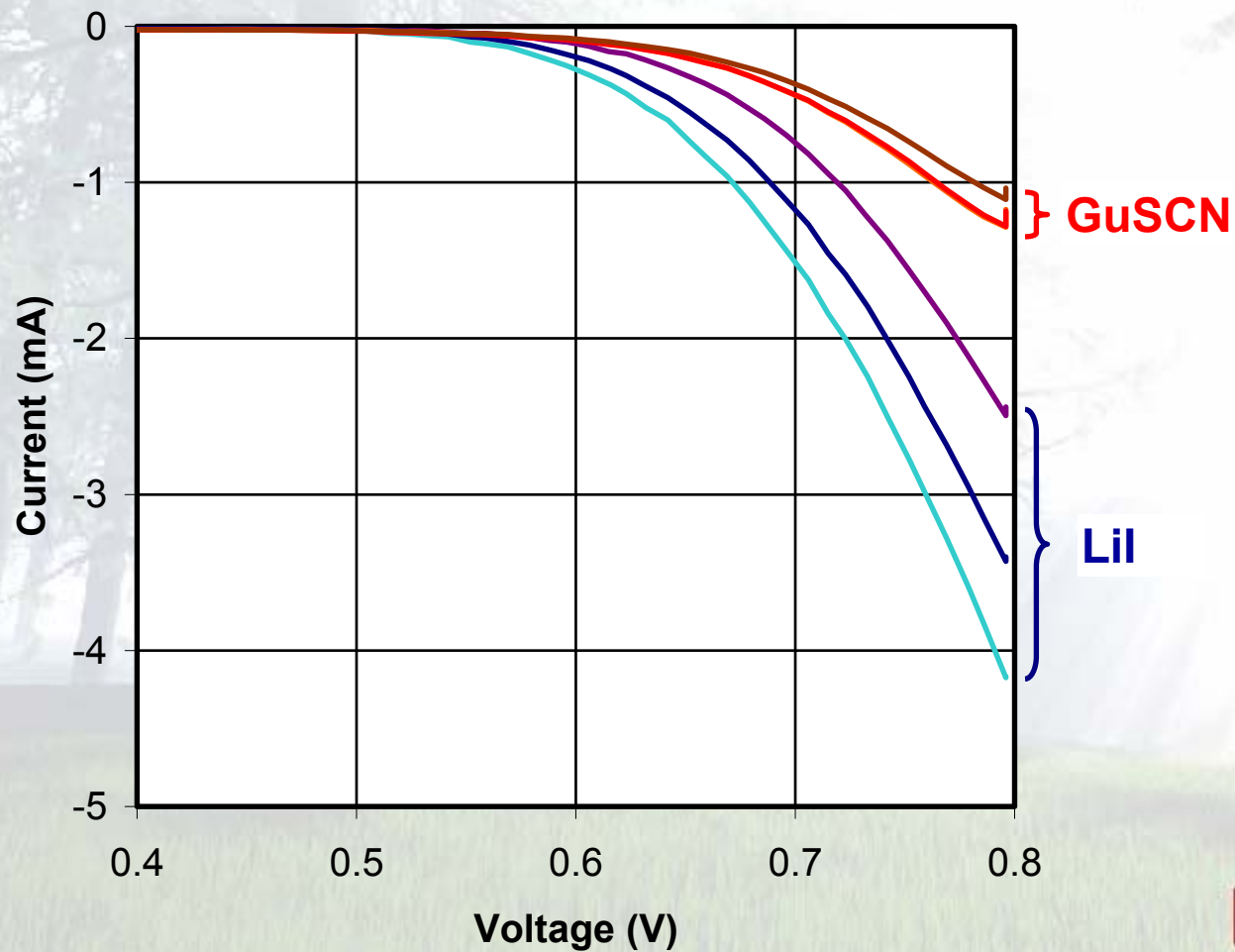
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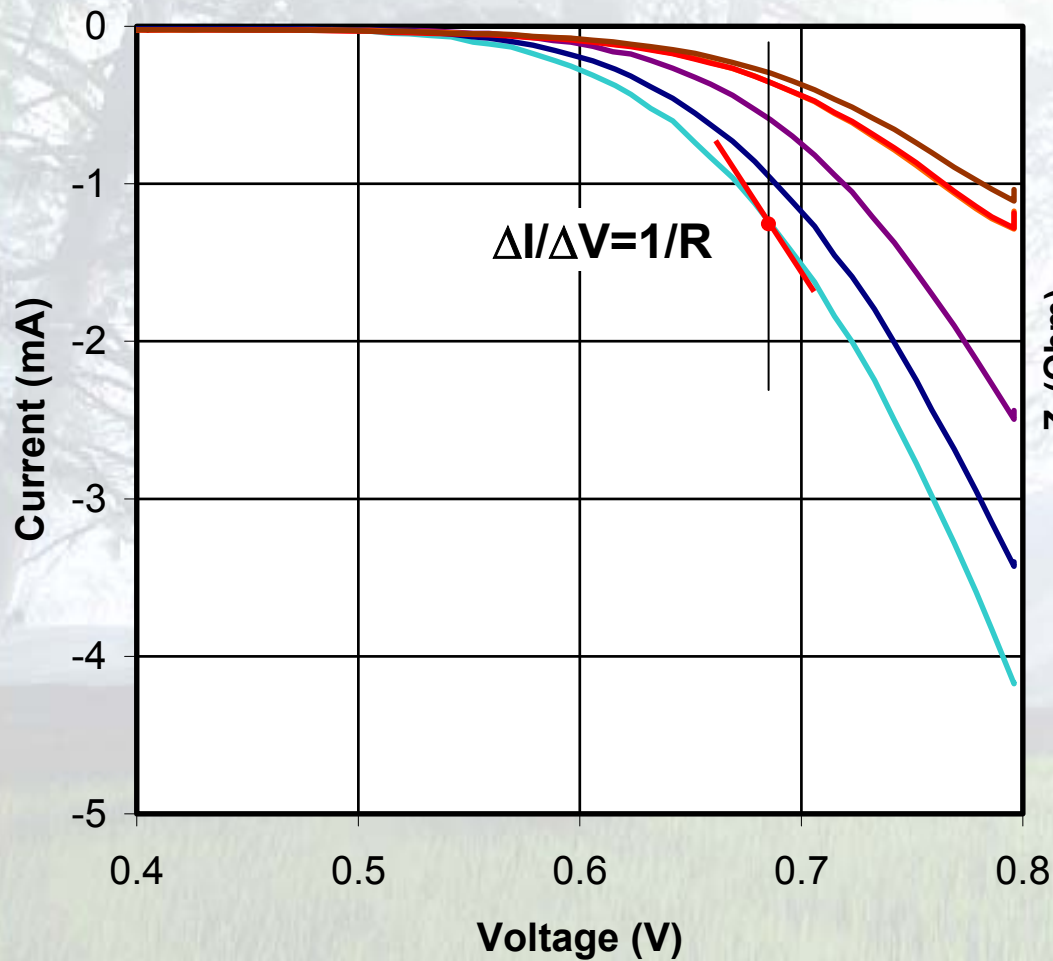
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Dark, I-V Plots
LiI vs GuSCN

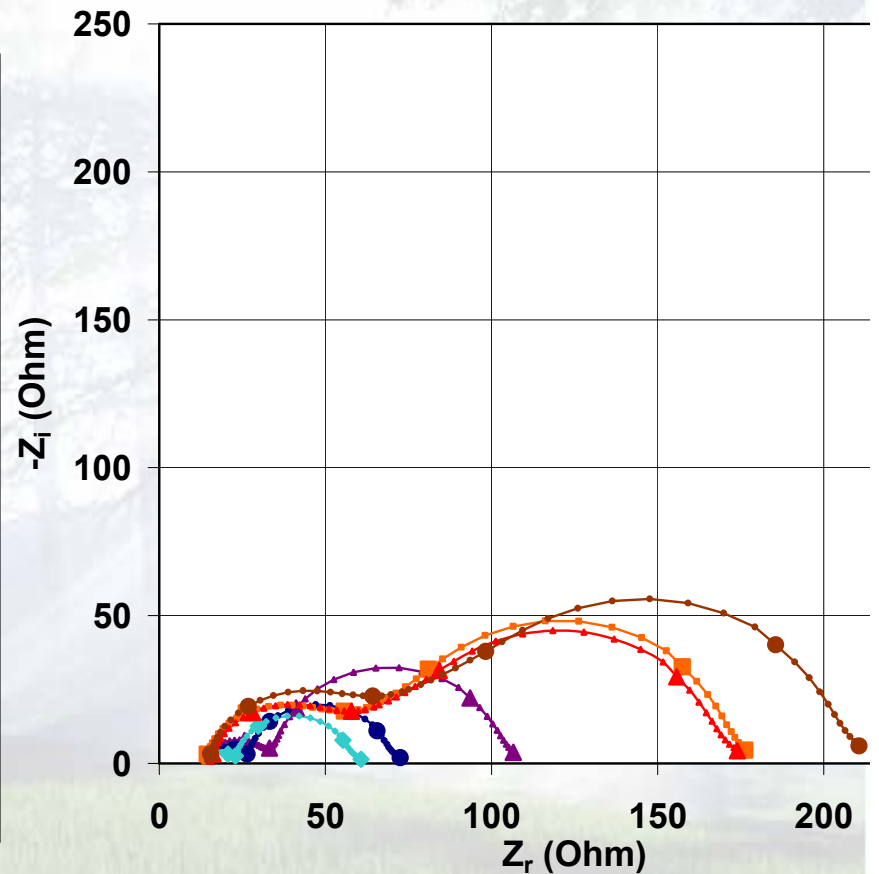


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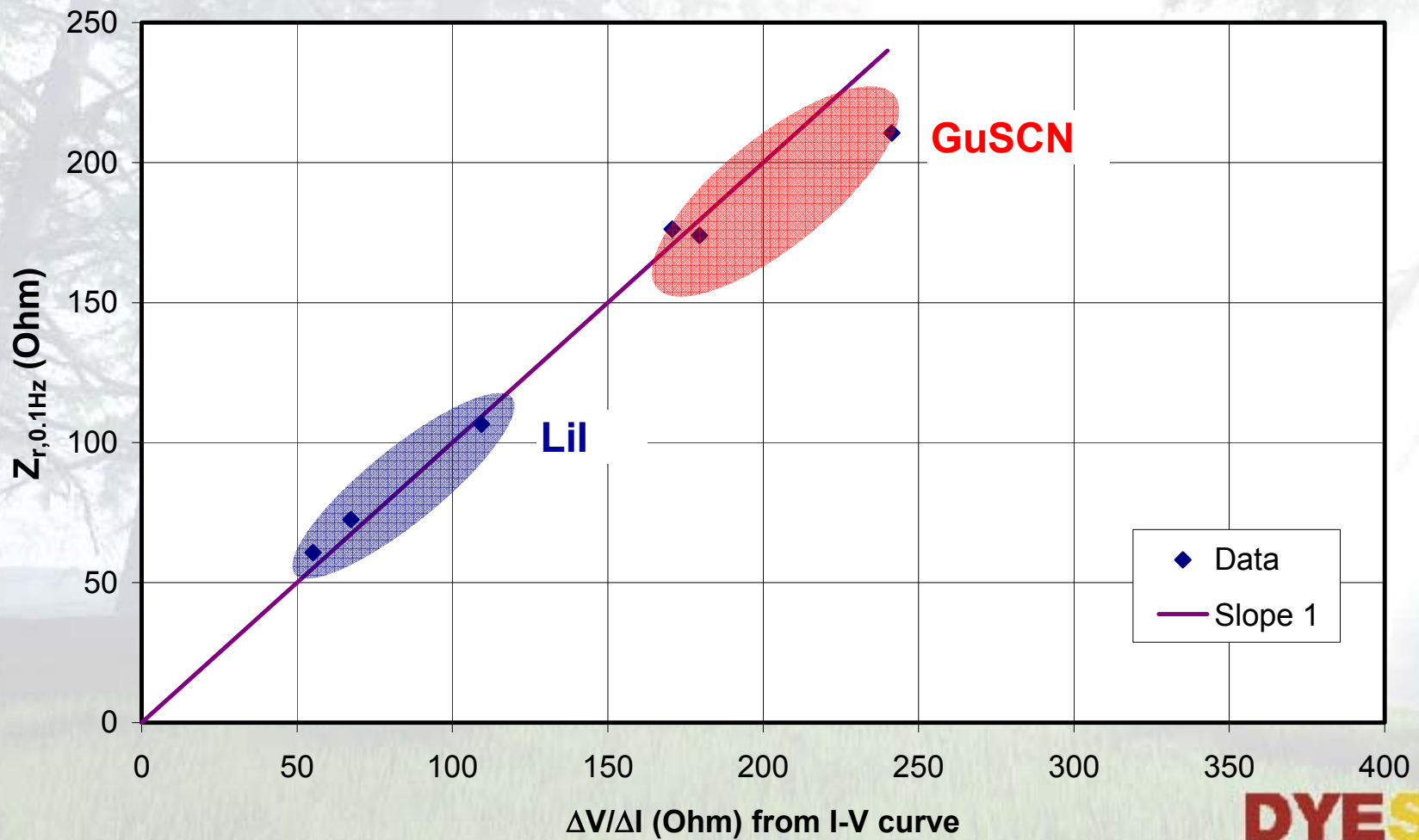


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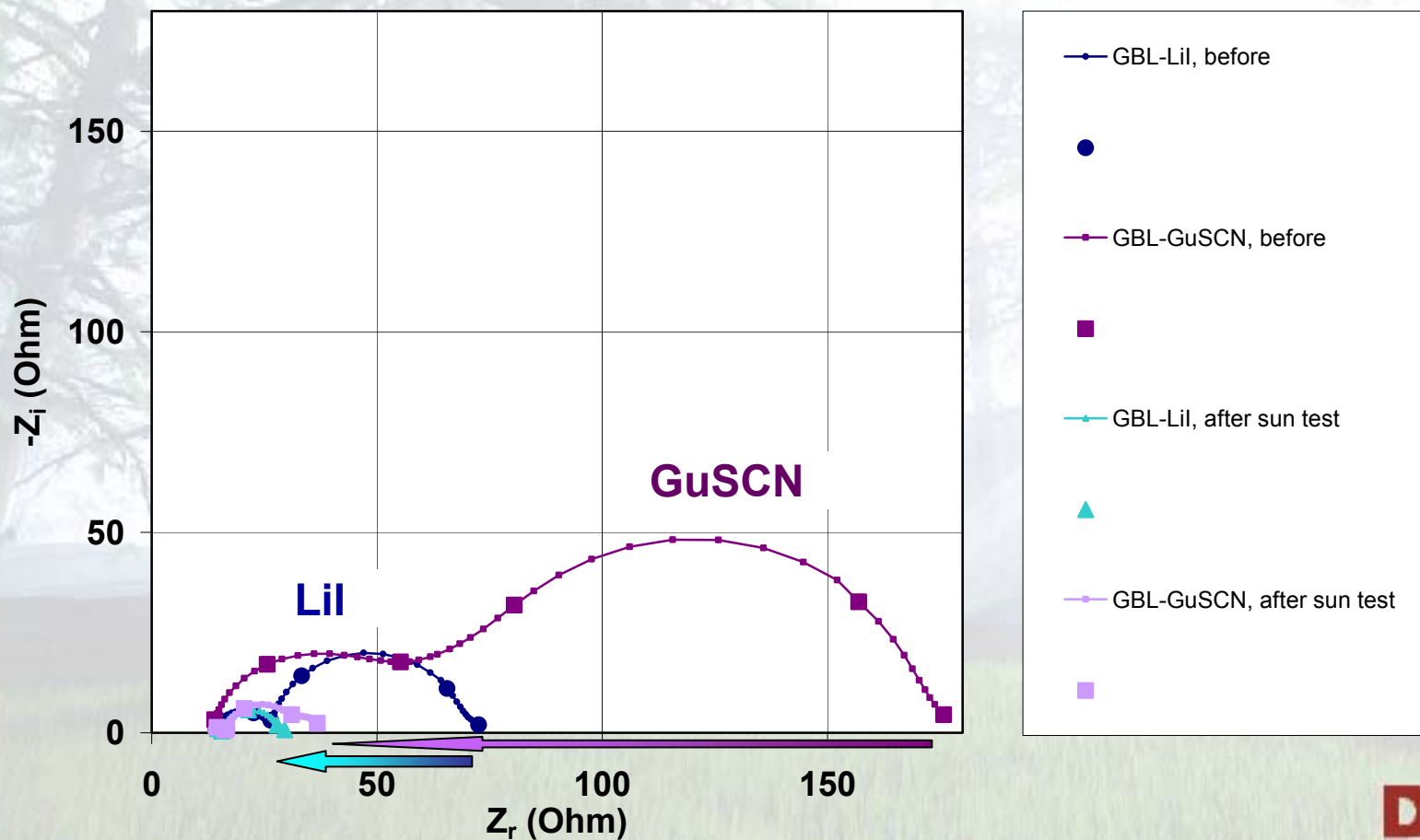
Influence of electrolyte composition (GBL)

I-V vs AC impedance data
dark, 0.68V, Lil vs GuSCN



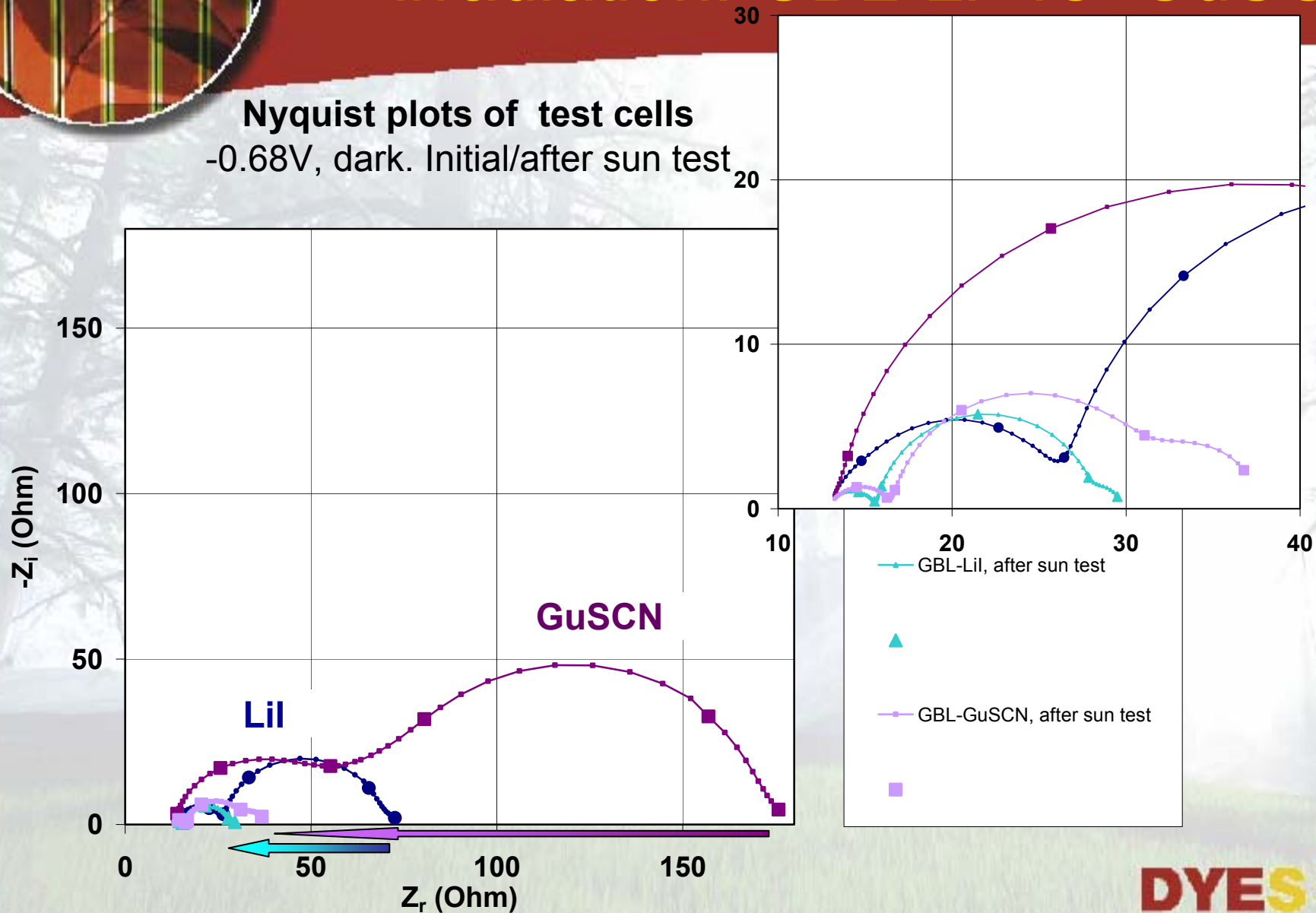
Influence of long term irradiation: GBL-Lil vs. GuSCN

Nyquist plots of test cells
-0.68V, dark. Initial/after sun test



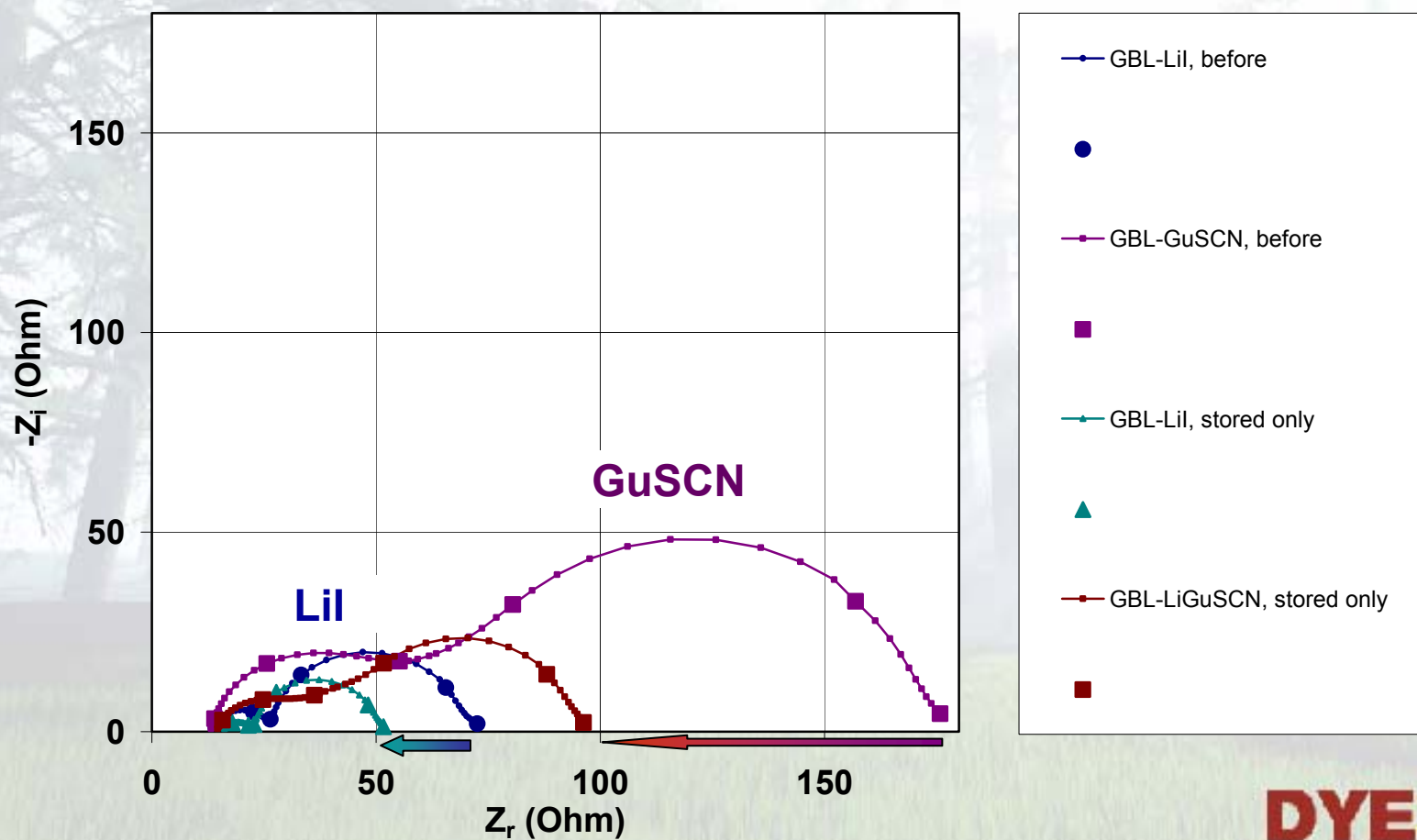
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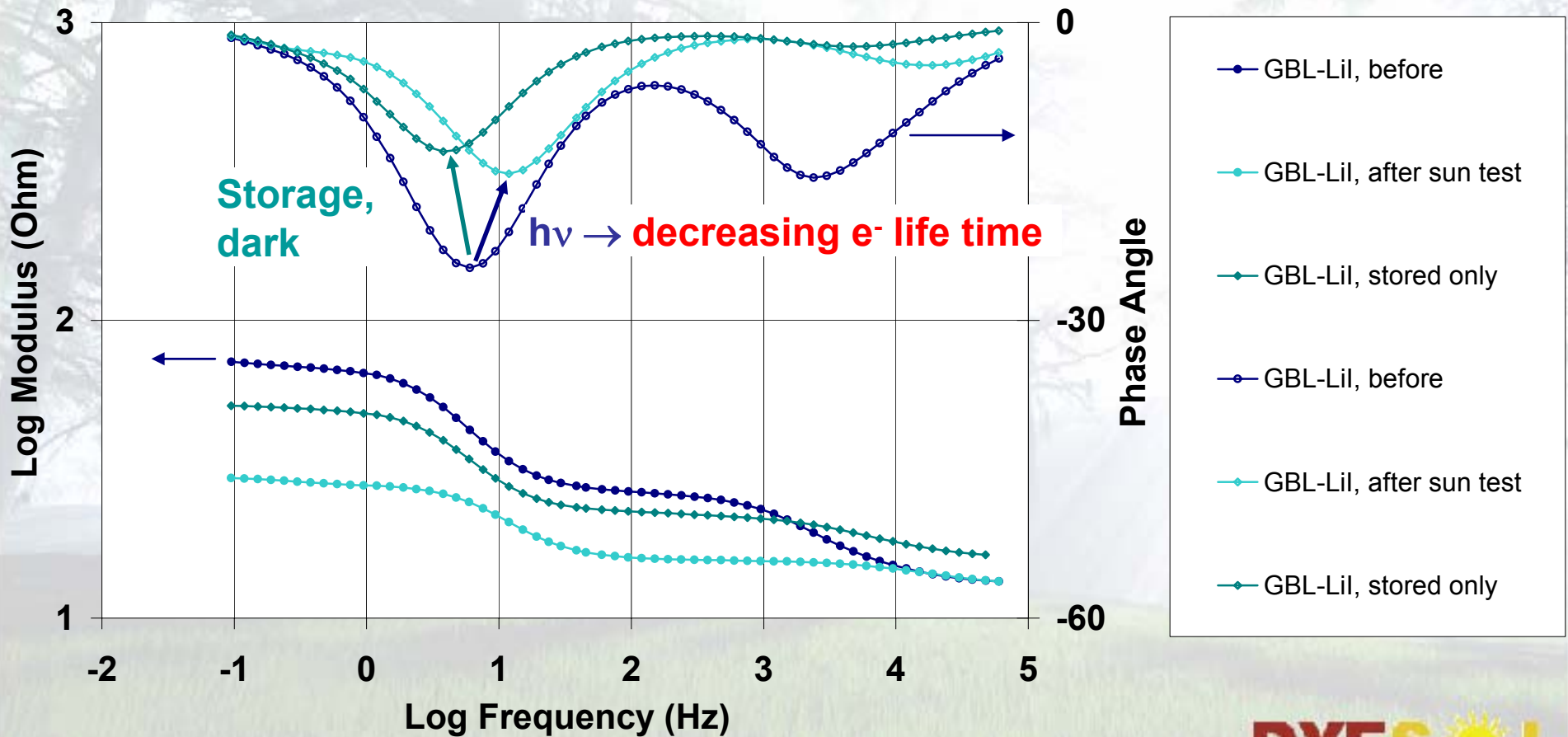
Influence of long term storage (dark): GBL-LiI vs. GuSCN

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-0.68V, dark. Initial/after storage in dark



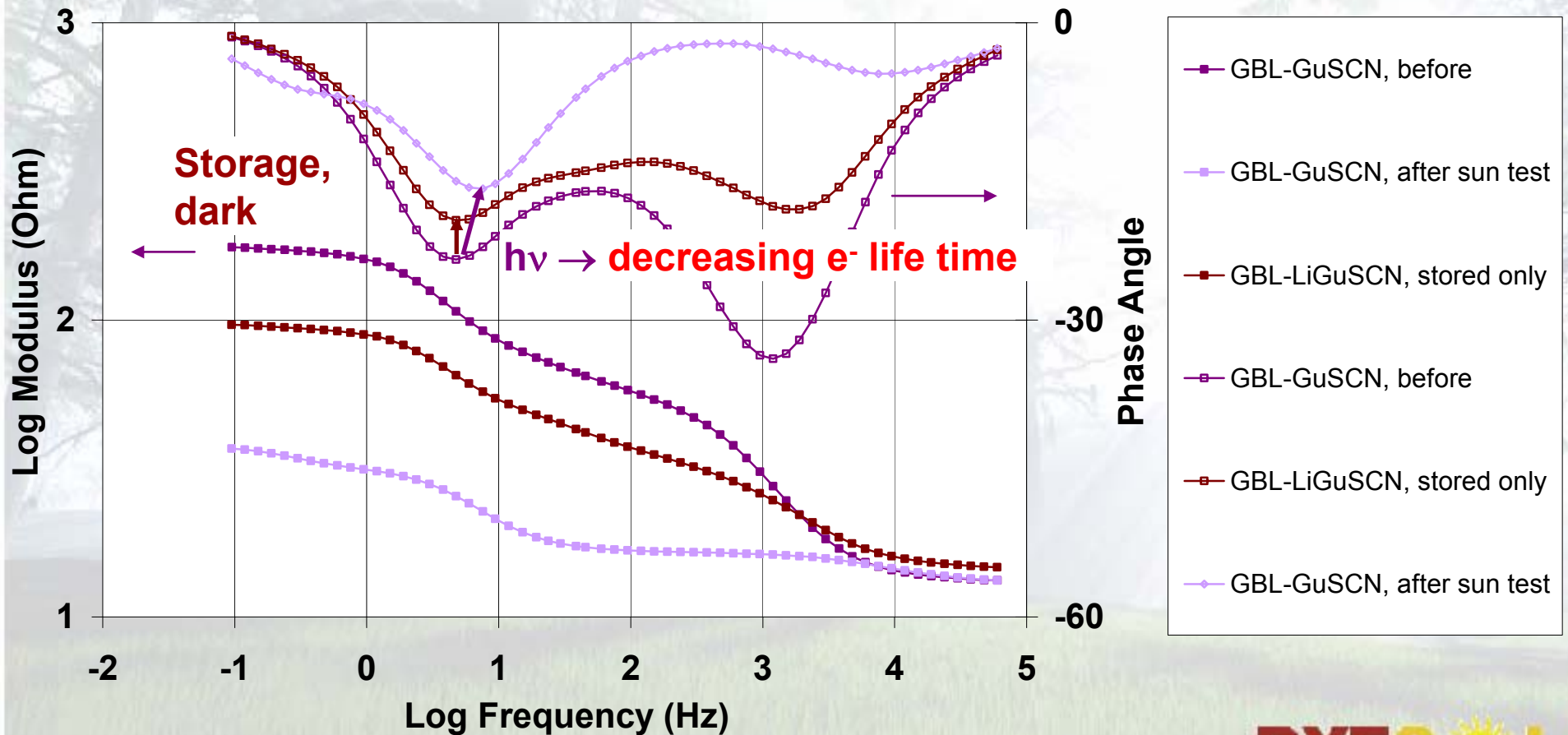
Influence of long term $h\nu$ or storage (dark): GBL-LiI

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Influence of long term $h\nu$ or storage (dark): GBL-GuSCN

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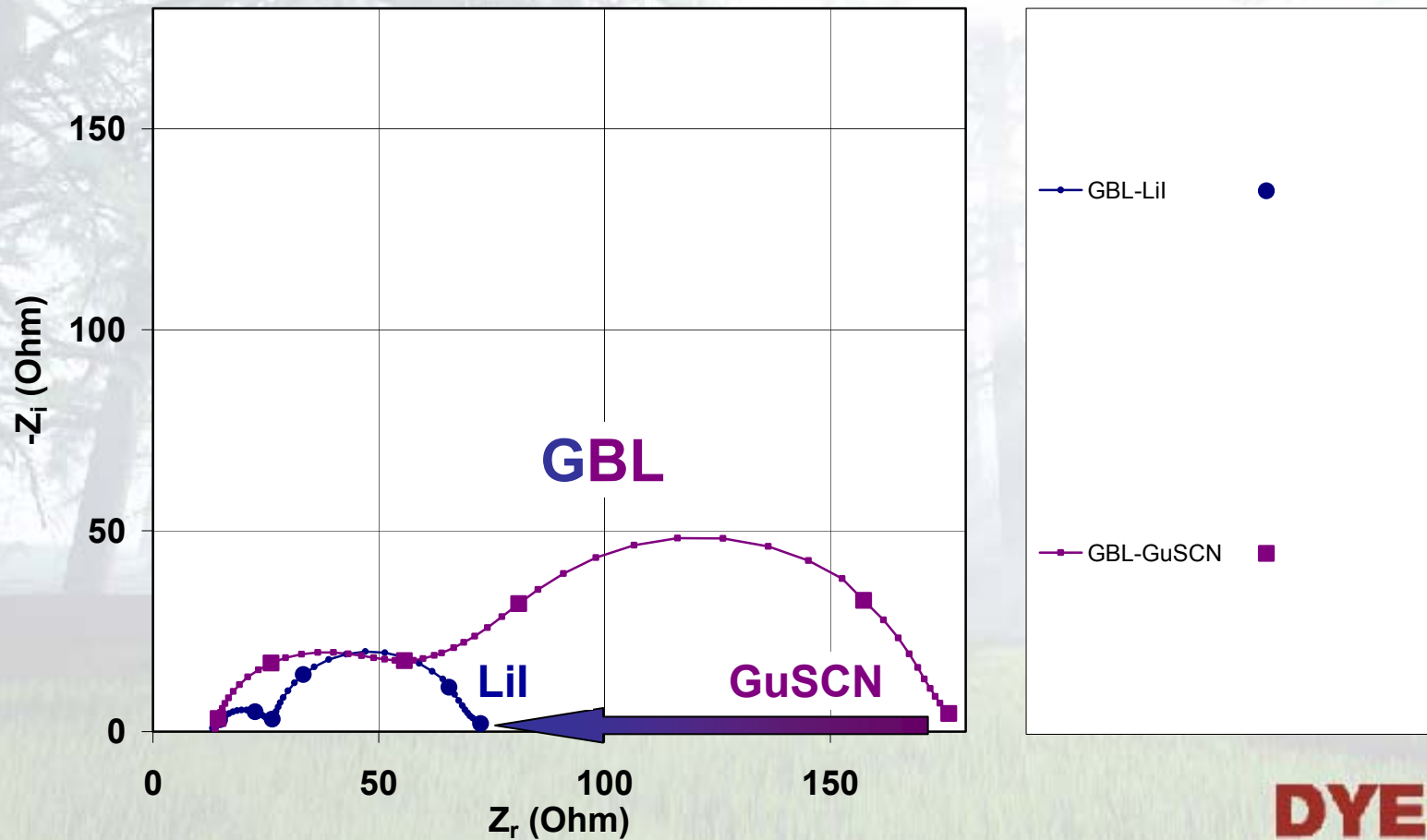


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- Long term ambient temperature storage in the dark leads to some decrease of R_{ct} (Pt) and R_{back} reaction as well, however to a much lesser degree. The electron life time is not lowered significantly through long term storage in the dark.

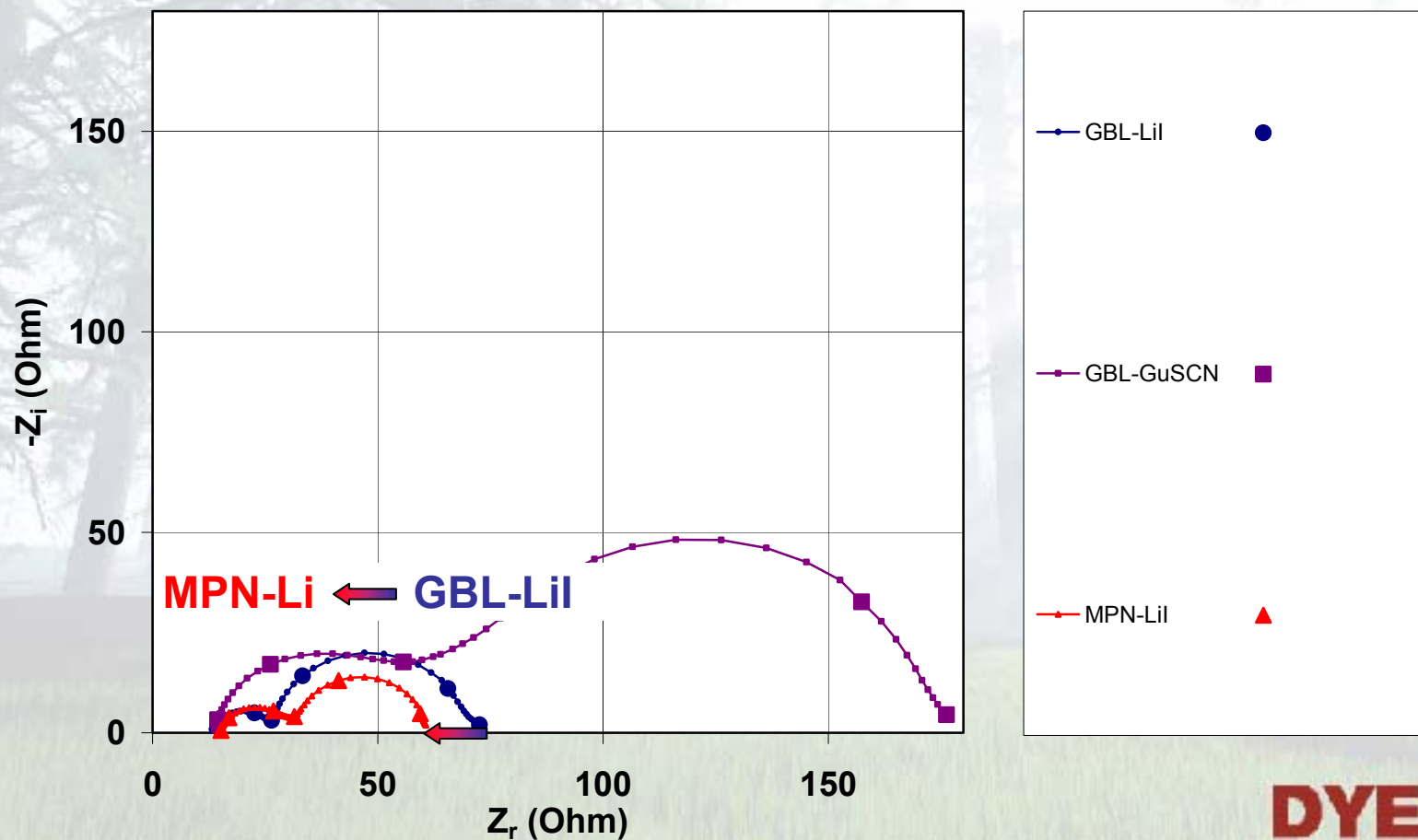
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Nyquist plots of test cells
-0.68V, dark



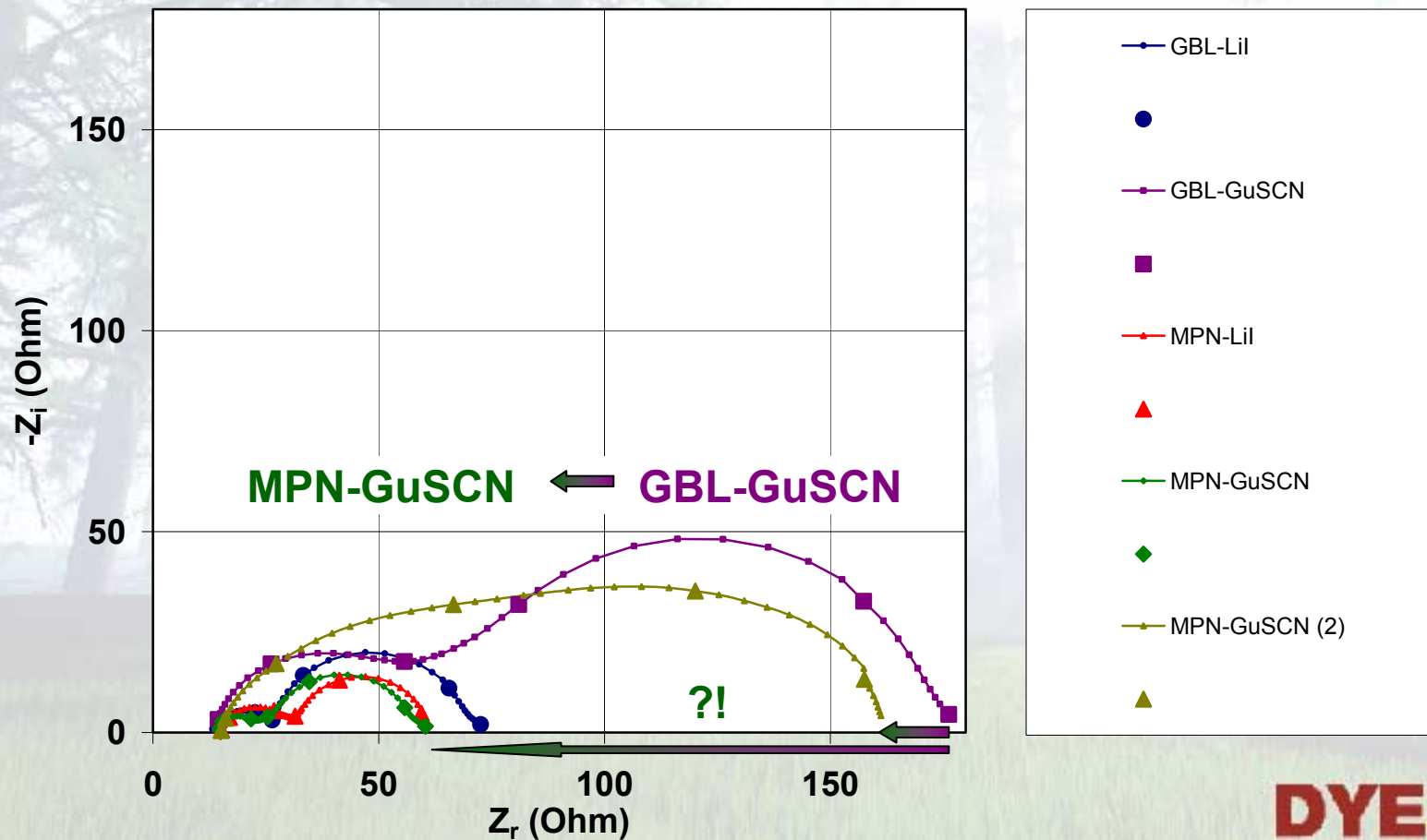
Influence of electrolyte composition (GBL/MPN-based)

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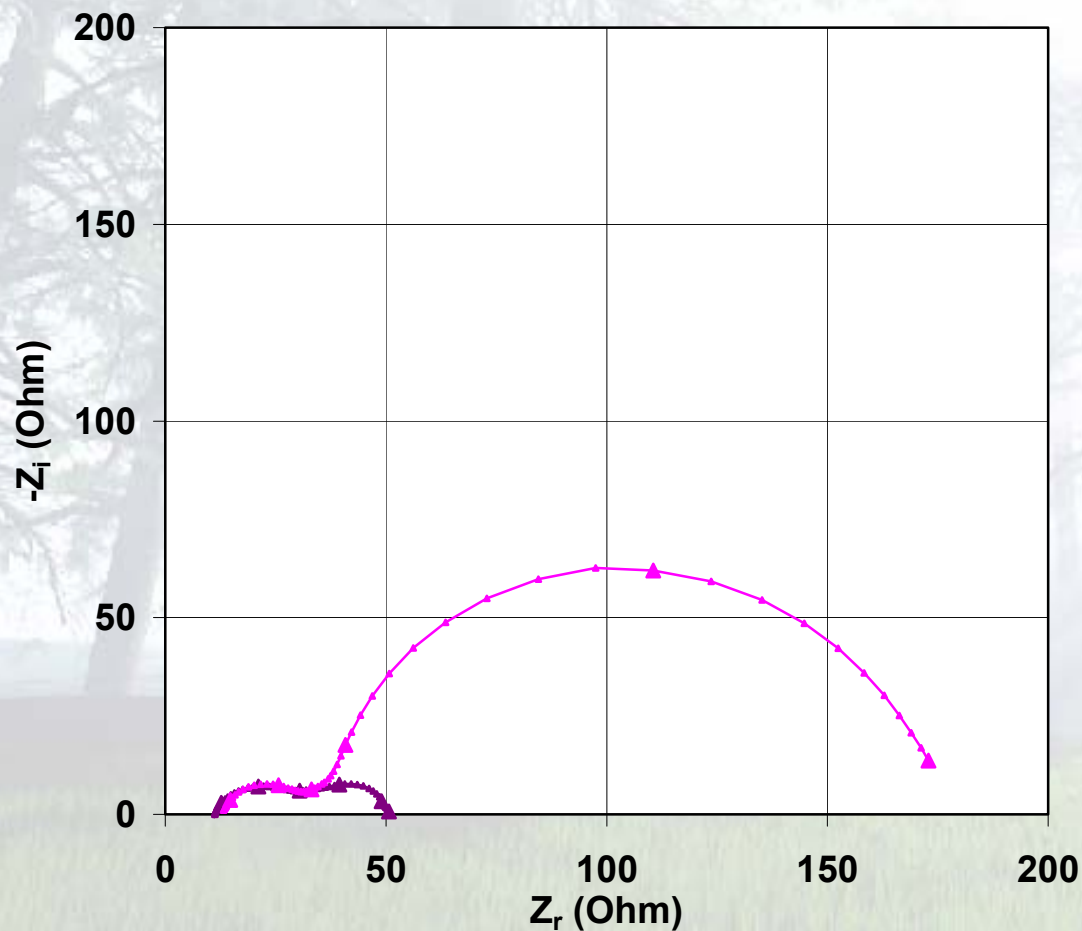


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- The 2 types of AC impedance spectra for MPN/GuSCN are not understood at this stage.

Influence of dye and surface modification

Nyquist plots of test cells
MPN - Lil



—●— N-719, surface unmodified

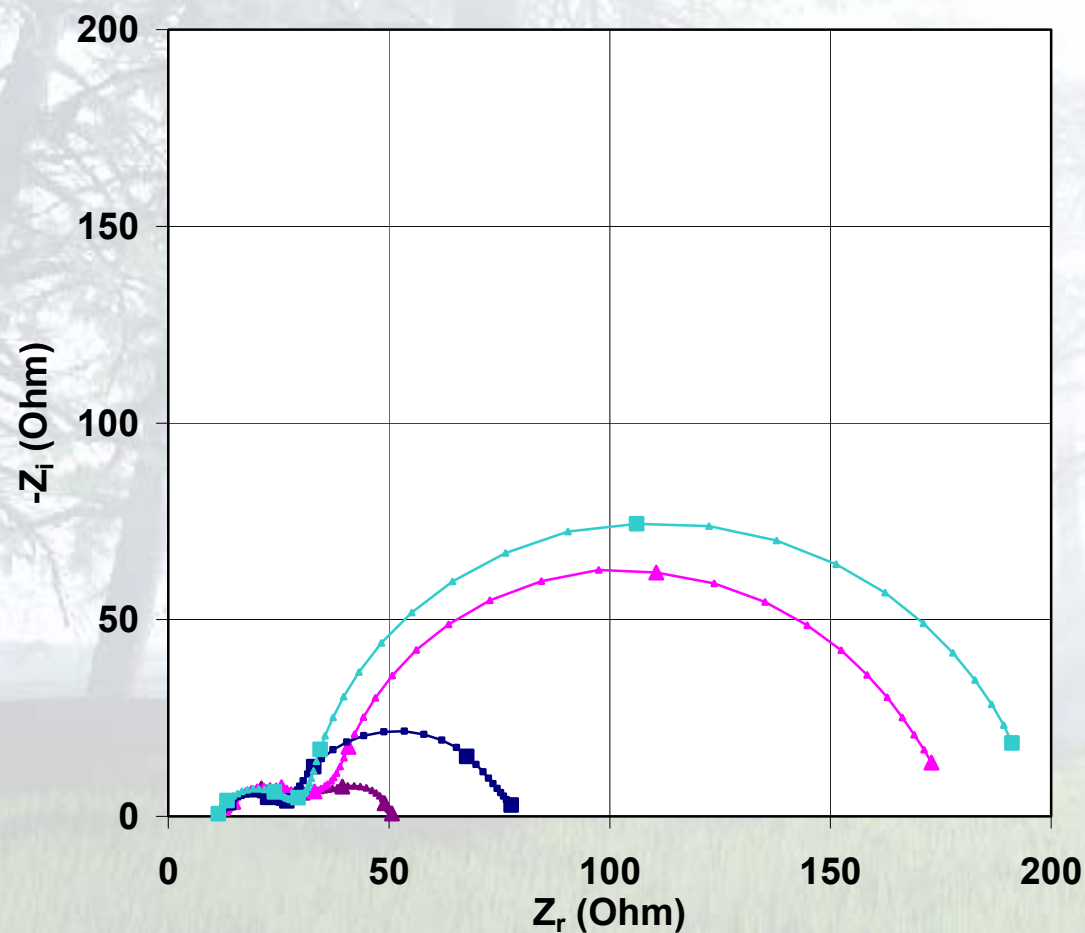


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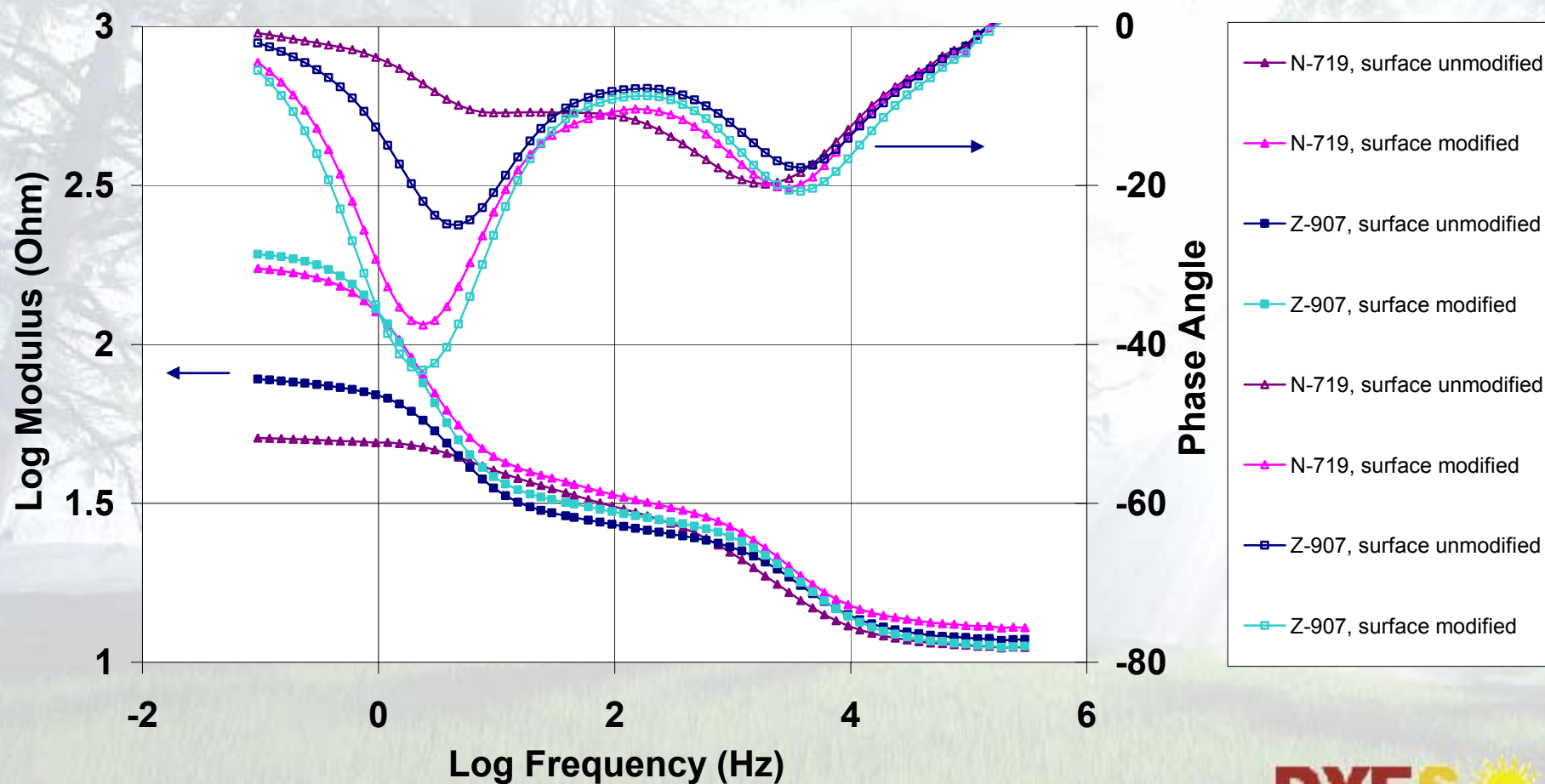
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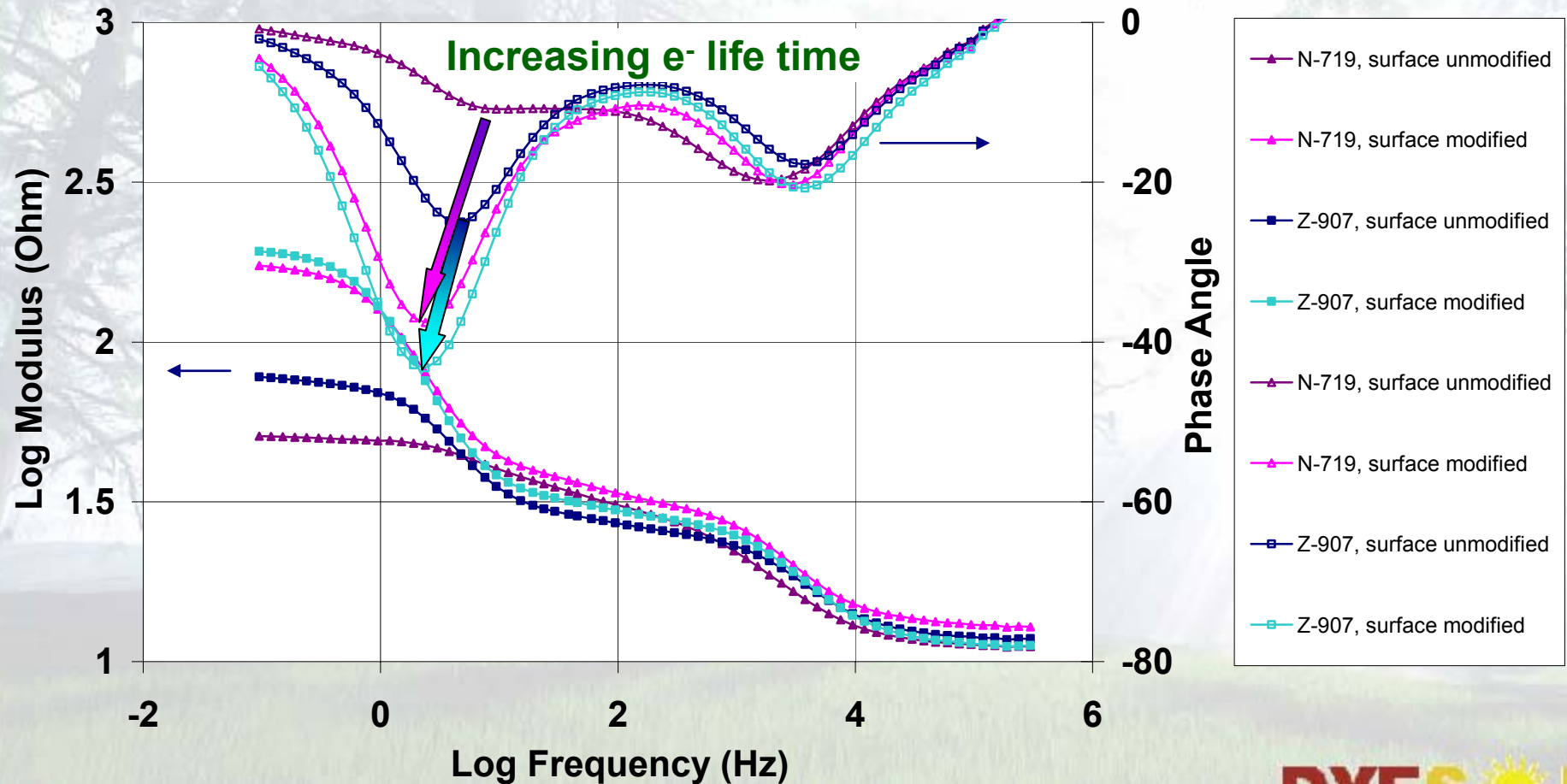
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Bode plots of of test cells
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Influence of dye and surface modification

- Dye chemistry and/or surface modification can have significant influence on the back reaction rate and the electron life time.

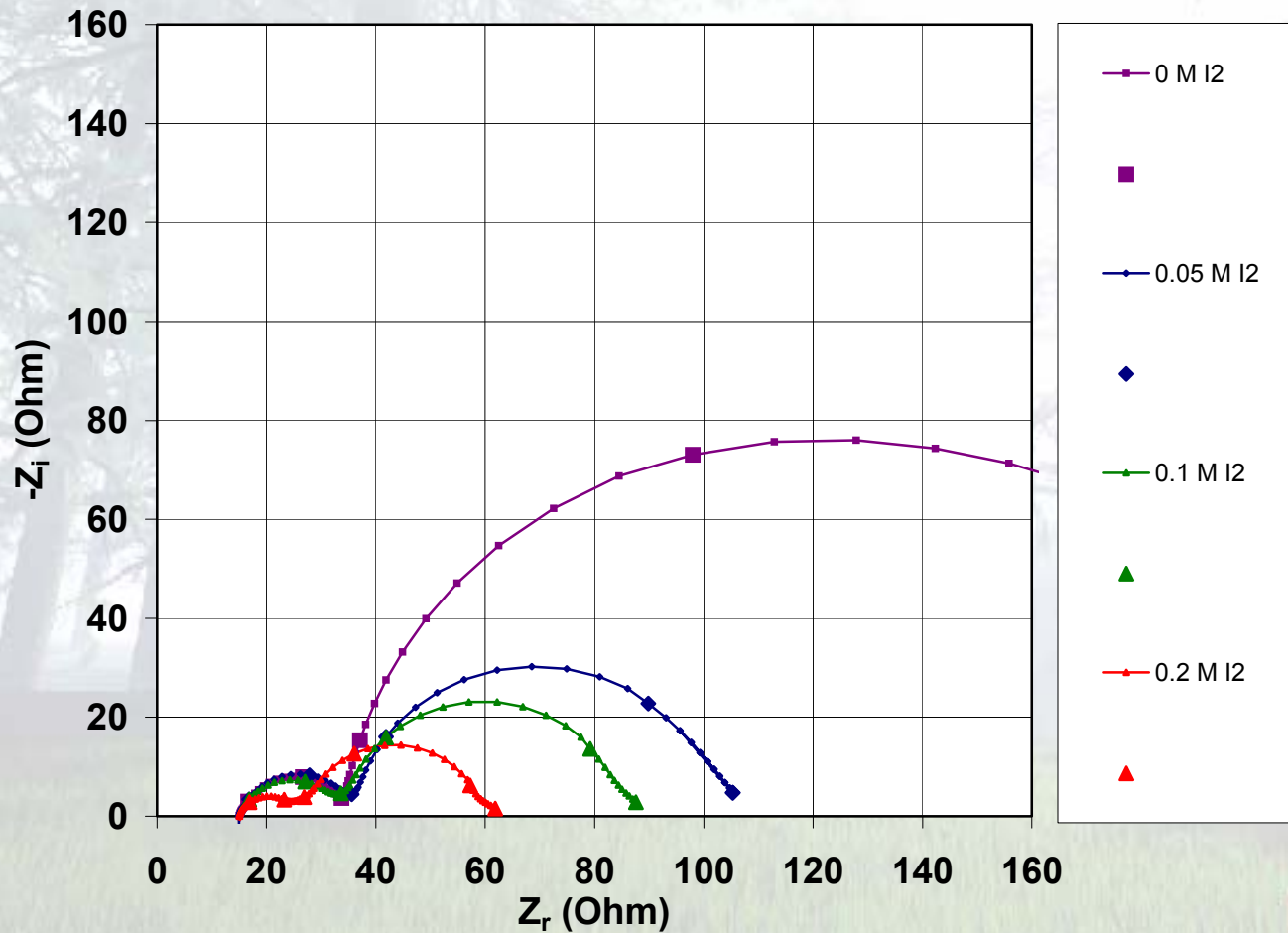


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- Long term testing is underway.

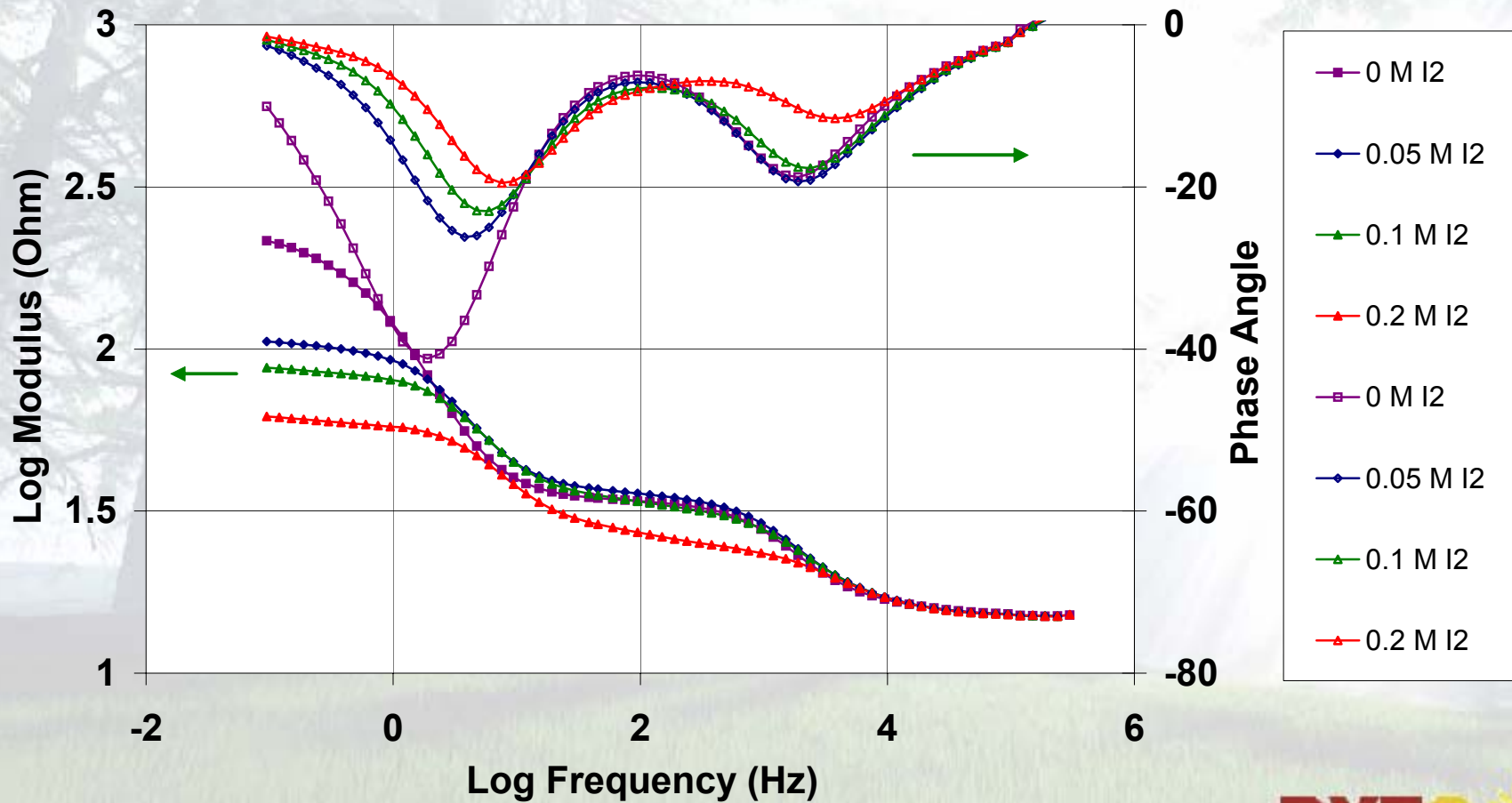
Influence of I_2 concentration

Nyquist plots of test cells
MPN/GuSCN - Initial Data



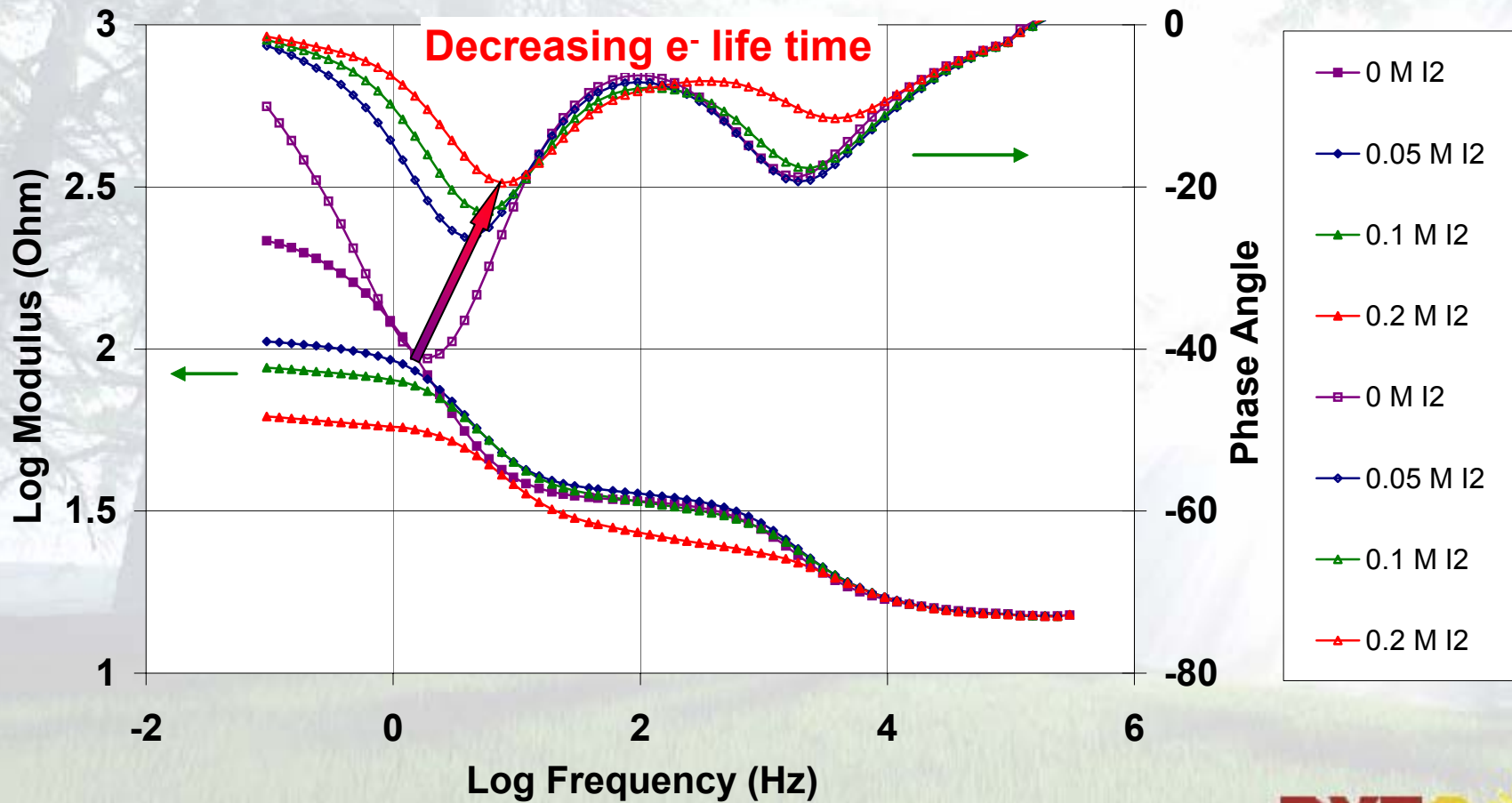
Influence of I₂ concentration

Bode plots of of test cells
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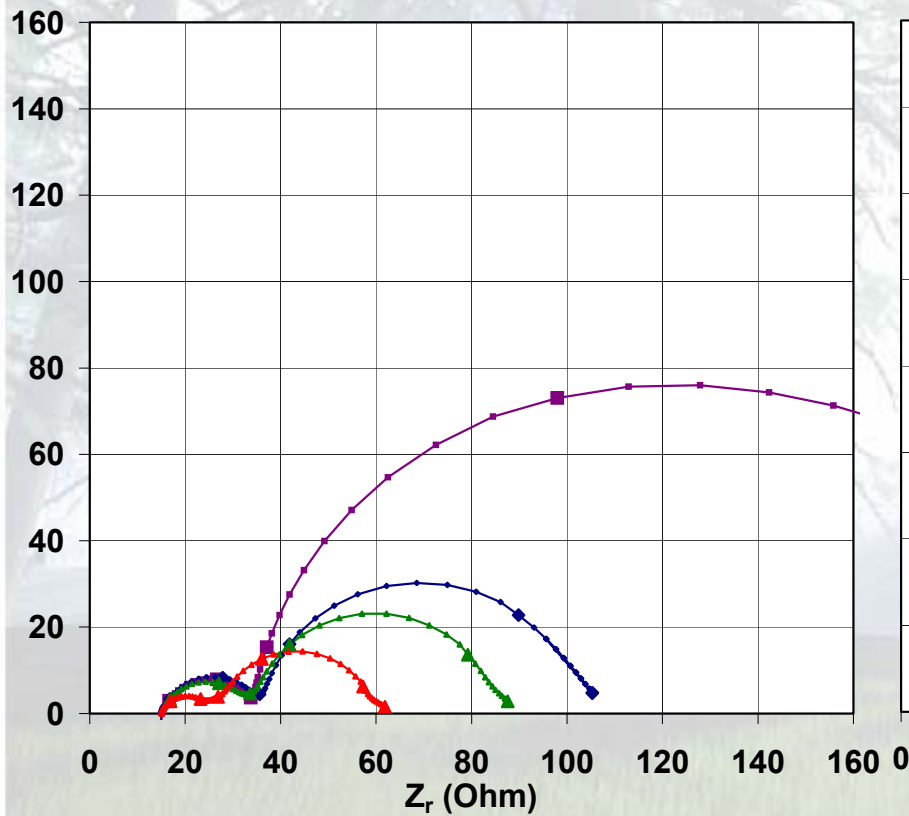
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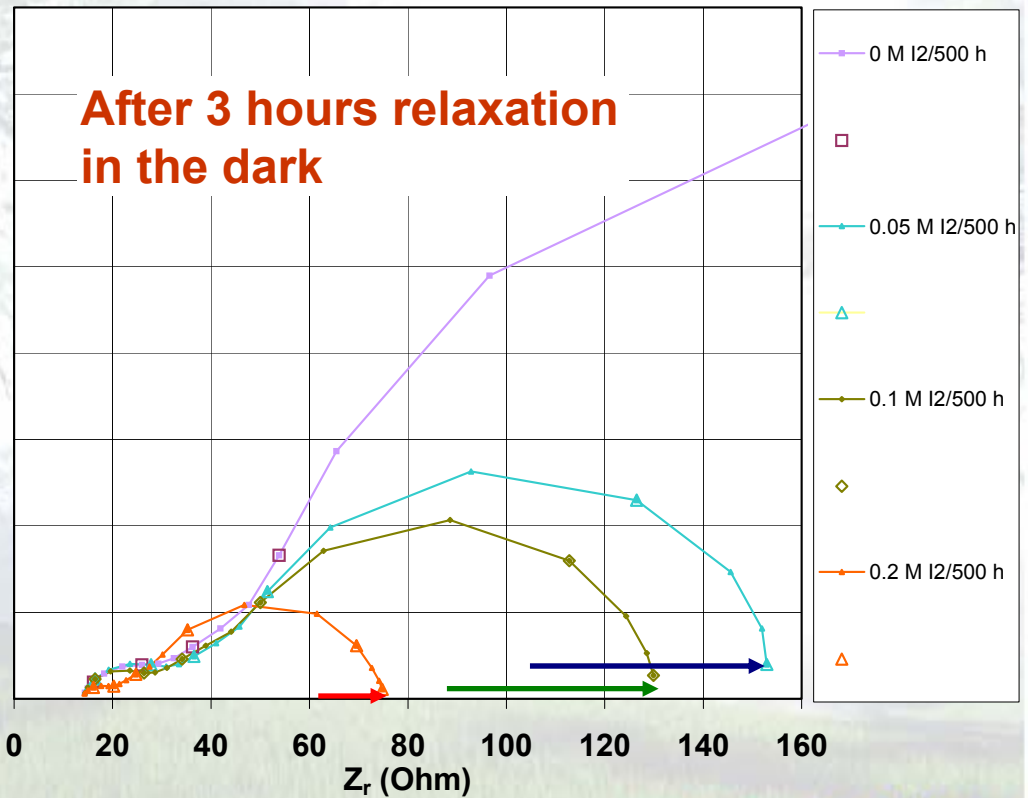


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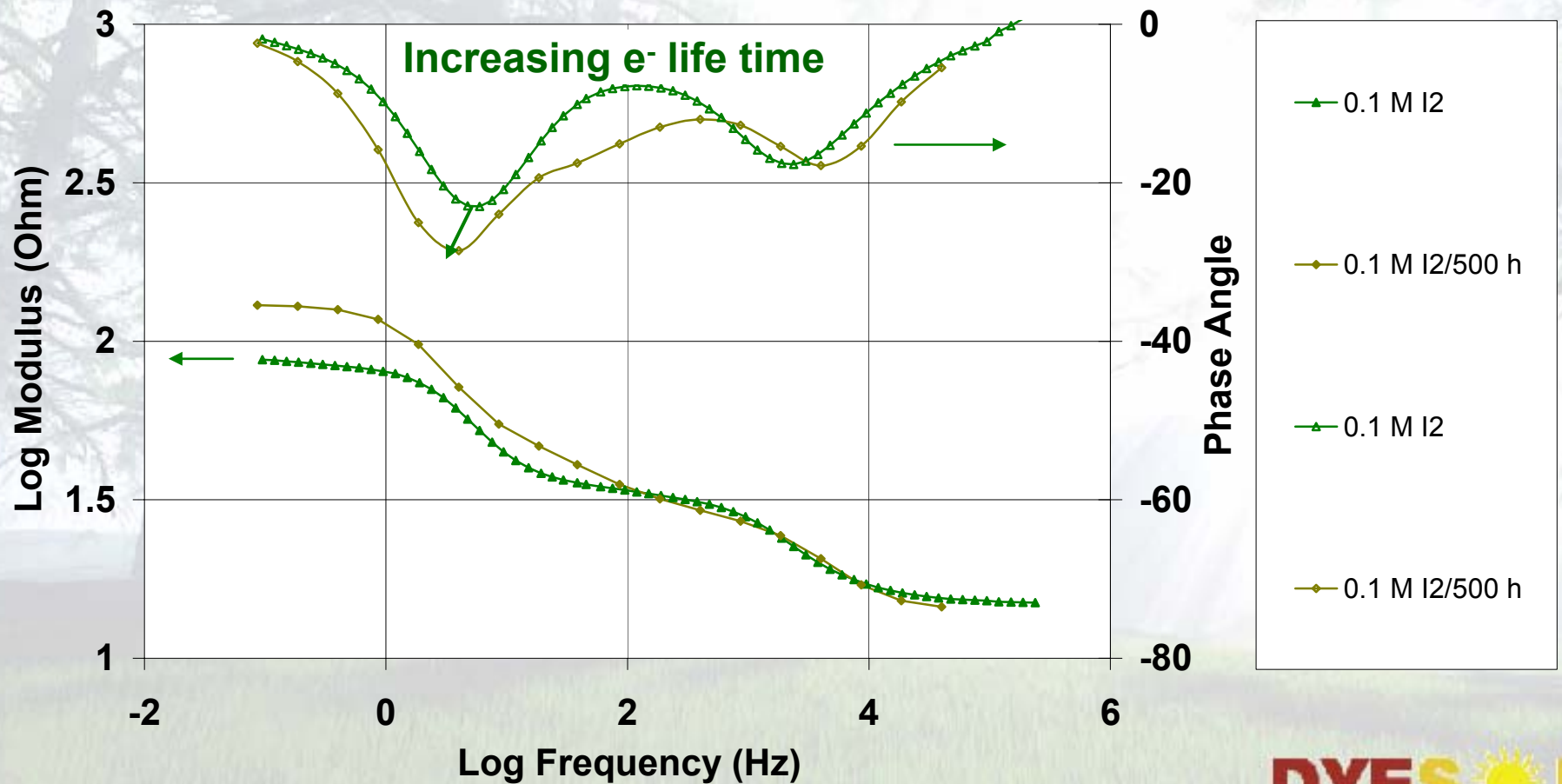


Nyquist plots of test cells
MPN/GuSCN - After 500 h sun test



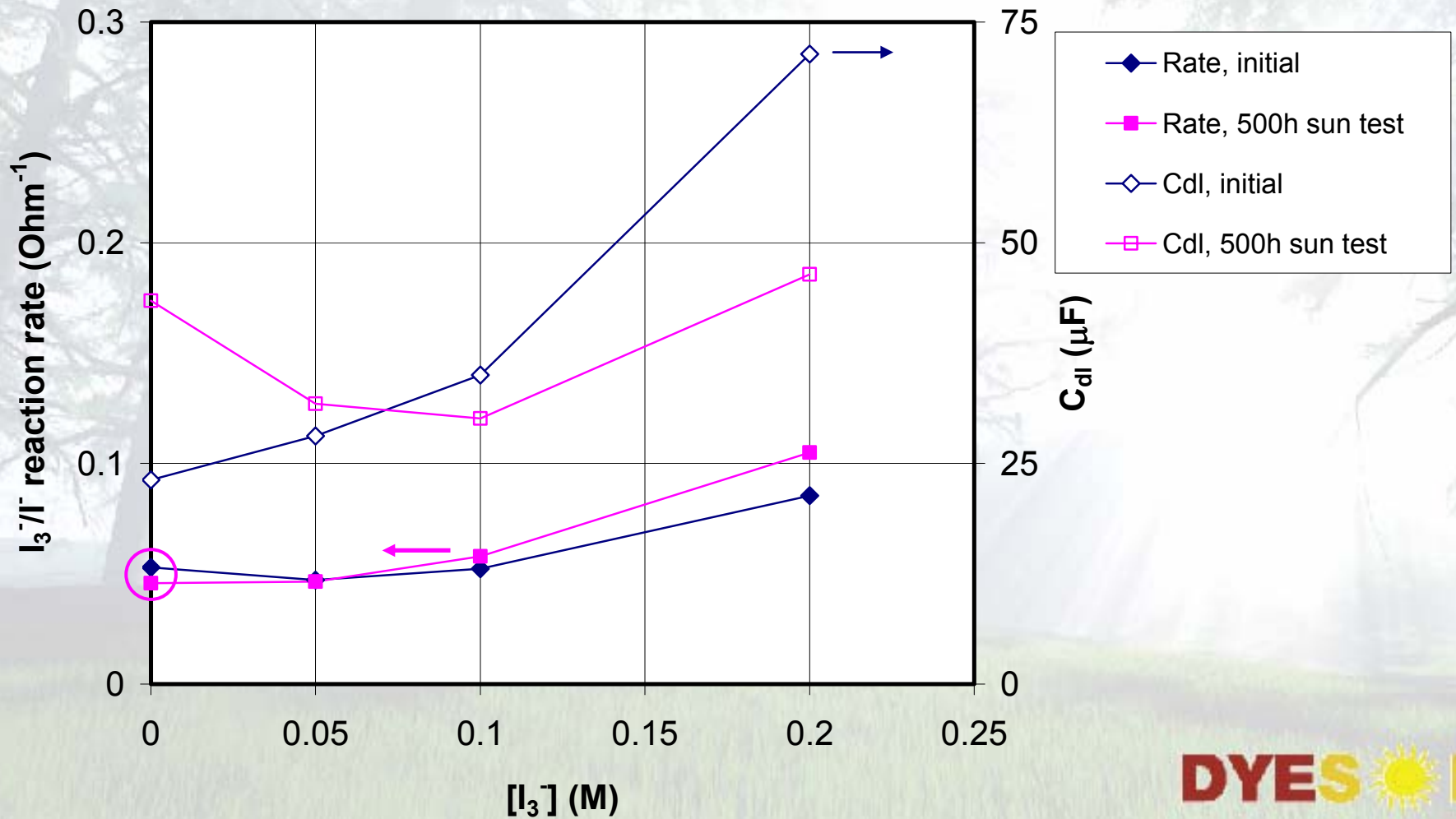
Influence of I_2 concentration

Bode plots of test cells - 0.1 M I_2
Initial Data vs after 500 h sun test



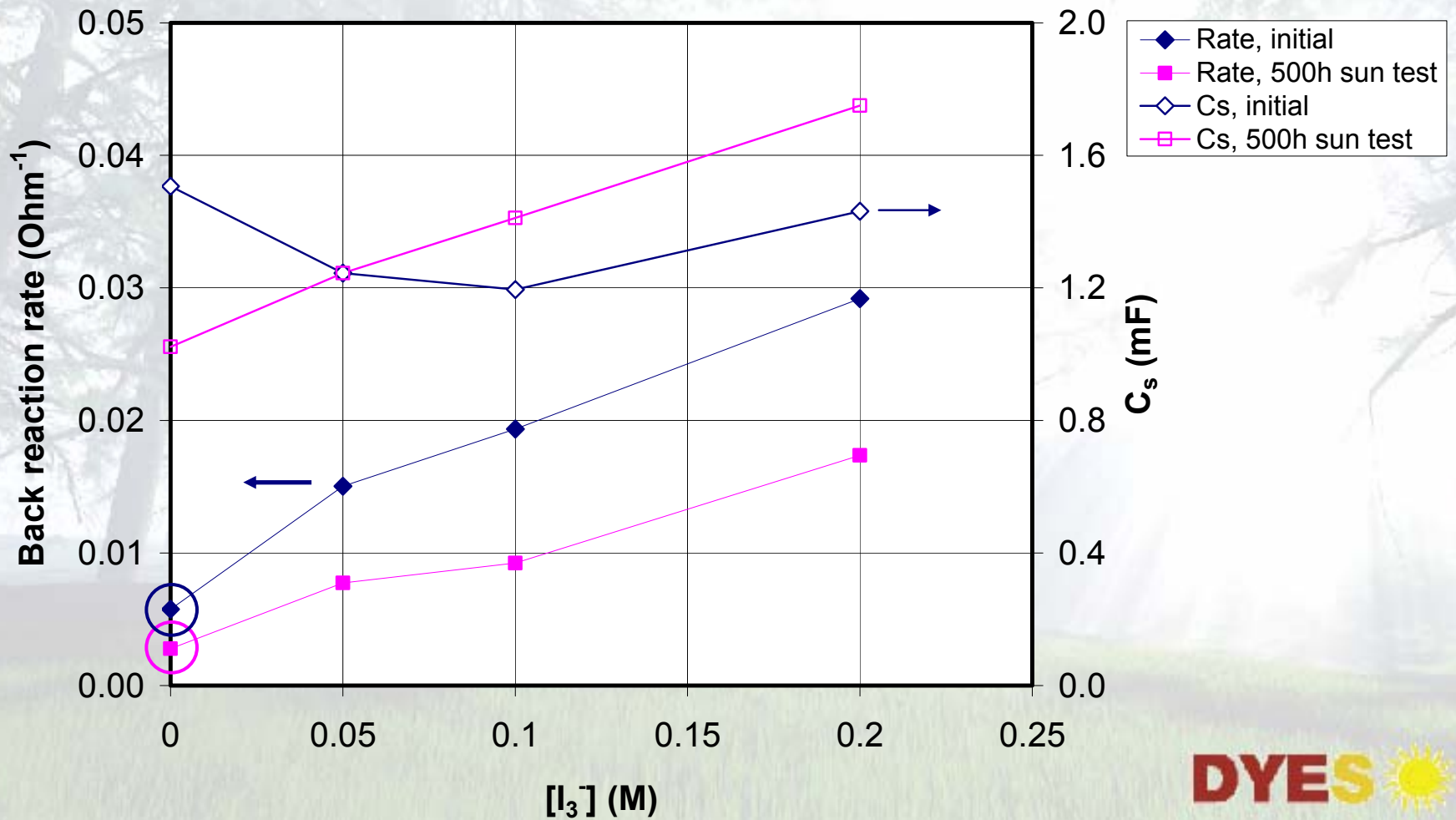
Influence of I_2 concentration

Initial CE(Pt) data vs 500h sun test
MPN-GuSCN



Influence of I_2 concentration

Initial TiO_2 data vs 500h sun test
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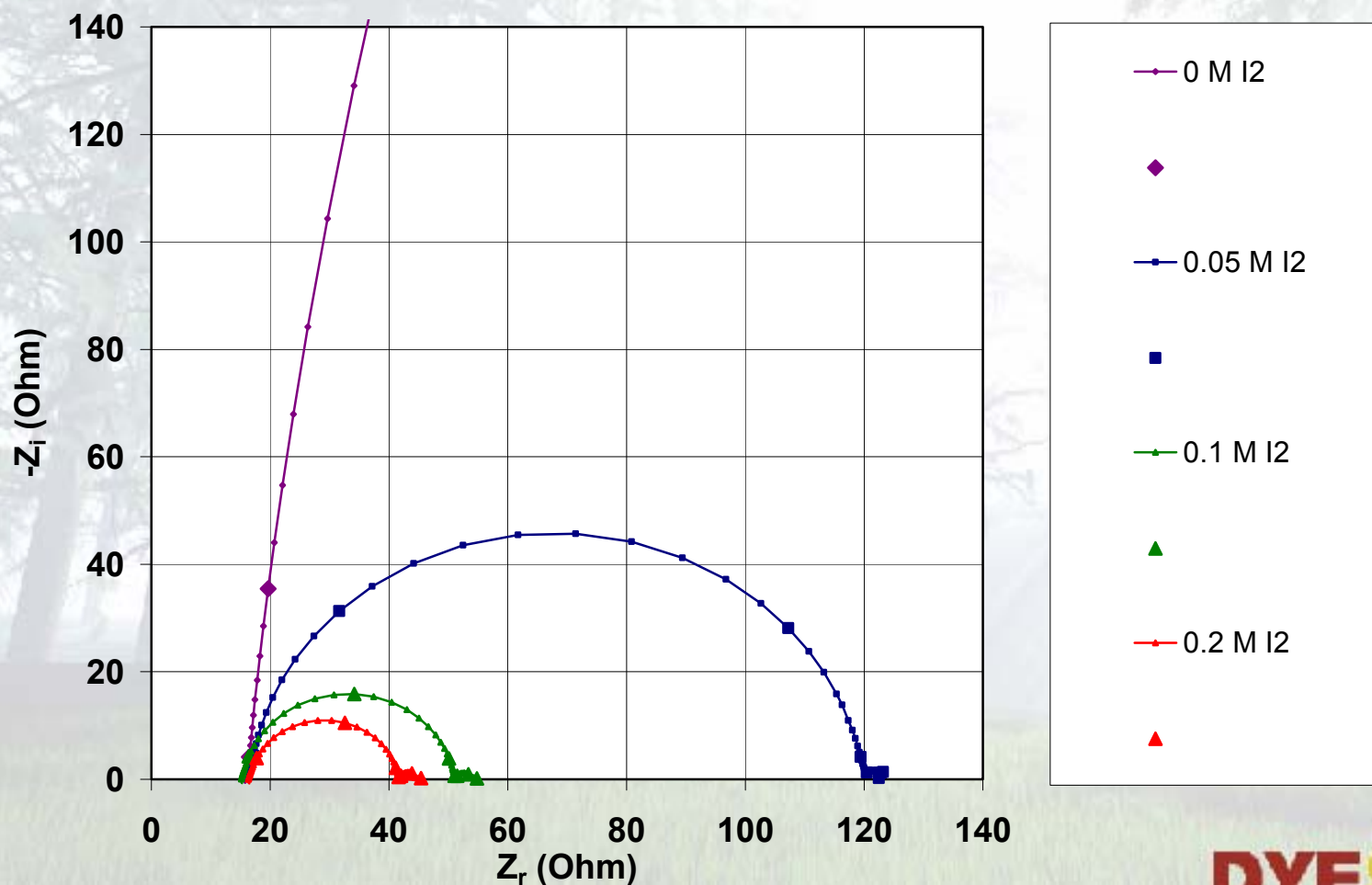
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Redox species responsible for zero I_2 effects ???

Influence of I_2 concentration on symmetrical Pt-Pt cells

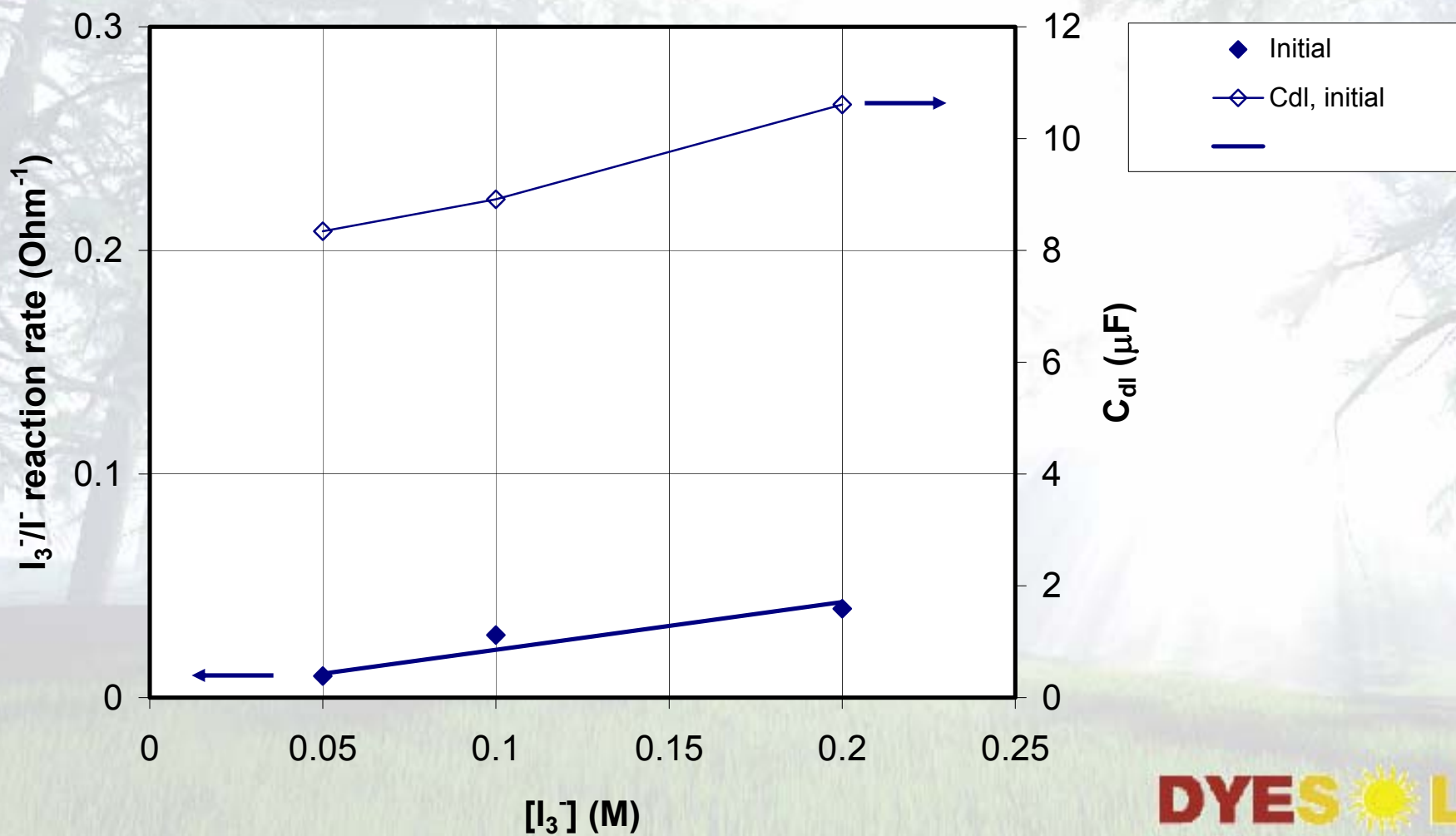
Nyquist plots of Pt-Pt cells

Initial



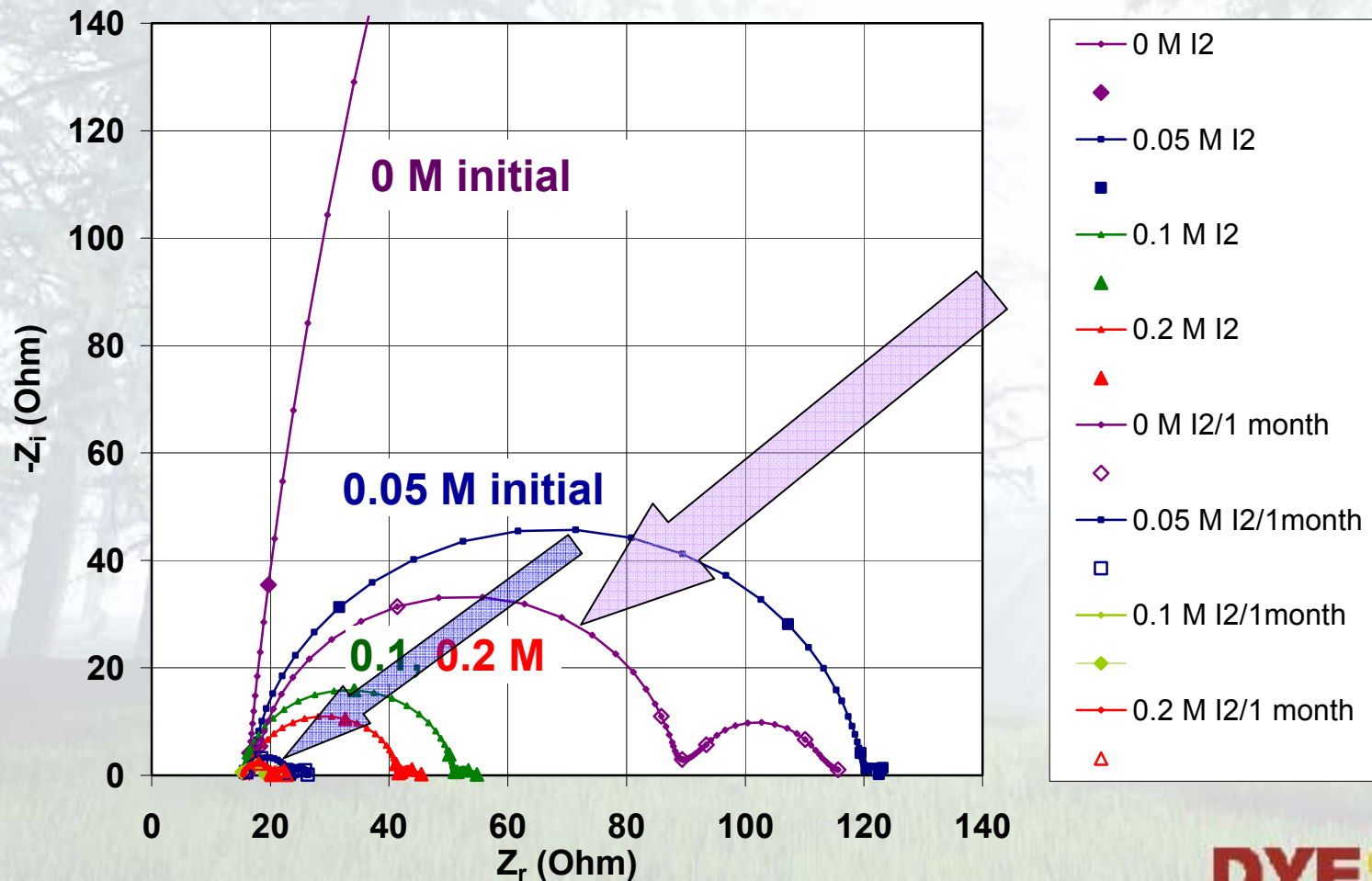
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Pt-Pt cells. Initial data



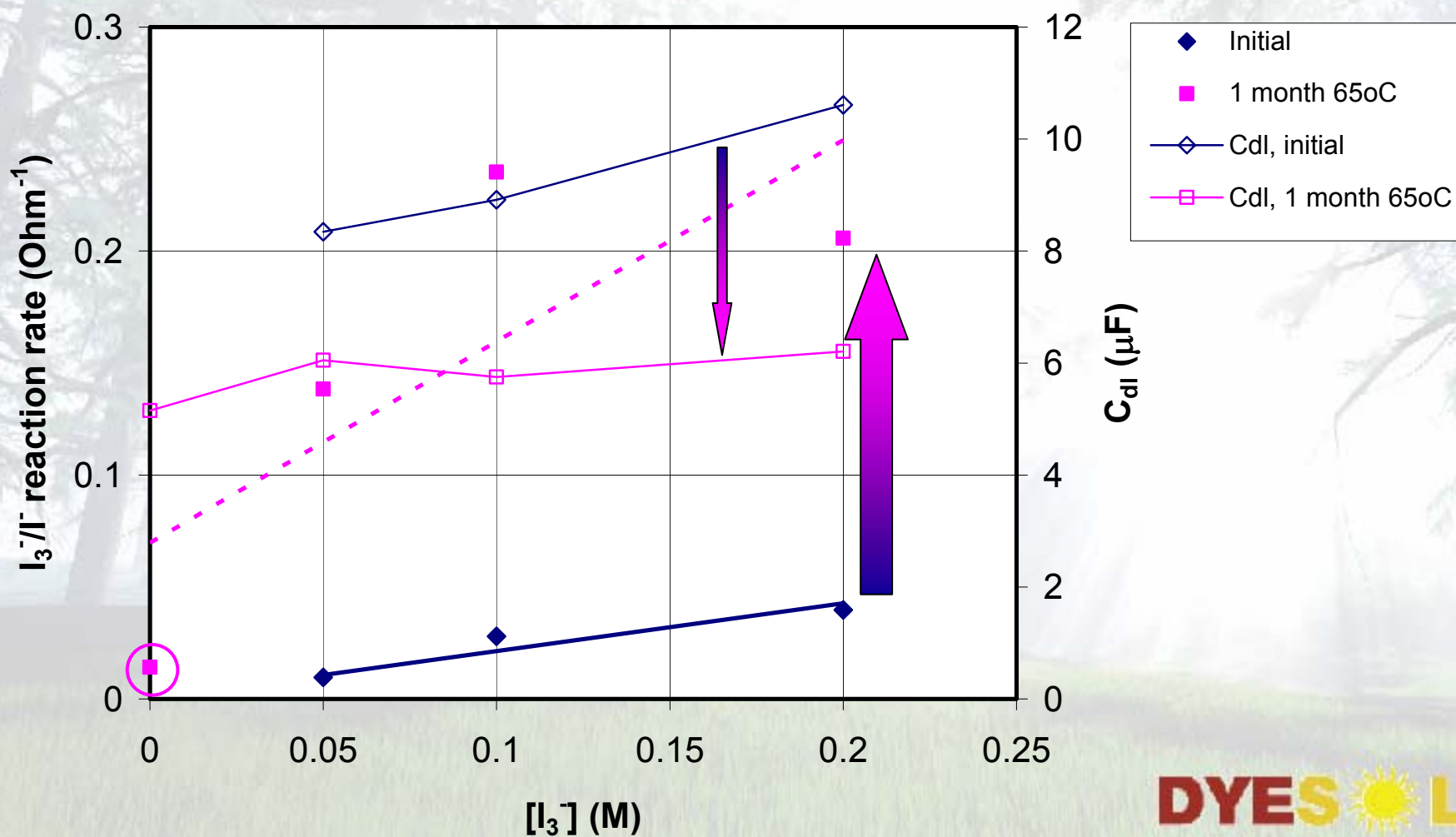
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Nyquist plots of Pt-Pt cells
Initial and after 1 month at 65°C



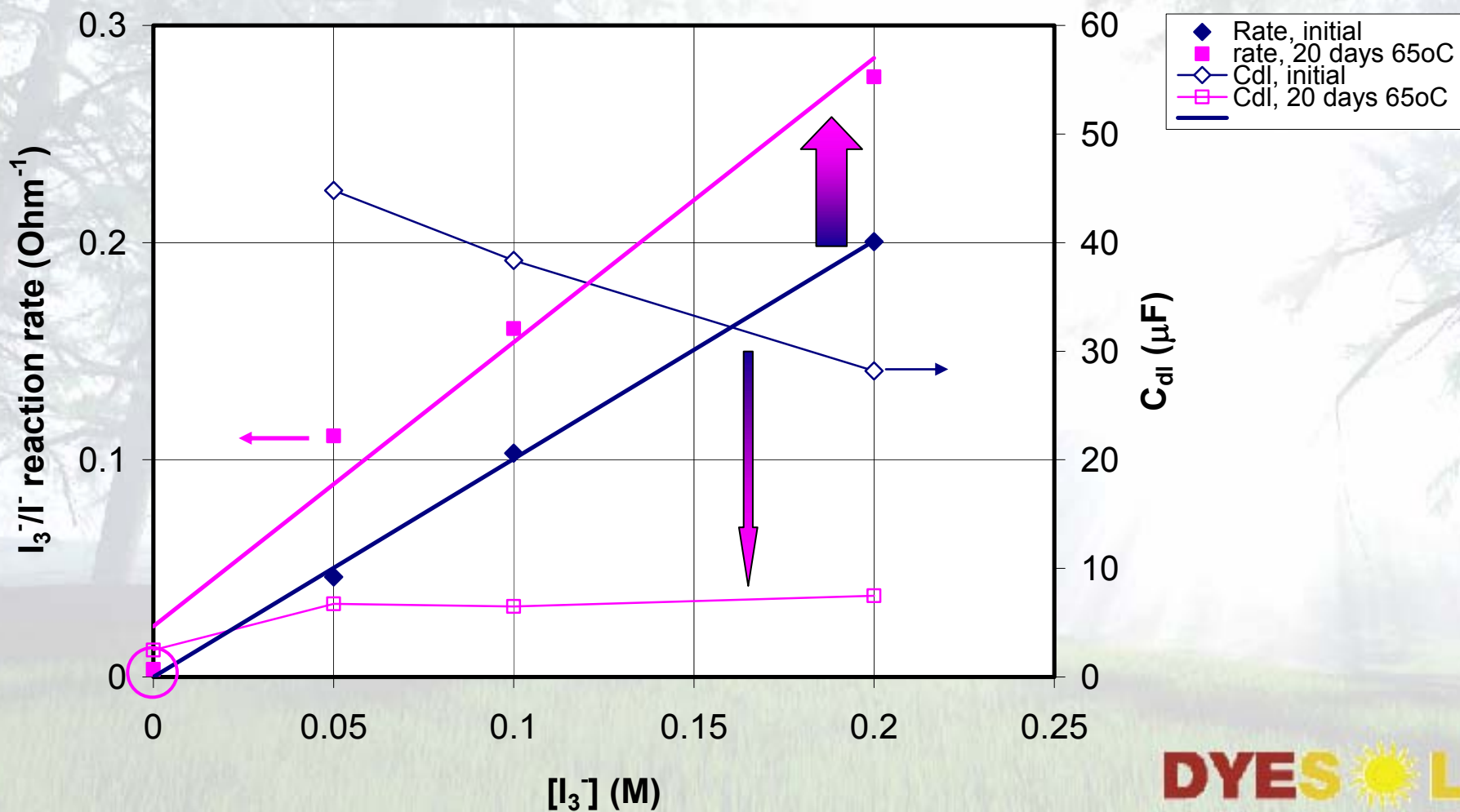
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Pt-Pt cells. Initial data vs 1 month 65°C



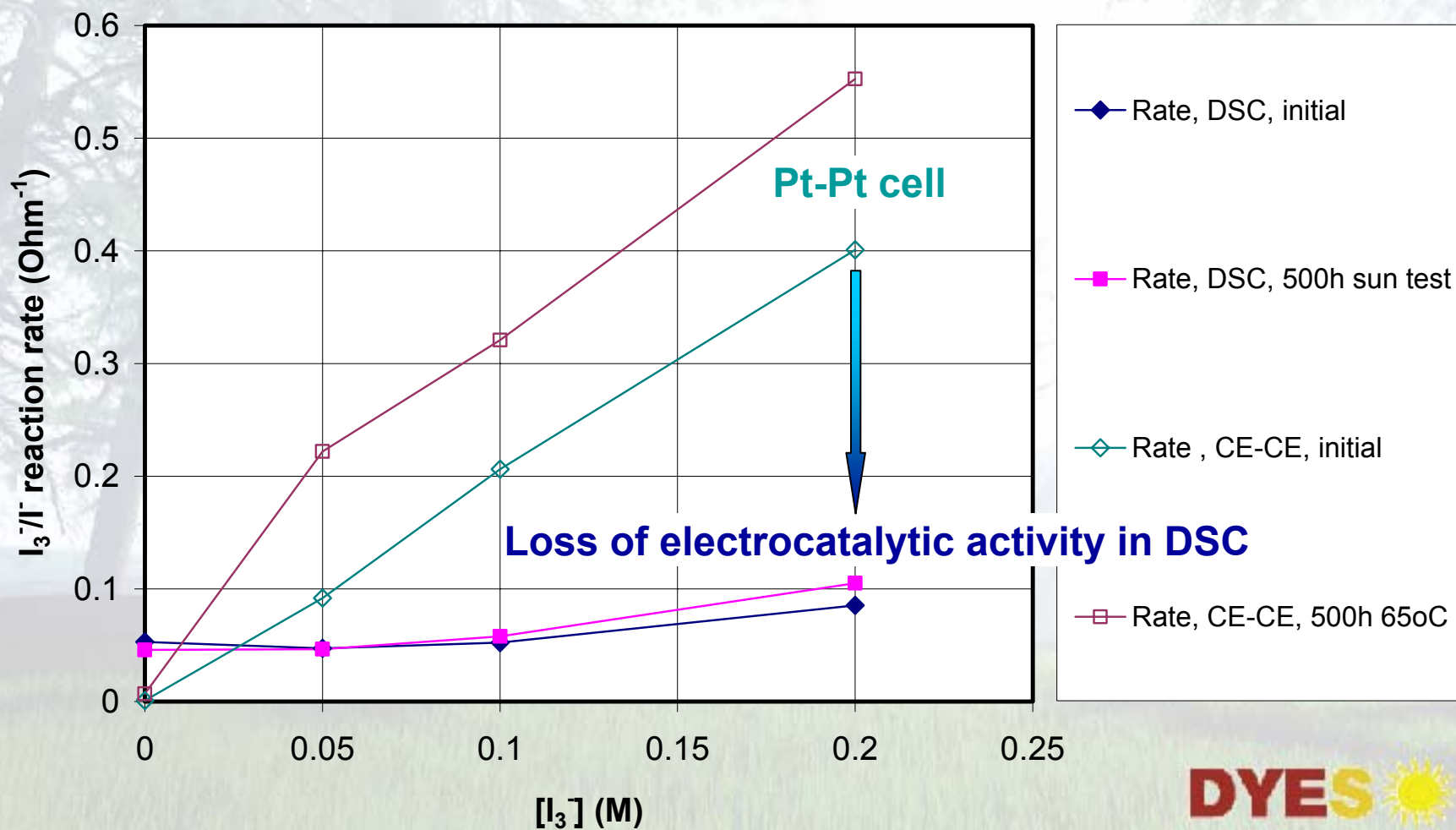
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Pt-Pt cells - Initial data vs 20d 65°C



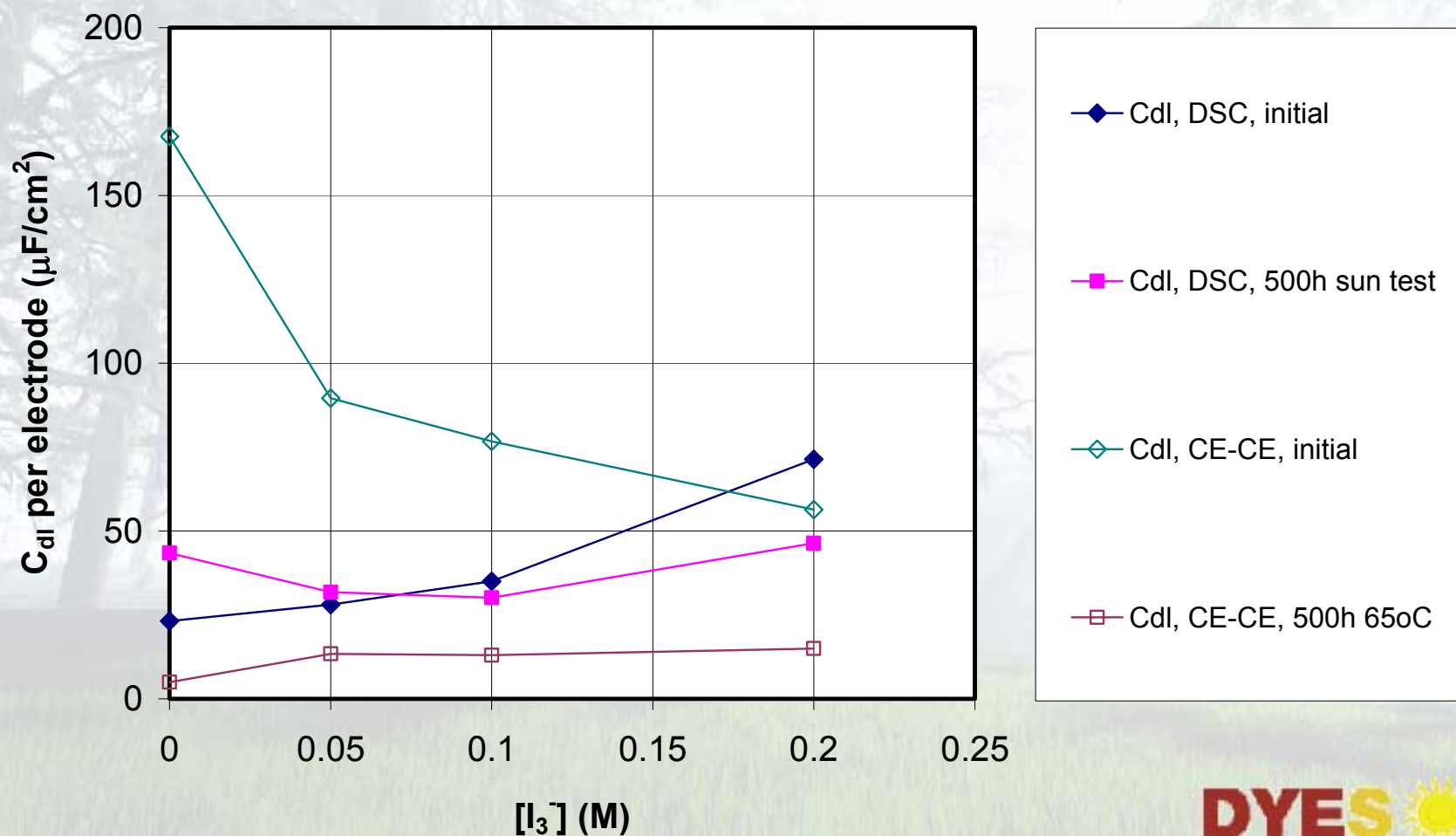
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DSC vs Pt-Pt symmetrical cell
Rate per electrode. MPN-GuSCN



Influence of I_2 concentration on symmetrical Pt-Pt cells


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 C_{dl} per electrode. MPN-GuSCN





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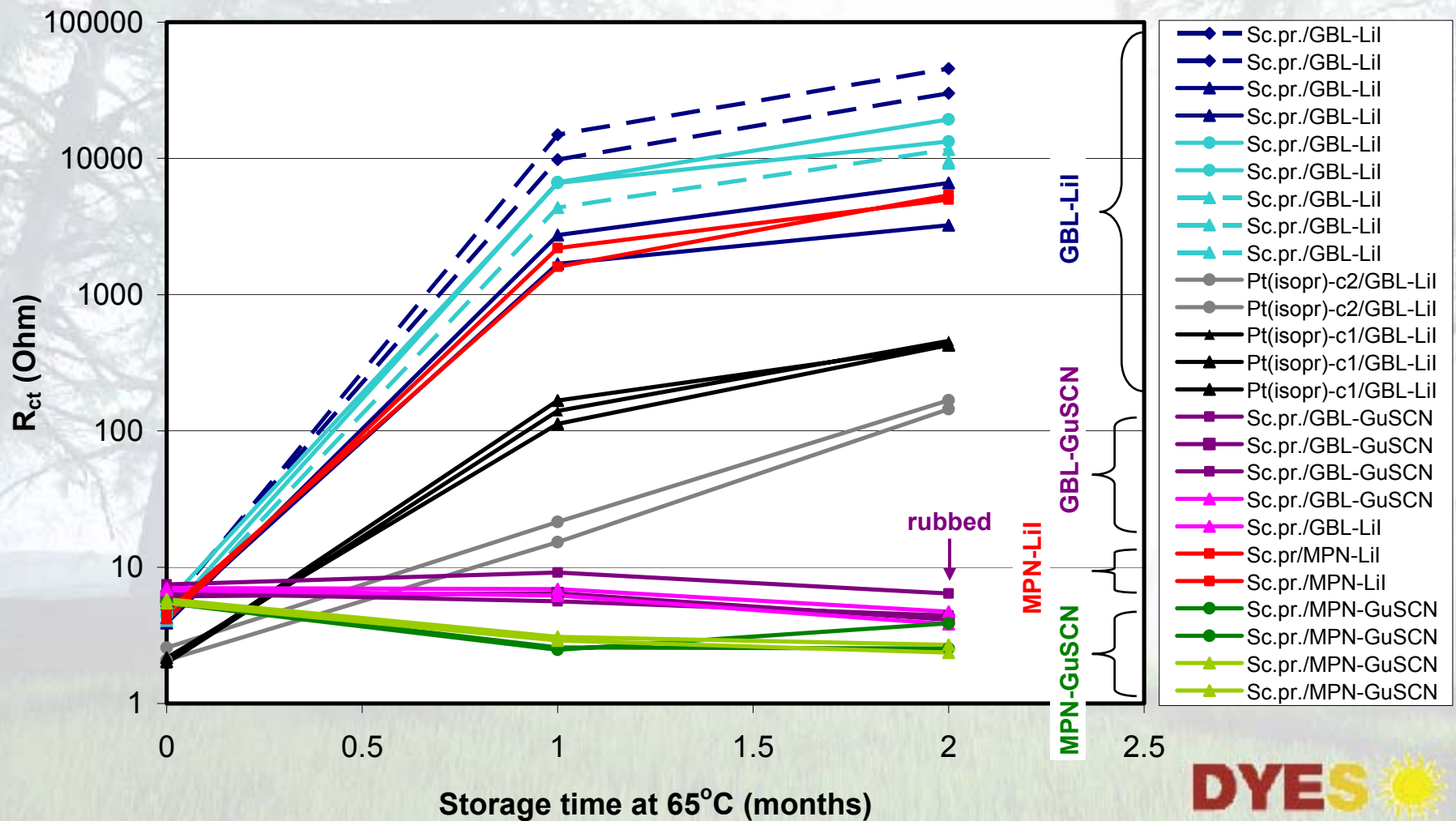


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- R_{ct} is ~ 4 times higher in DSCs than in symmetrical Pt-Pt cells (for $0.2 \text{ M } I_2$)

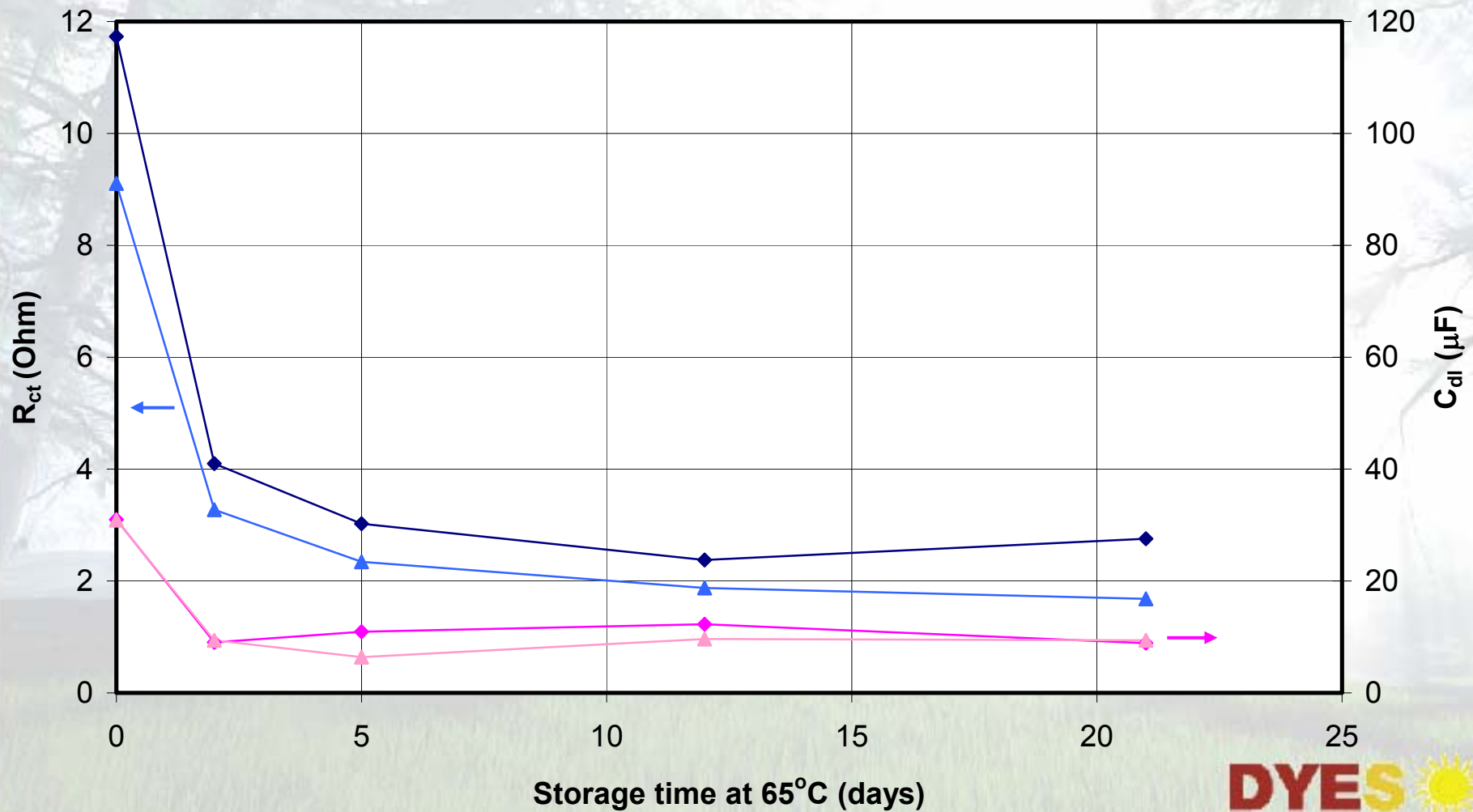
Influence of electrolyte composition on stability of Pt-Pt cells


Symmetrical Pt-Pt cells, stored at 65°C



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Symmetrical Pt-Pt cells, MPN-GuSCN, stored at 65°C.





Influence of electrolyte on symmetrical Pt-Pt cells

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GBL-Lil (sc.pr.) \sim MPN-Lil (sc.pr.) \gg GBL-Lil (Pt-isopr.)
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- There are many complex chemical effects at play in DSCs. Lil **increases $R_{ct}(\text{Pt})$ of Pt-Pt cells** upon 65°C storage and **decreases $R_{ct}(\text{Pt})$ in DSCs**, particularly when illuminated. This indicates that the dyed TiO_2 surface is responsible for the creation of some redox-active species through desorption (dye?) or a chemical process.



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- **There is a complex chemistry at play at the TiO_2 as well as at the Pt interface, depending on electrolyte composition, surface treatment, illumination, etc.**
- **Understanding the mechanistic effect of impurities and additives on performance and long term stability is still in its infancy.**
- **There are indications of a significant involvement of one or several non- I_3^-/I^- redox couples.**



Acknowledgements

- **Michael Bertoz**
- **Graeme Evans**
- **Paul Moonie**
- **Ravi Harikisun**
- **Paul Murray**
- **Lynne Meredith**