



DEGRADACIÓN DE BATERÍAS

Dra. Erika Teliz

A complex network diagram with nodes of various sizes and colors (dark blue, light grey, yellow) connected by thin lines. The background is a light purple gradient with faint circular patterns.

Modos de degradación

Técnicas y resultados

Técnicas dinámicas y estudios termodinámicos

Ensayos de capacidad

V_{gen} y V_{app} y efecto de I

Ensayos a potencial de circuito abierto

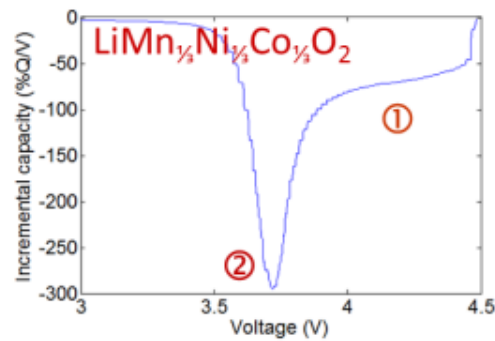
- GITT
- Ciclado a baja velocidad y pseudo OCV.
- EMF

Espectroscopía de impedancia electroquímica: EIS

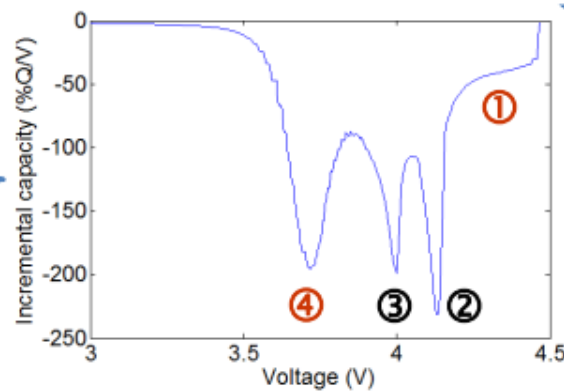
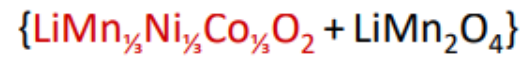
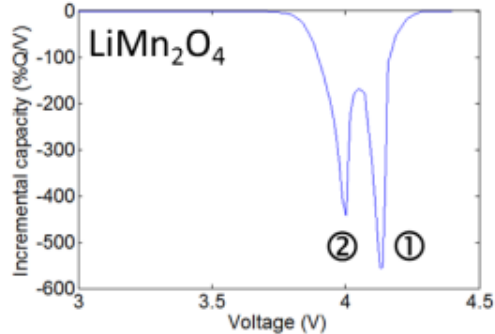
Espectroscopía electroquímica de voltaje: EVS

- IC
- DV

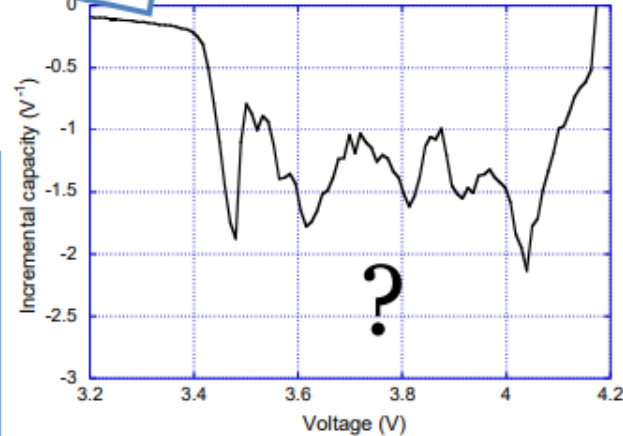
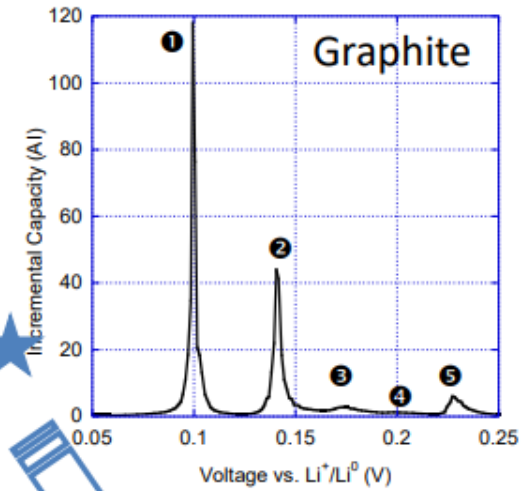
Análisis de capacidad incremental

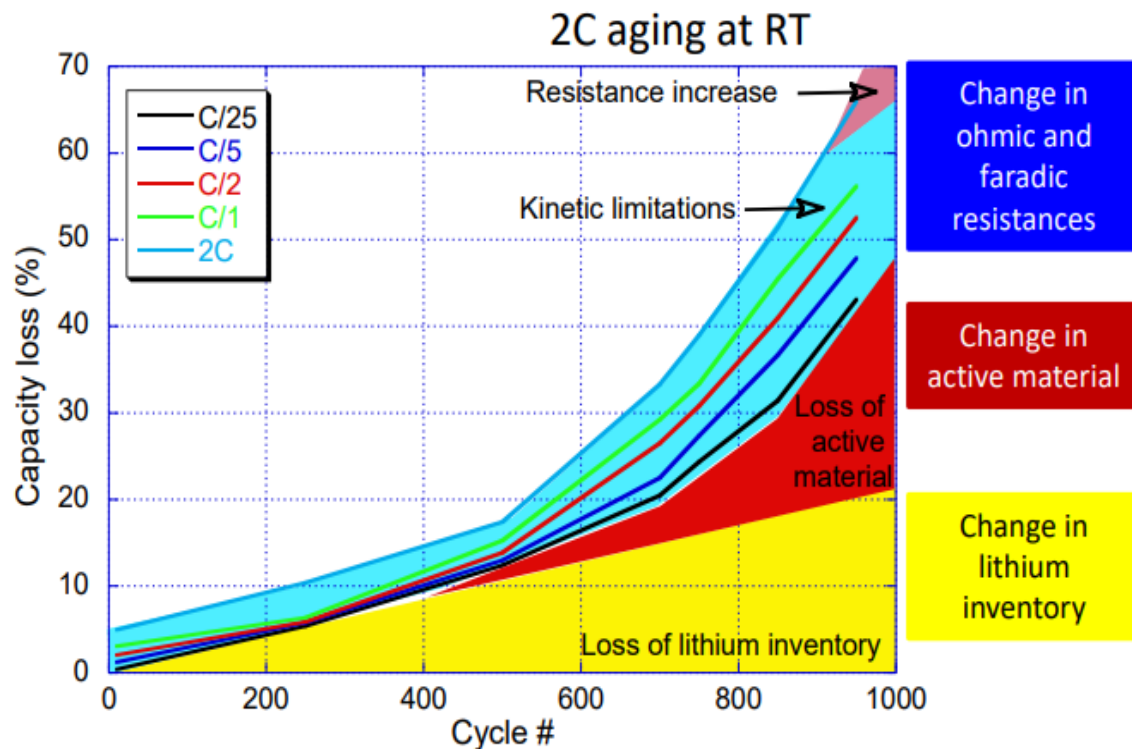
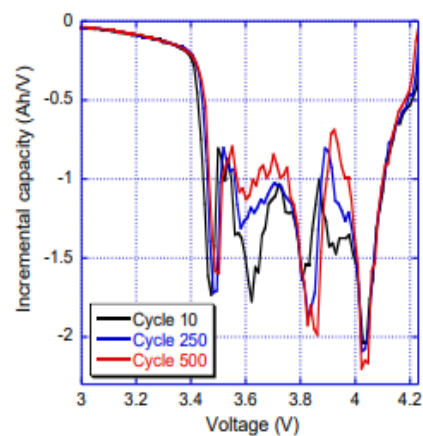


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Configuración de media celda vs celda completa:
Alta complejidad

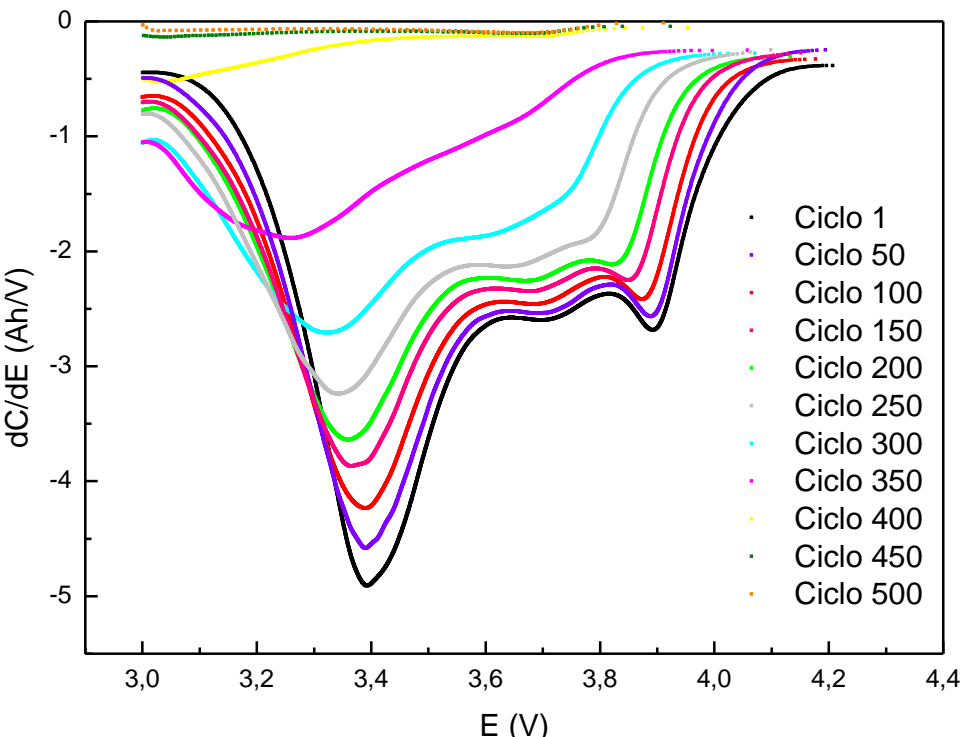




Change in ohmic and faradic resistances

Change in active material

Change in lithium inventory



M. Dubarry et al. *J. Power Sources*, **196** (2011), 10336
M. Dubarry et al. *J. Power Sources*, **196(7)** (2011), 3420
M. Dubarry et al. *J. Power Sources*, **194** (2009), 551

$$Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$

$$|Z(\omega)| = \sqrt{\text{Re}(Z(\omega))^2 + \text{Im}(Z(\omega))^2}$$

$$\phi(\omega) = \tan^{-1} \frac{\text{Re}(Z(\omega))}{\text{Im}(Z(\omega))}$$

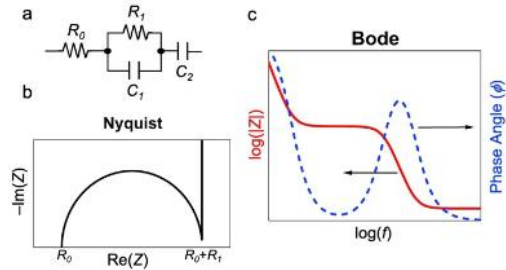
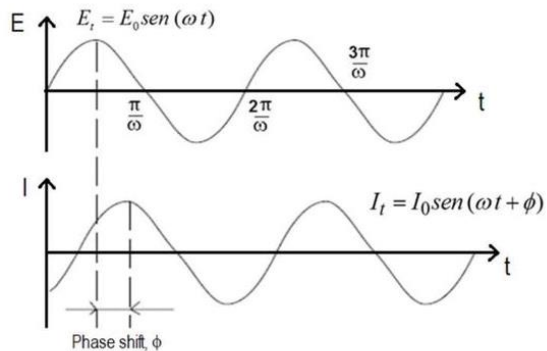
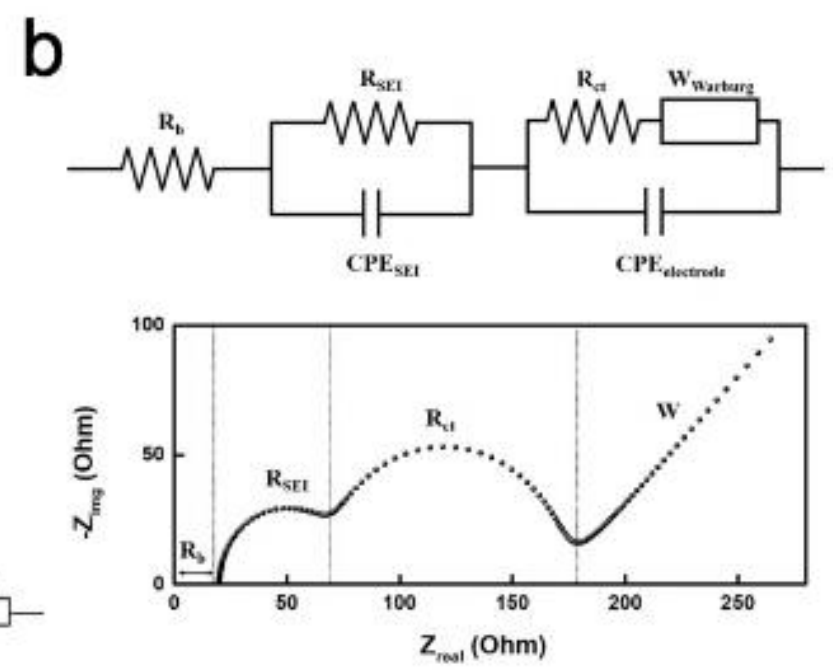
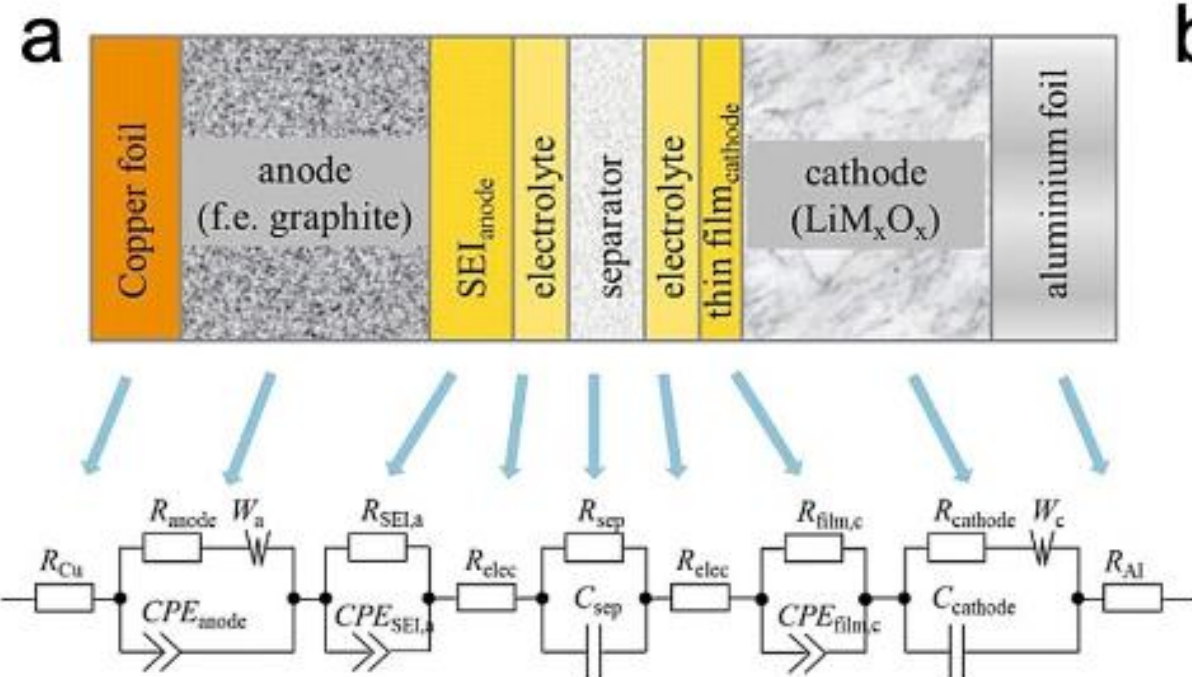
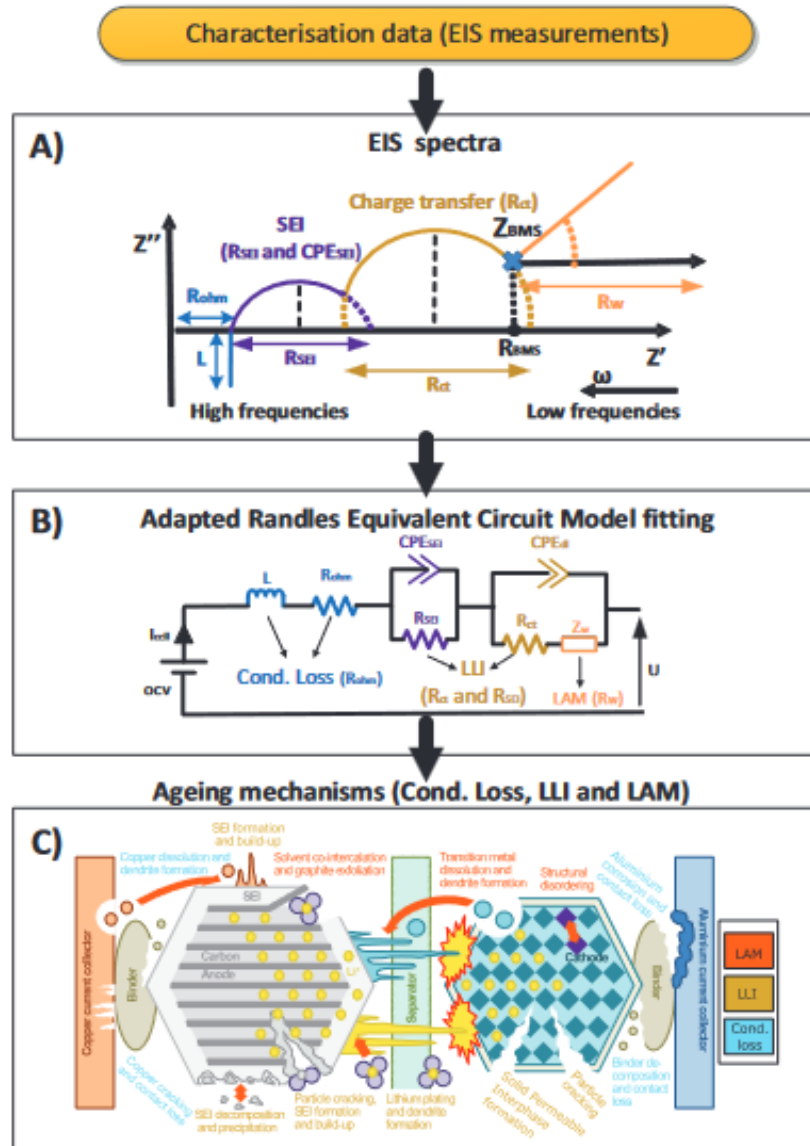


Figure 2. a) Equivalent circuit for single electron transfer and ion migration in the electrolyte. b) Nyquist plot of the real impedance against the imaginary impedance showing the resistance for the electrolyte. c) Bode plot of the magnitude of the impedance and phase angle against frequency.

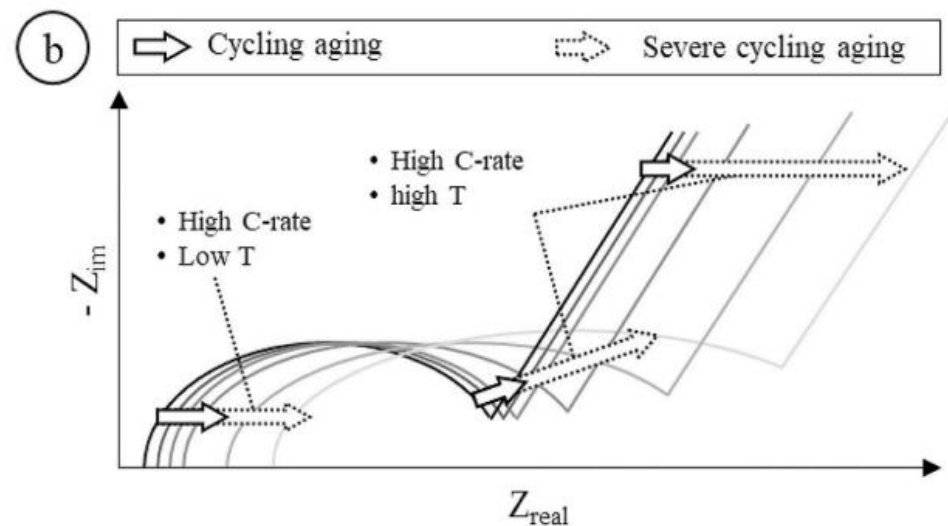
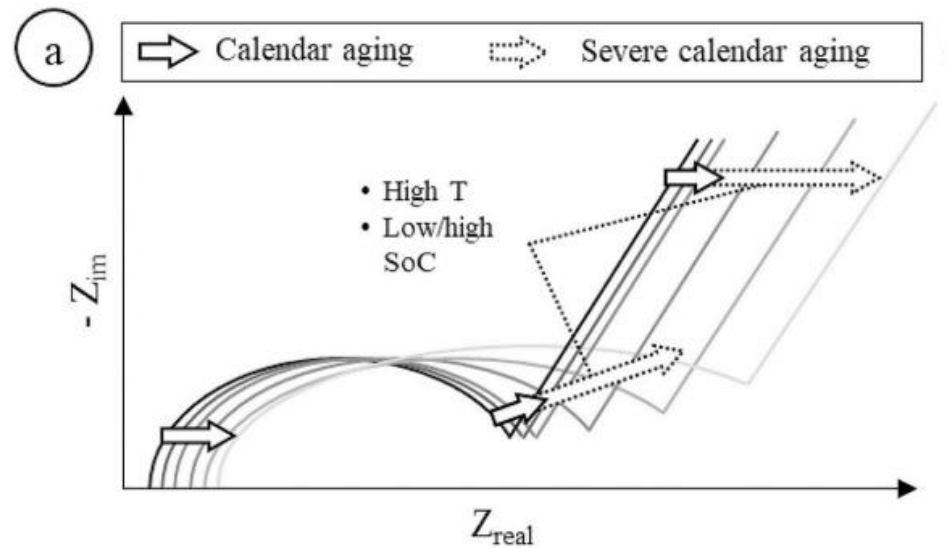
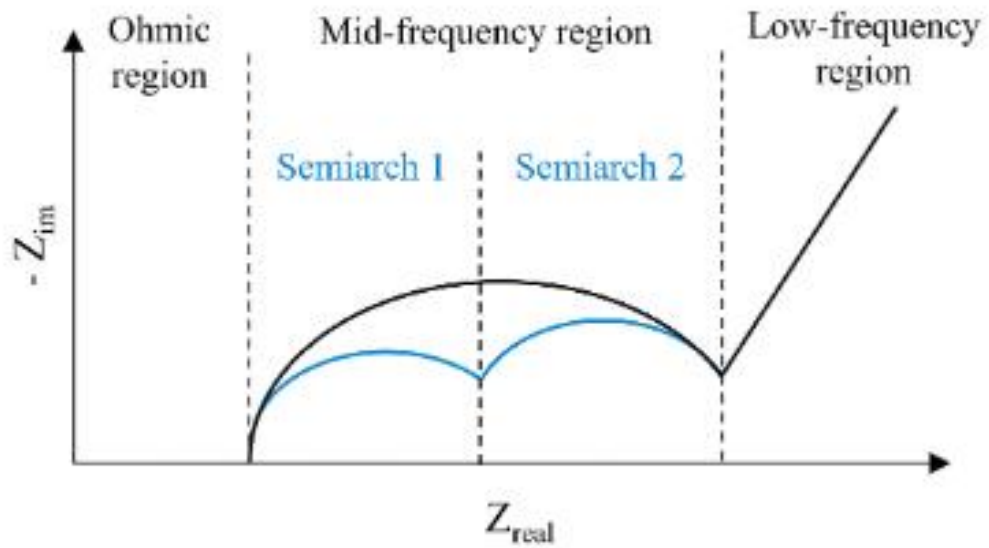
Espectroscopía de Impedancia Electroquímica: EIS







R [Ω]	Ageing mechanism	Ageing mechanism root cause
R_{ohm}	Cond. loss	Copper dissolution dendrite formation. Copper cracking and contact loss. Aluminium corrosion and contact loss. Binder decomposition and contact loss.
R_{SEI} and R_{ct}	LLI	SEI formation and build-up. SEI decomposition and precipitation. Solid permeable interphase formation. Particle cracking, pore clogging and particle disconnection.
R_w	LAM	Solvent co-intercalation and graphite exfoliation. Transition metal dissolution and dendrite formation. Structural disordering.

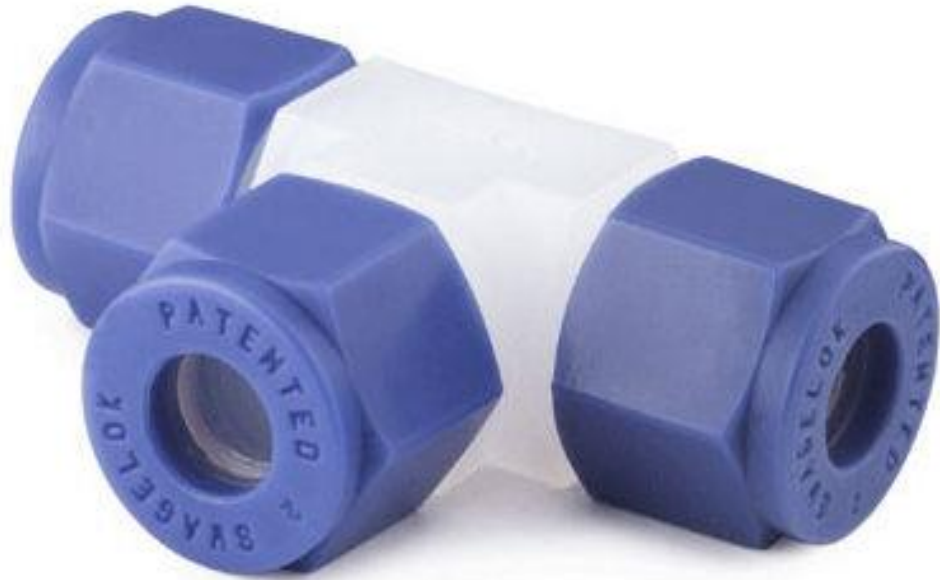




Algunos resultados

Celdas a escala de laboratorio LFP

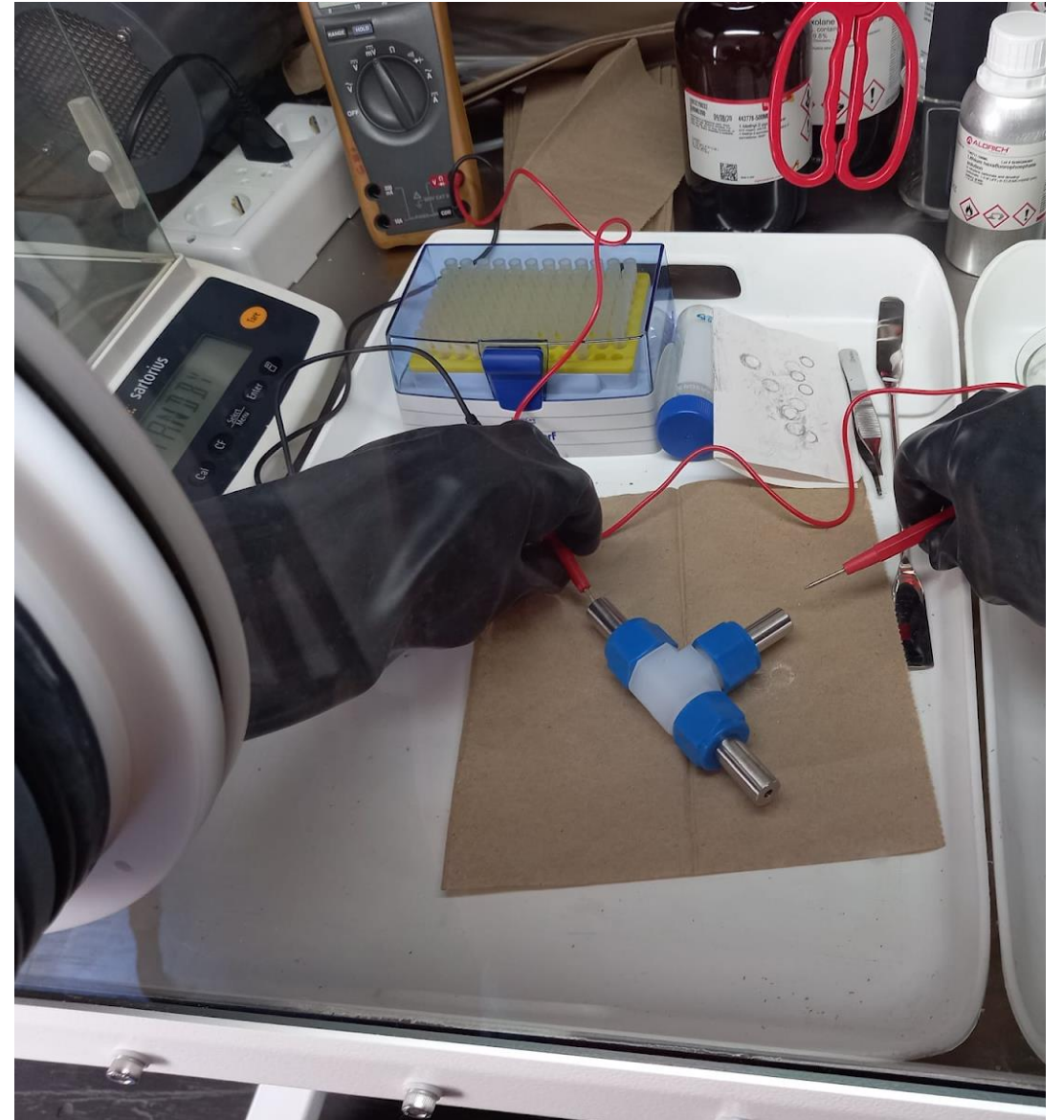
Baterías 18650 NMC



Desarrollo de nuevos materiales catódicos para baterías secundarias: ion-Litio

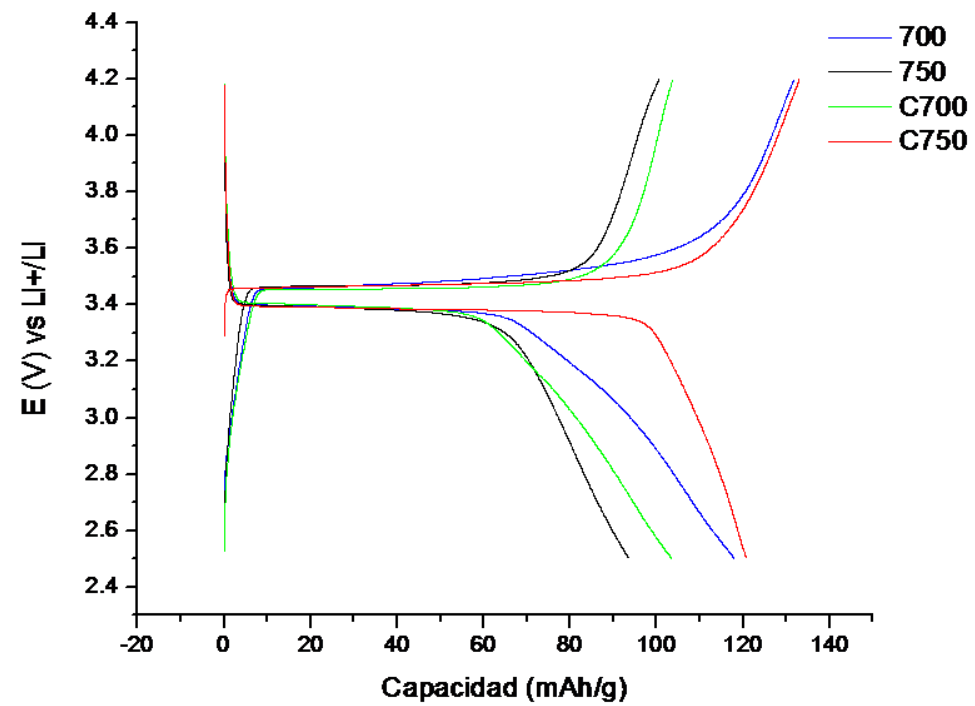
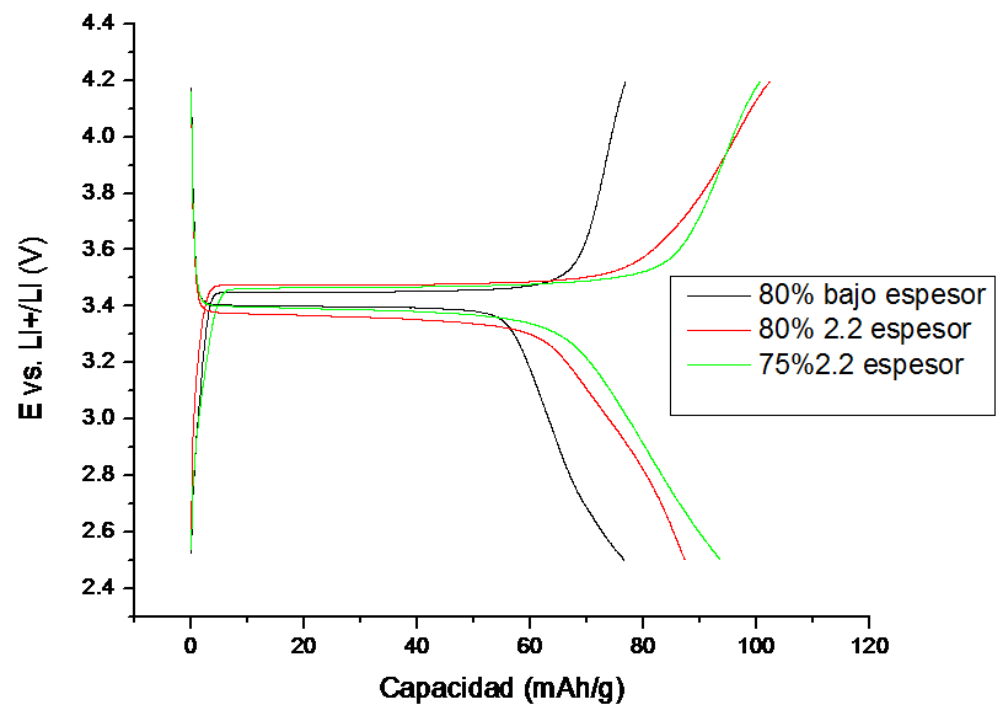
Para realizar la caracterización electroquímica se preparó una tinta mezclando la muestra de olivina sintetizada previamente con carbón y PDVF. La mezcla es pintada sobre una hoja de aluminio y secada en horno de vacío. De esta forma se obtiene el electrodo de trabajo. Como contra electrodo se utilizó litio metálico.

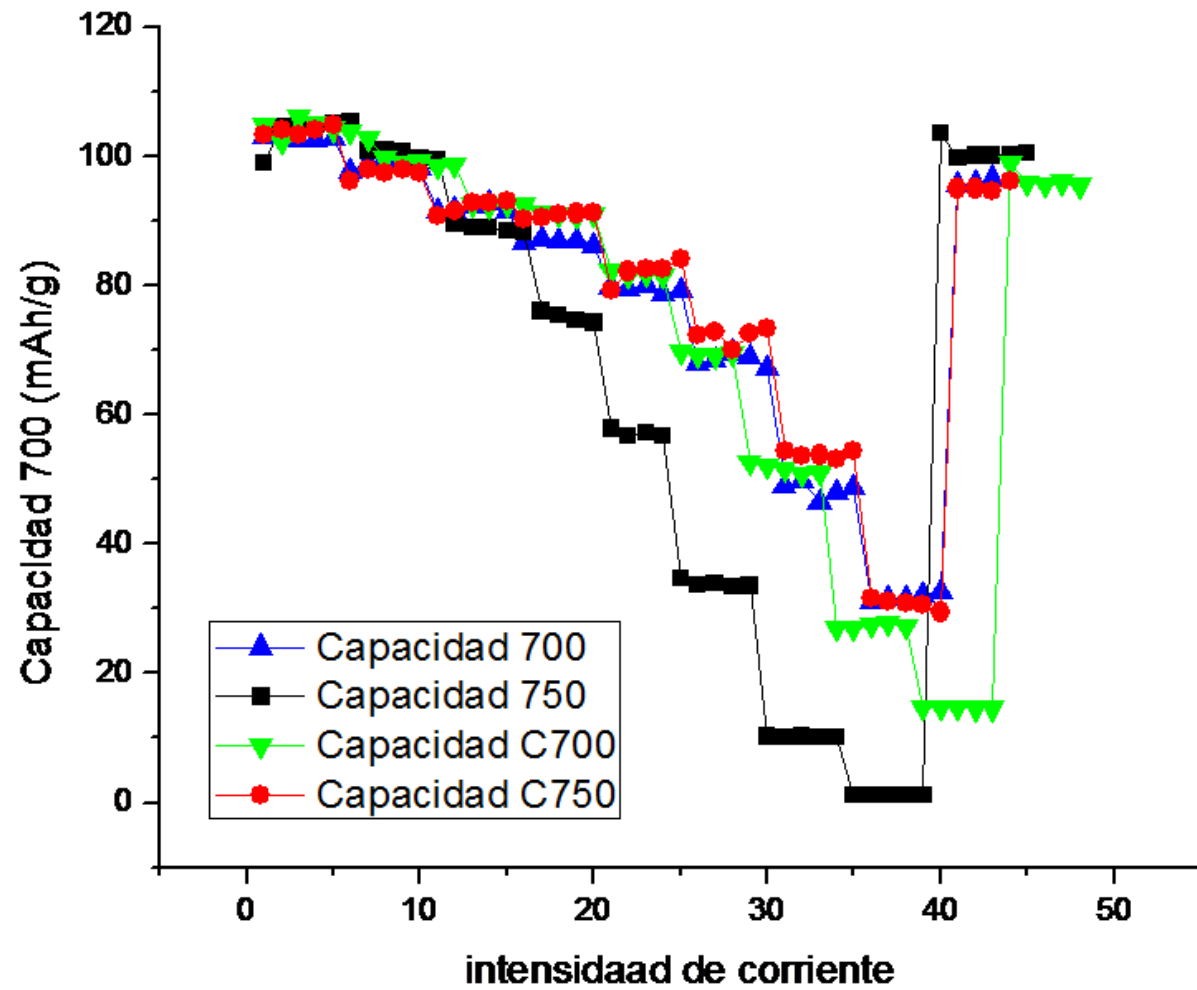
- **Electrodo de trabajo:** LiFePO_4
- **Contraelectrodo y referencia:** Litio metálico
- **Electrolito:** 1M de LiPF_6 en 1:1 (V:V) de EC:DMC
- **Separador:** Lana de vidrio





Equipamiento de laboratorio





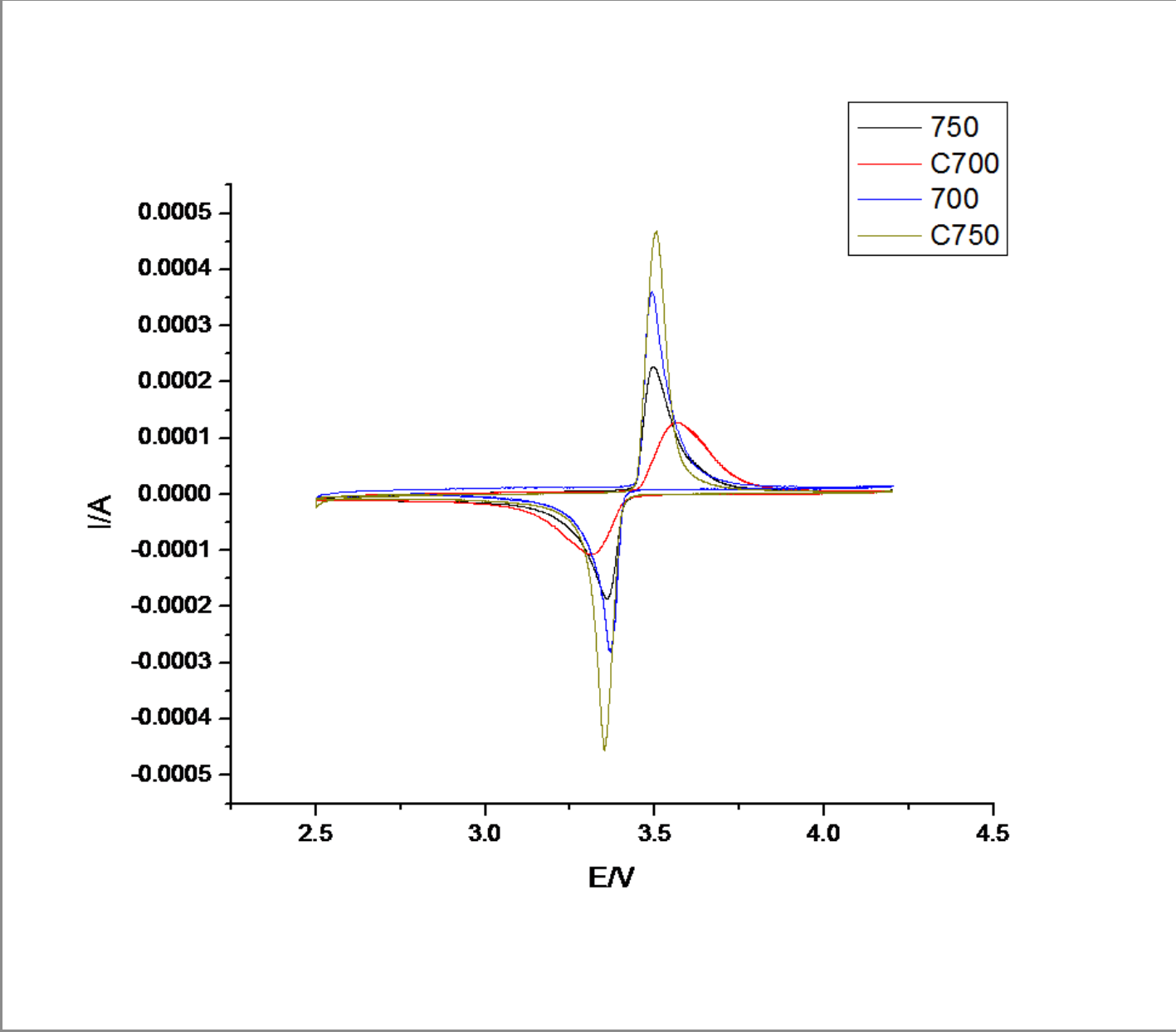
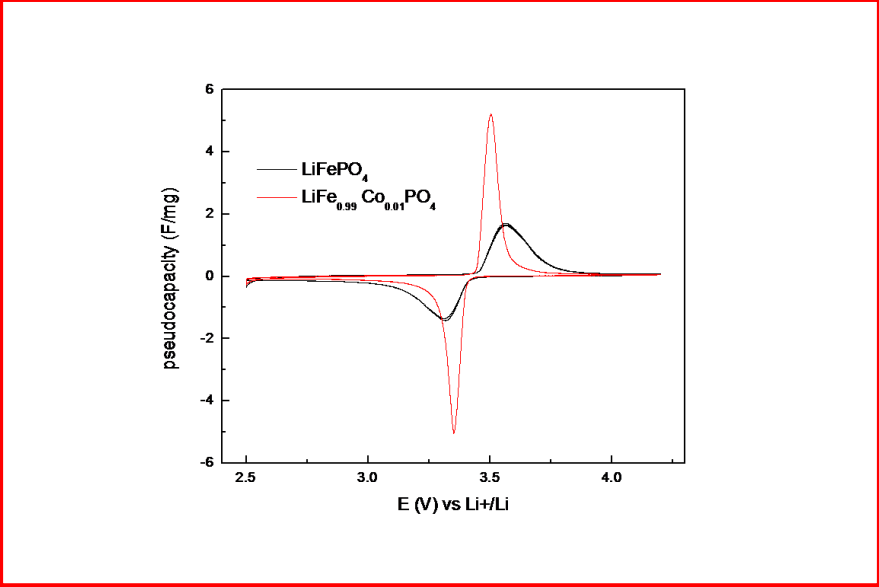
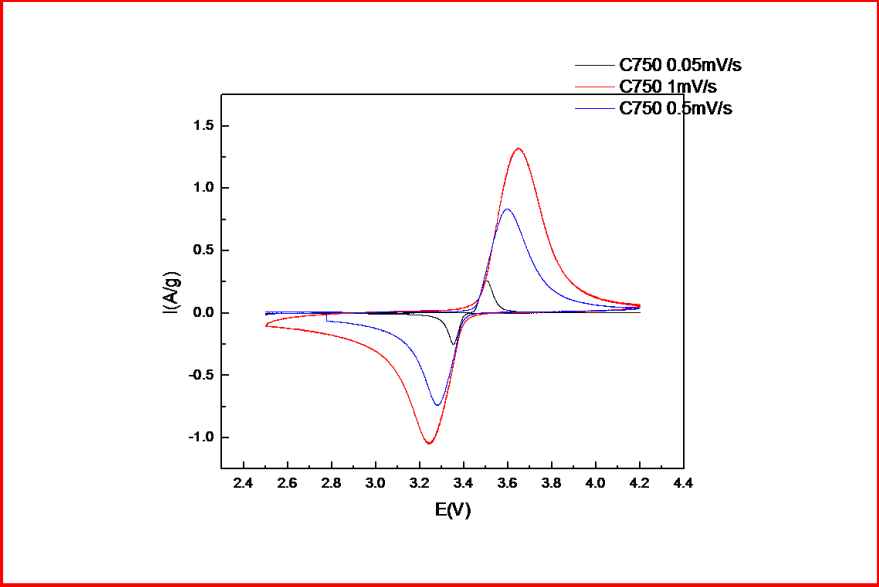


Table 3 Capacity (C), coulombic efficiency (C.E.), and $AD^{1/2}$ (anodic and cathodic) parameters from Randles-Sevcik equation

Sample	C (mAh g ⁻¹)	C.E. (%)	$AD^{1/2}$ (cm ³ s ^{-1/2})	$AD_{cat}^{1/2}$ (cm ³ s ^{-1/2})
LiFePO ₄	90	93	2.9×10^{-6}	2.6×10^{-6}
LiFe _{0.99} Co _{0.01} PO ₄	120	91	1.2×10^{-5}	9.6×10^{-6}

$$i_p = 2.69 \times 10^5 n^{3/2} AD^{1/2} C v^{1/2}$$

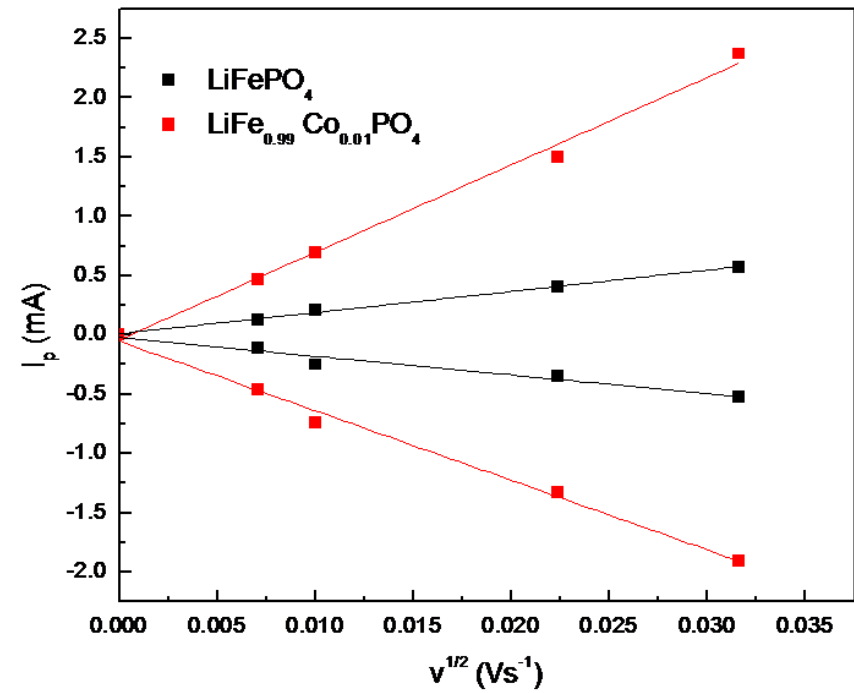
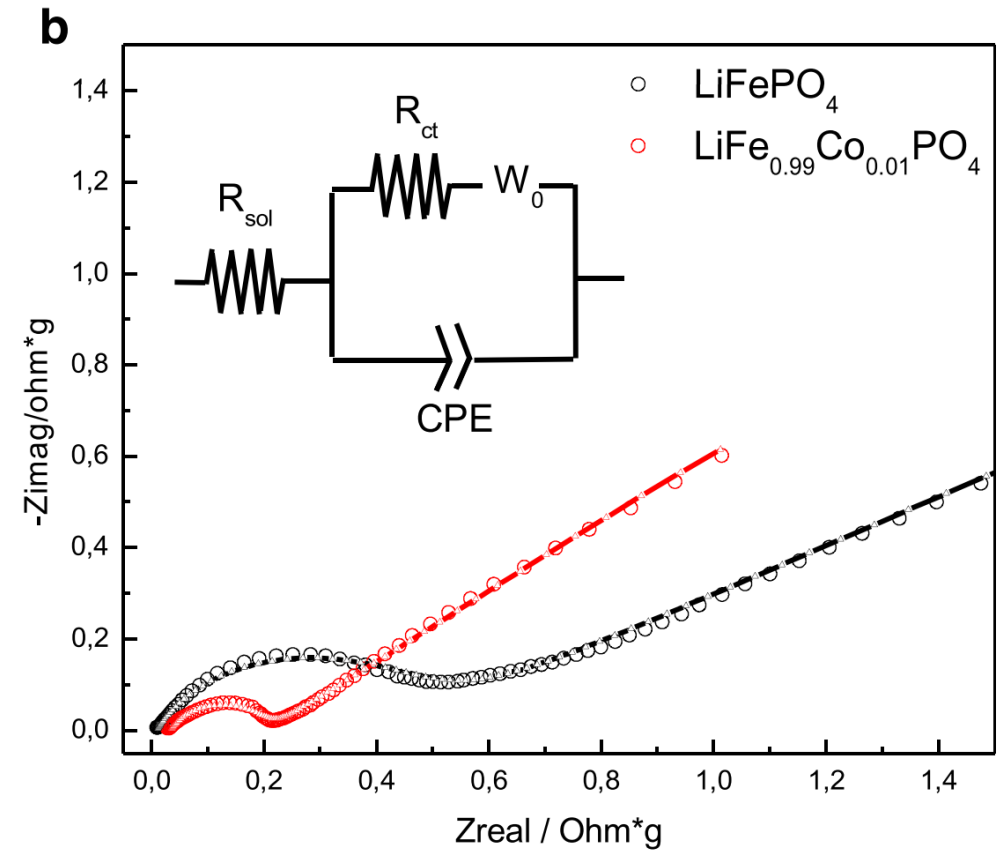


Table 5

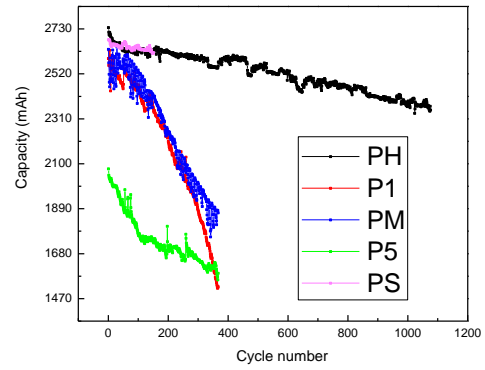
τ_{ct} and σ_w fitting parameters for doped (C700 y C750) and pure (700 y 750) samples at 25%, 50% and 75% SOC.

SOC	700		750		C700		C750	
	τ_{ct} (s)	$\sigma_w^{-0.5}$ ($\Omega \cdot s$)	τ_{ct} (s)	$\sigma_w^{-0.5}$ ($\Omega \cdot s$)	τ_{ct} (s)	$\sigma_w^{-0.5}$ ($\Omega \cdot s$)	τ_{ct} (s)	$\sigma_w^{-0.5}$ ($\Omega \cdot s$)
75%	0.0012	42	0.0017	84	0.0018	82	0.0006	37
50%	0.0013	68	0.0013	139	0.0016	140	0.0006	47
25%	0.0011	84	0.0010	213	0.0013	232	0.0005	68

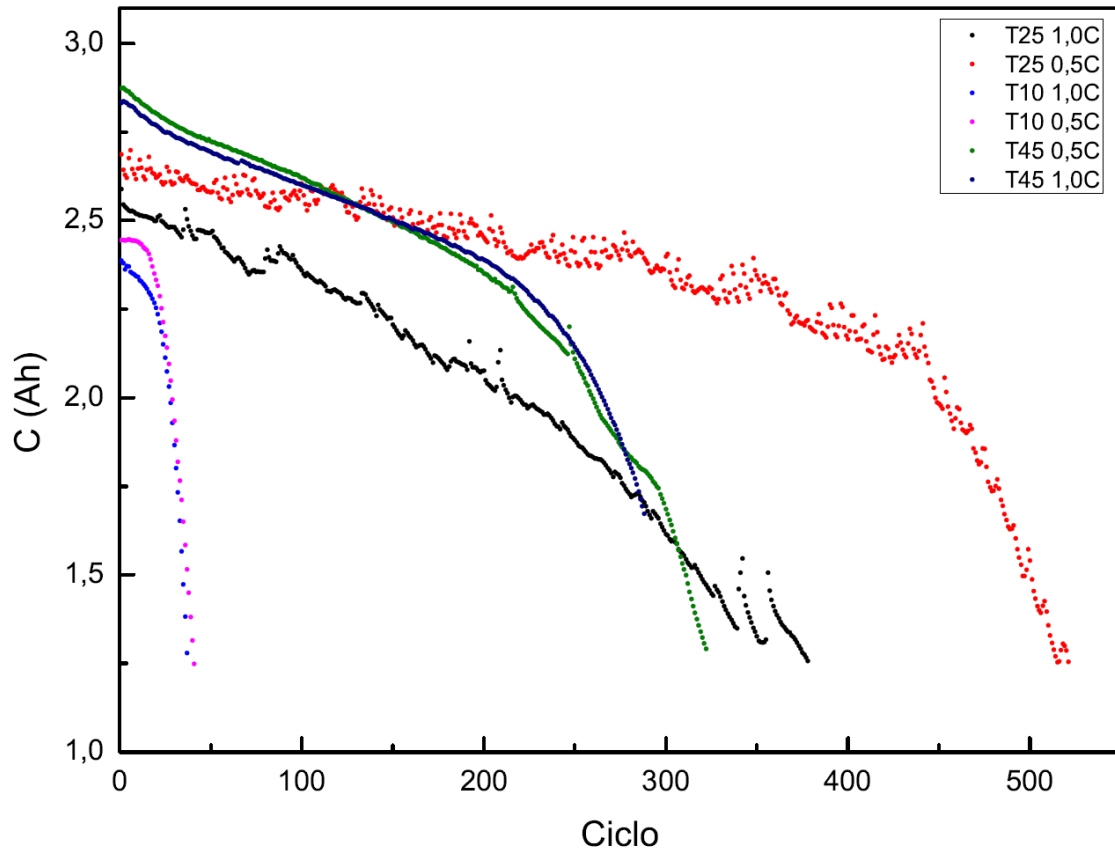




Baterias comerciales



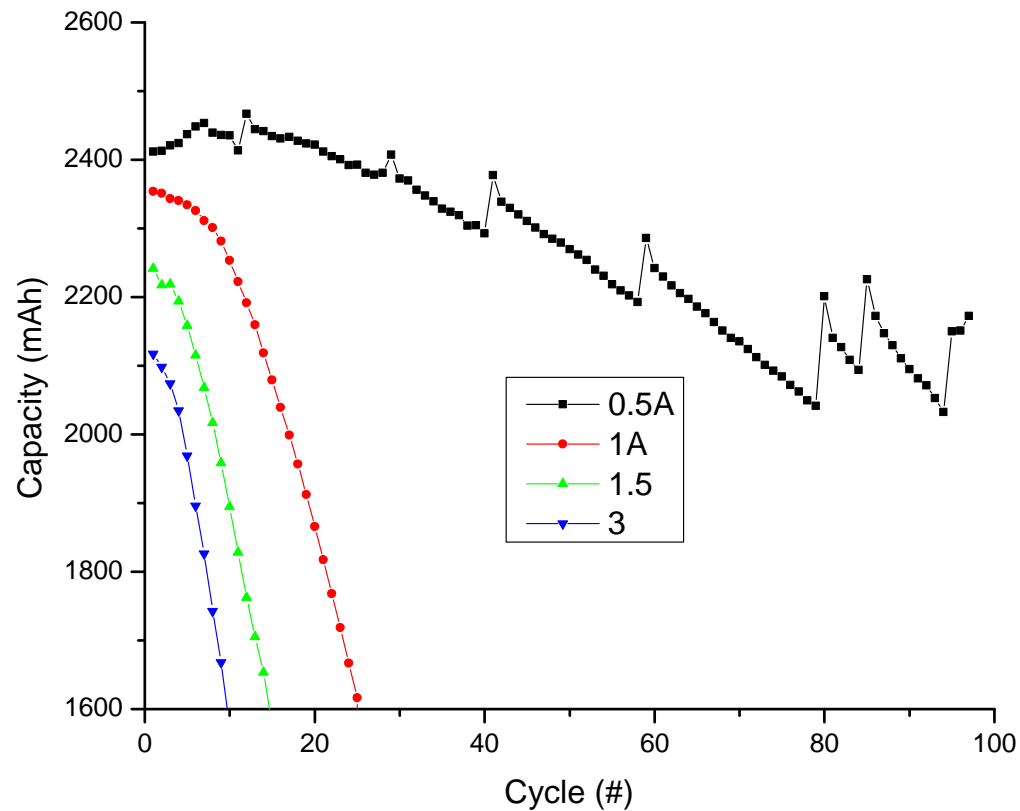
Estudios a diferentes temperaturas y velocidades de descarga



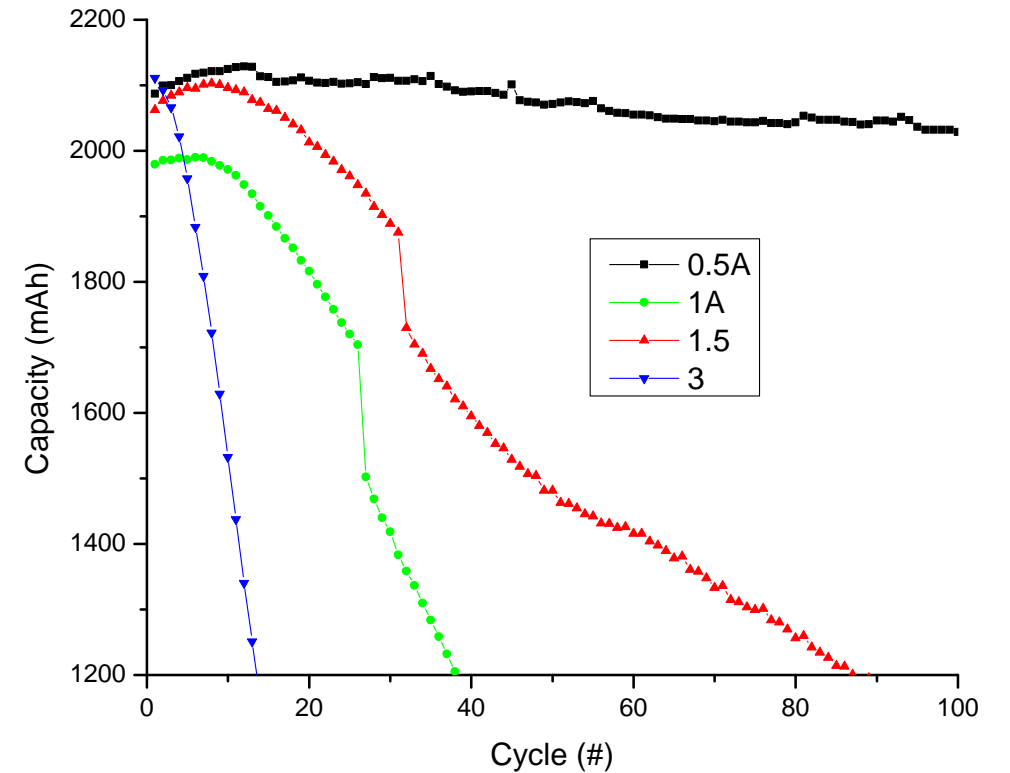
T (°C)	I (A)	C (Ah)
10	1.30	2.44
10	3.00	2.39
25	1.30	2.69
25	3.00	2.59
45	1.30	2.87
45	3.00	2.83

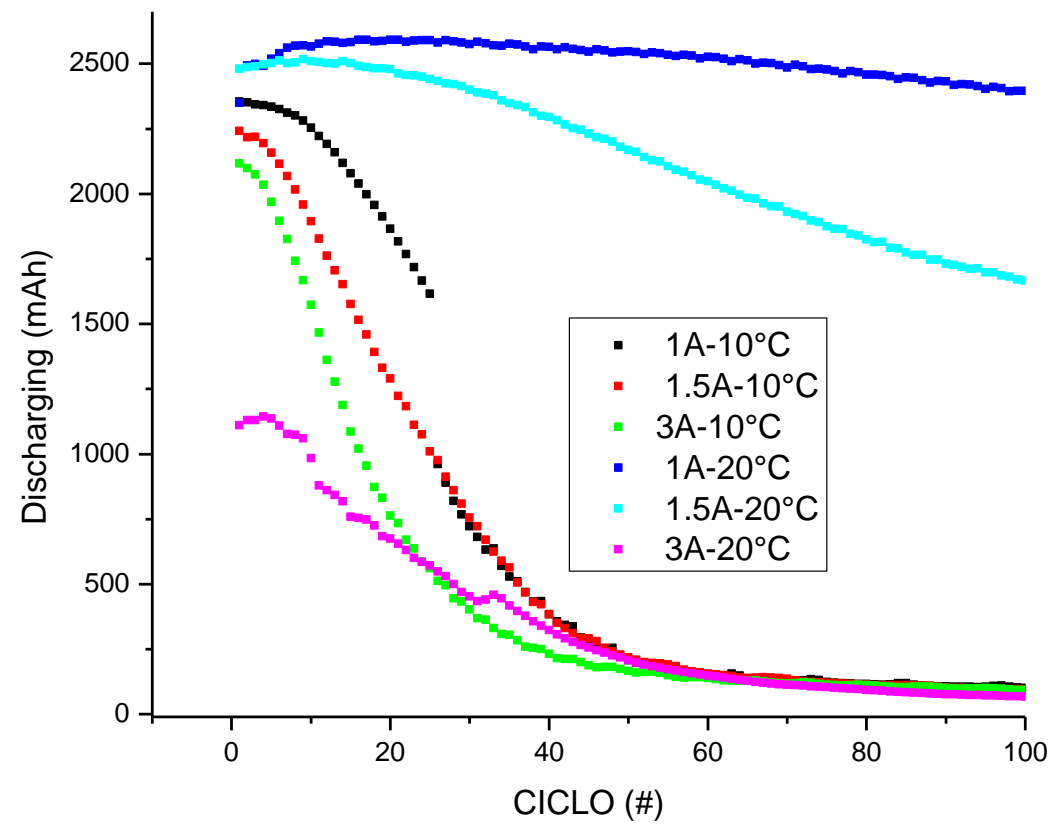
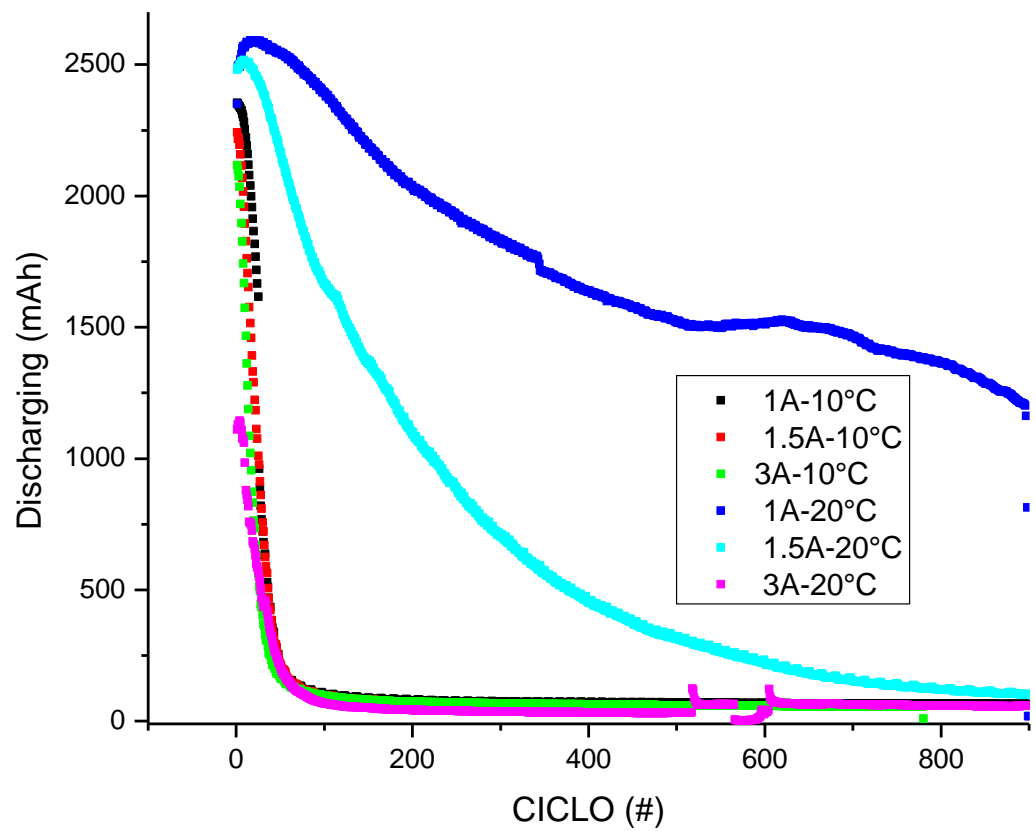
Estudios a baja temperatura y diferentes velocidades de carga

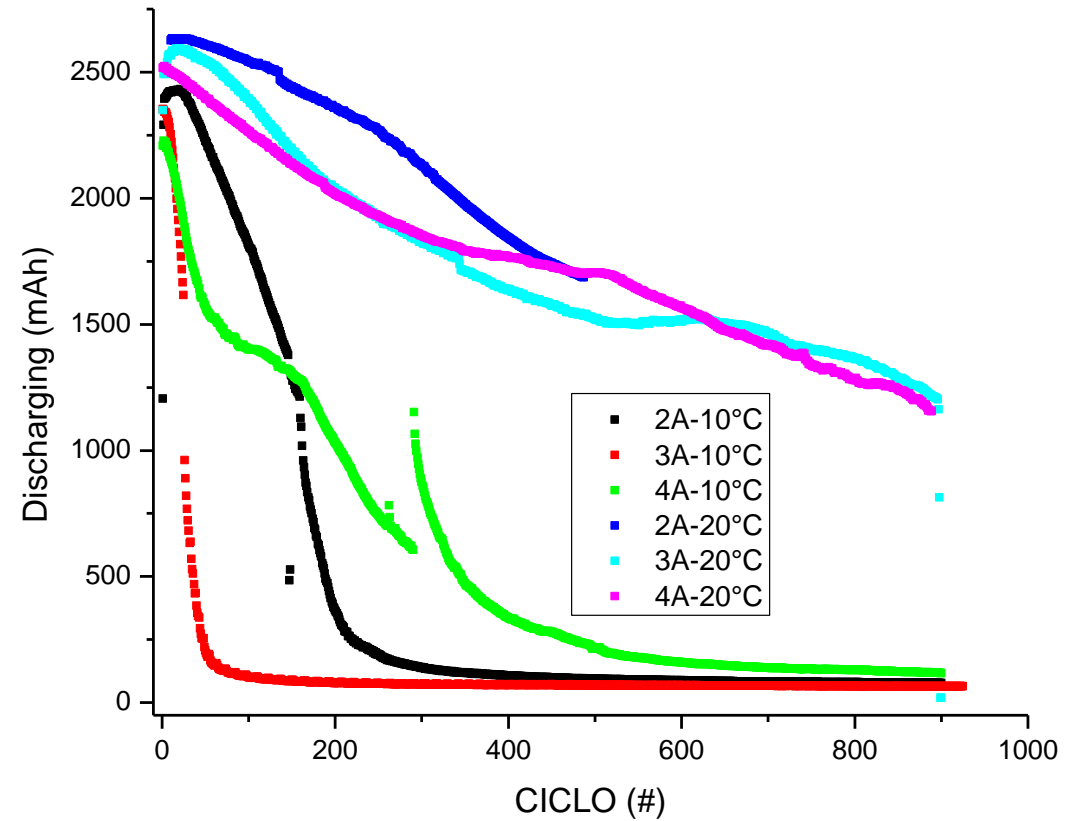
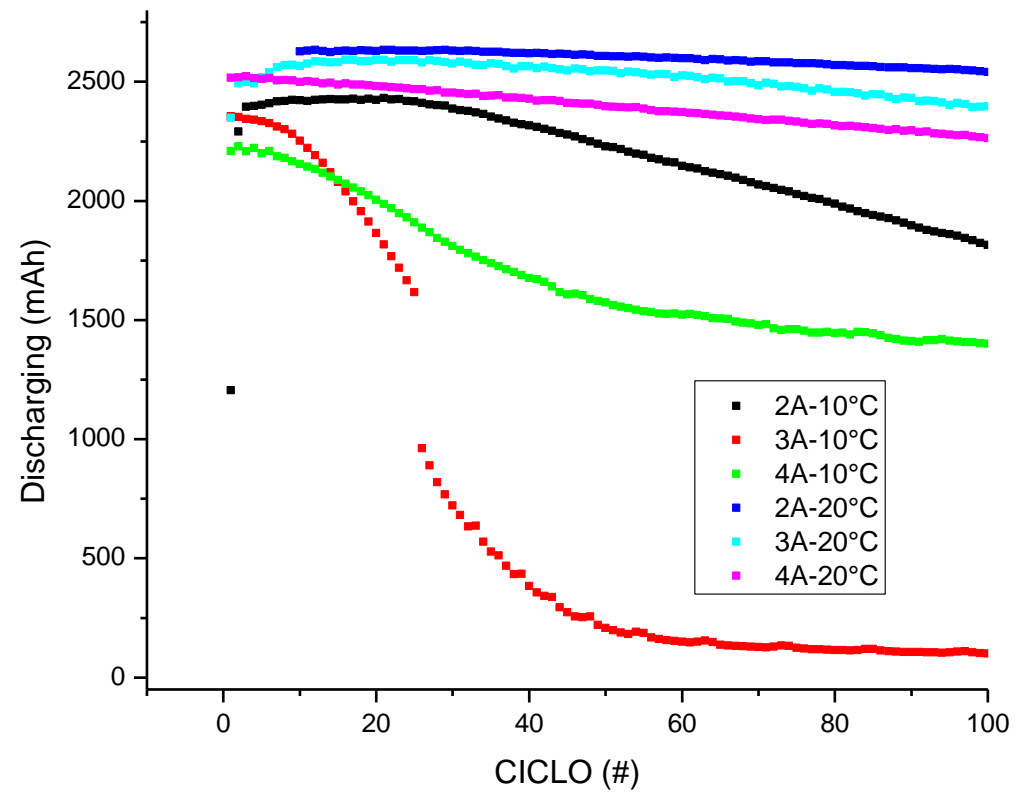
Carga CC

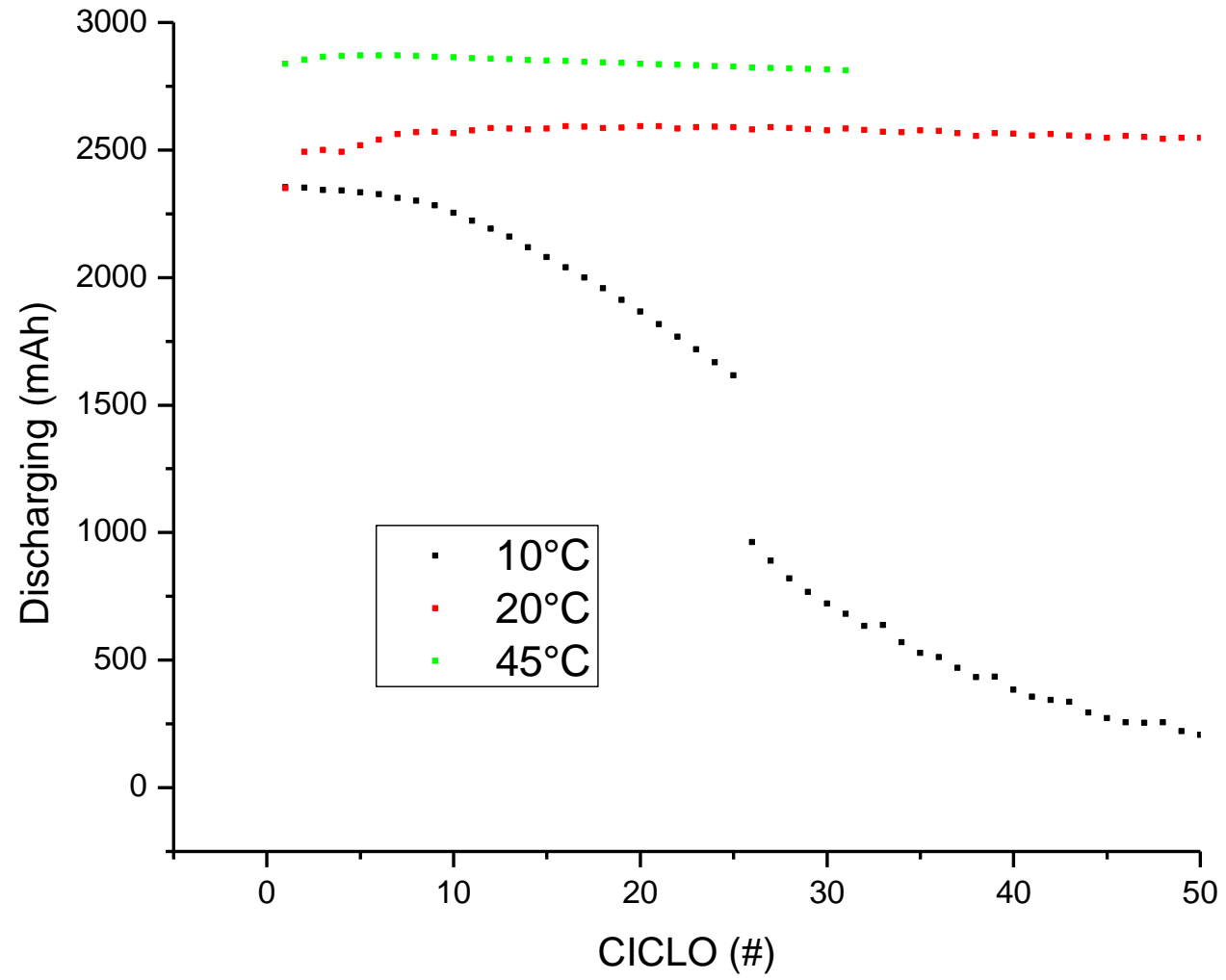


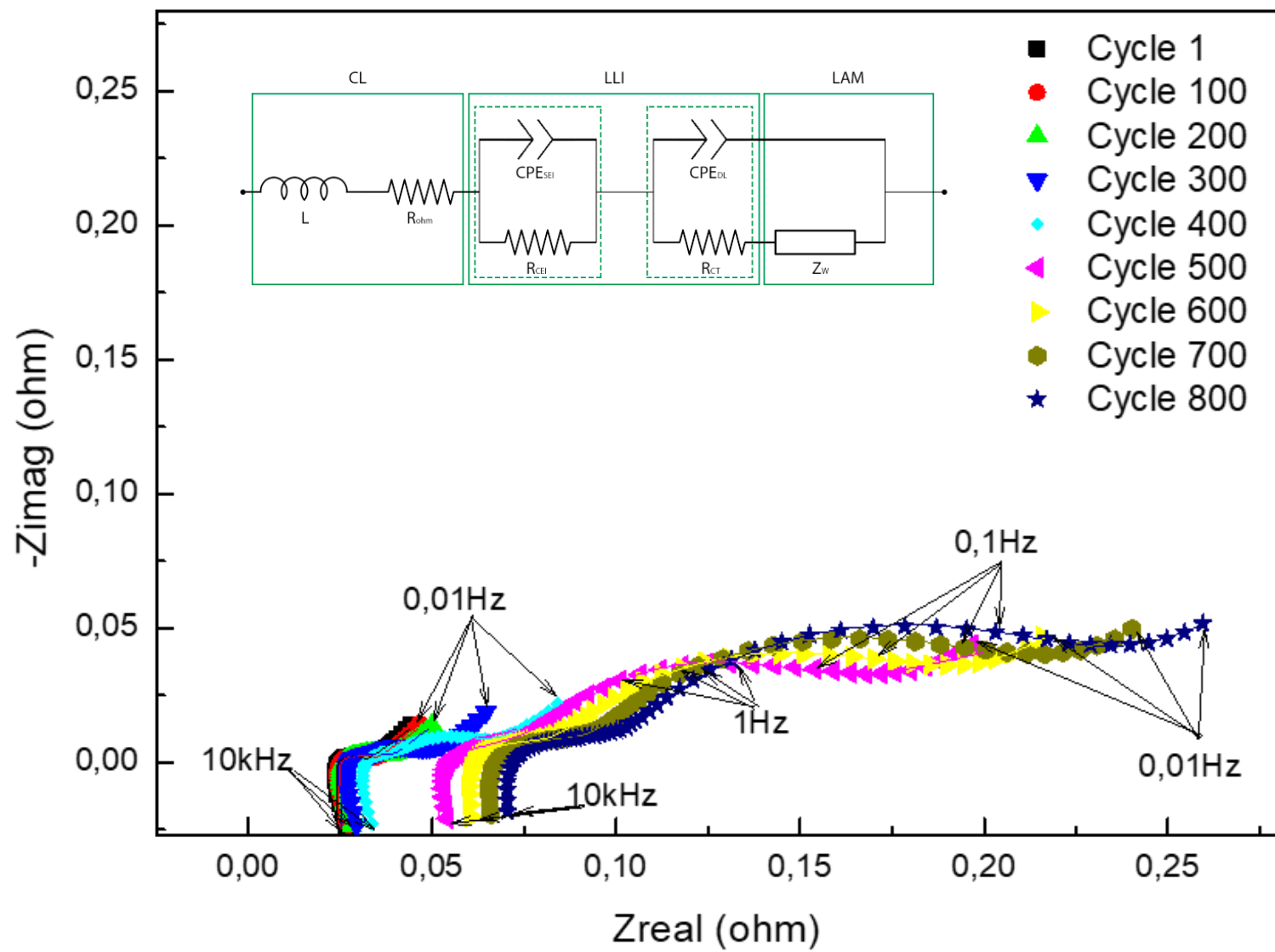
Carga CCCV









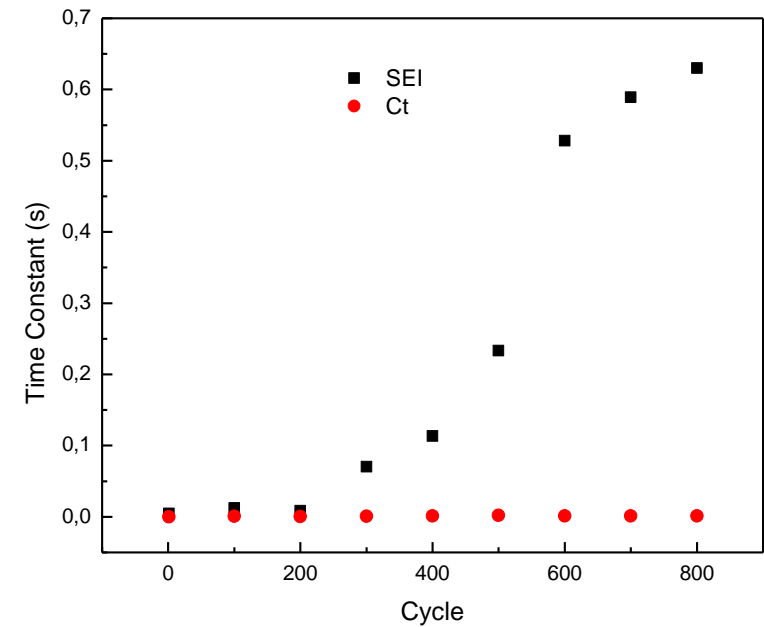
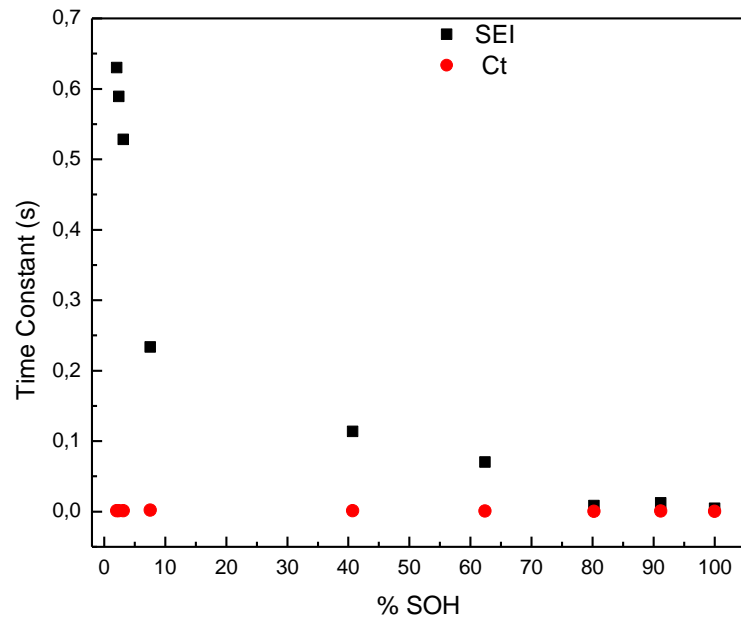
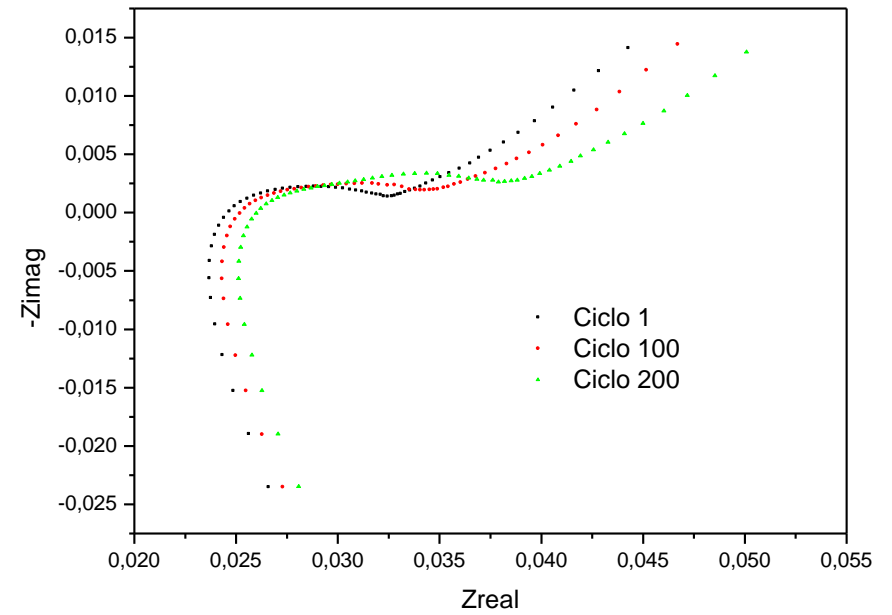
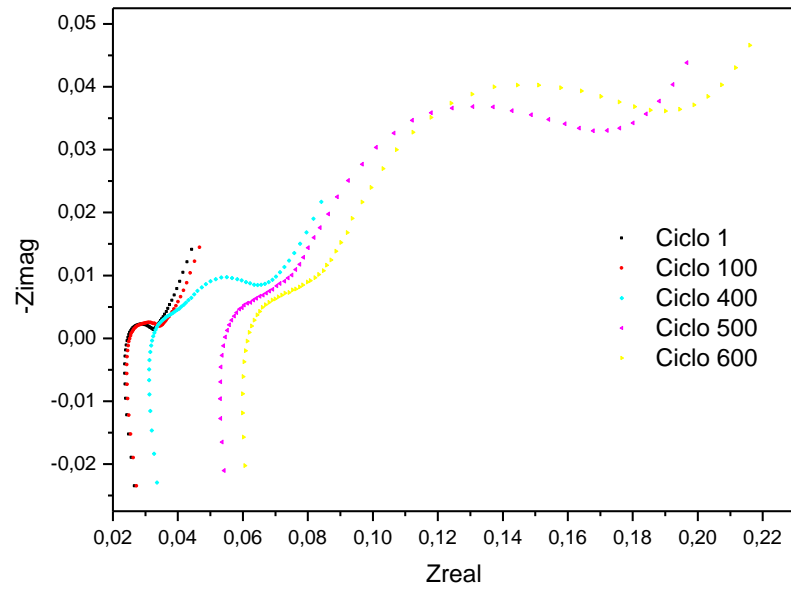


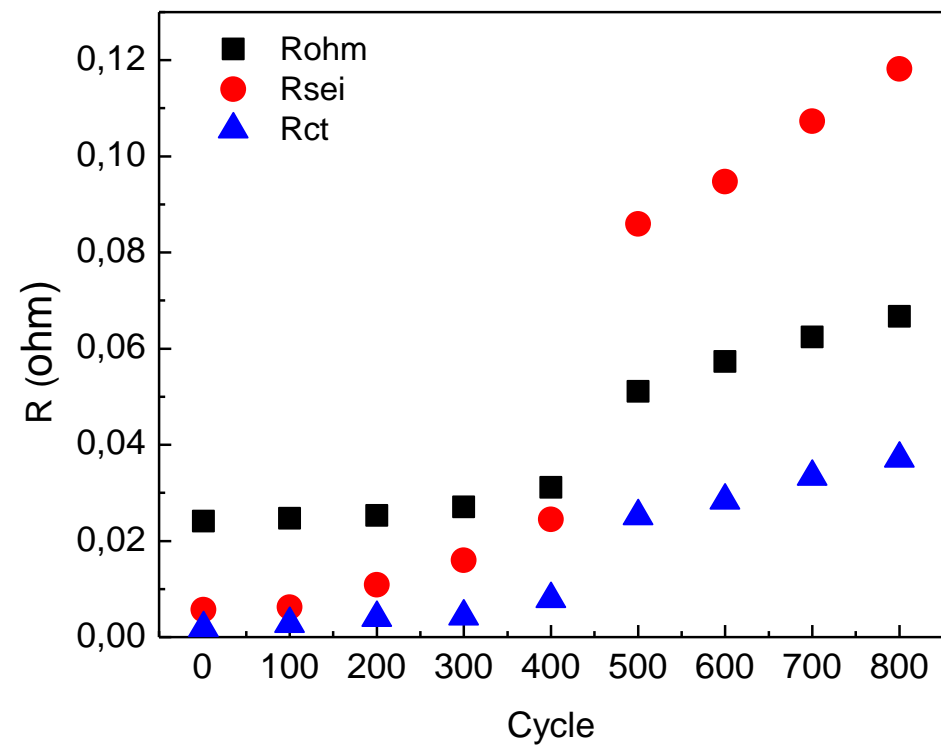
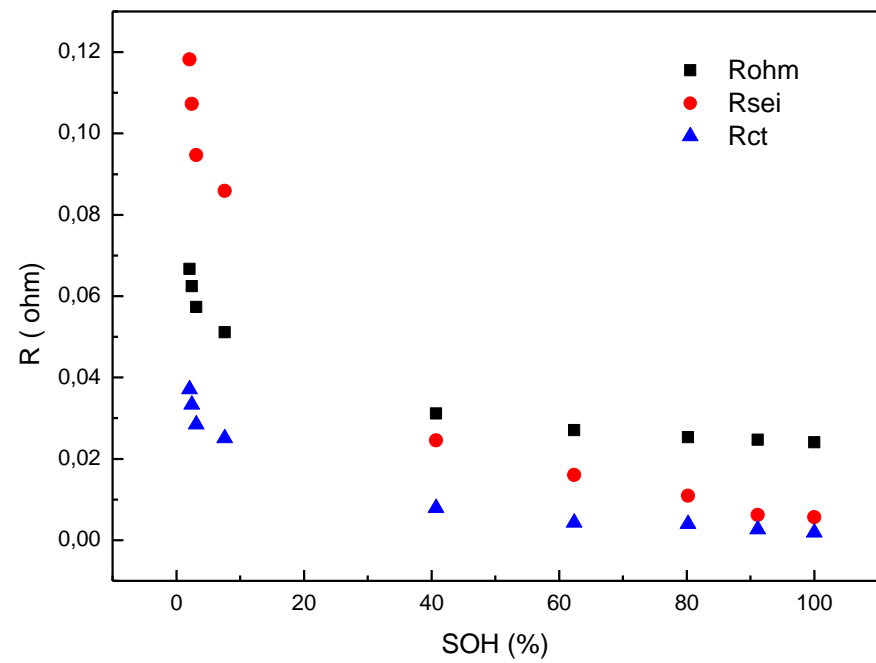
Cycle	$R_{ohm} (\Omega)$	$R_{sei} (\Omega)$	$R_{ct} (\Omega)$	$Y_0 (S.s^{1/2})$	$L (10^9 H)$	$CPE_{SEI} (S.s^{a1})$	a_1	$CPE_{dl} (S.s^{a2})$	a_2
1	0.02408	0.0057	0.0018	222	381	2.5	0.79	0.06	1
100	0.02468	0.0062	0.0027	221	381	5.7	0.76	0.23	1
200	0.02530	0.0109	0.0040	192	388	9.3	0.48	0.35	0.82
300	0.02704	0.0160	0.0043	171	379	10	0.69	0.54	0.87
400	0.03114	0.0245	0.0079	140	373	8.9	0.70	0.72	0.76
500	0.05110	0.0251	0.0251	73.4	390	10	0.95	1.20	0.56
600	0.05732	0.0947	0.0284	69.8	352	6.5	0.76	0.96	0.53
700	0.06242	0.1073	0.0333	66.6	345	6.2	0.77	0.86	0.52
800	0.06670	0.1182	0.0371	65.1	337	5.9	0.78	0.79	0.52

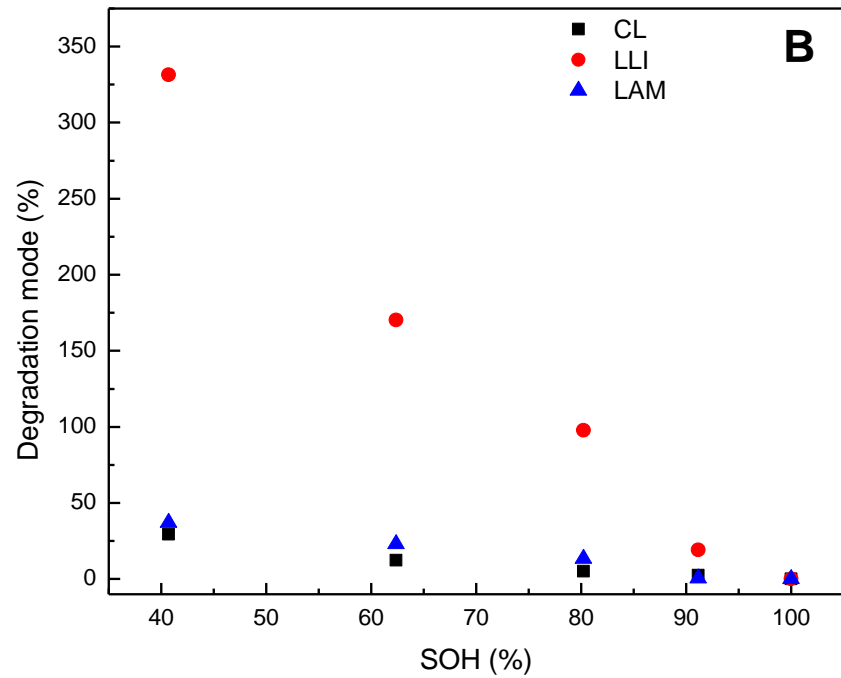
$$Z_w = \sigma w^{-1/2} (1 - j)$$

$$Y_0 = \frac{1}{\sigma\sqrt{2}}$$

$$D_{Li} = \frac{R^2 T^2 Y_0^2}{A^2 C^2 n^4 F^4}$$



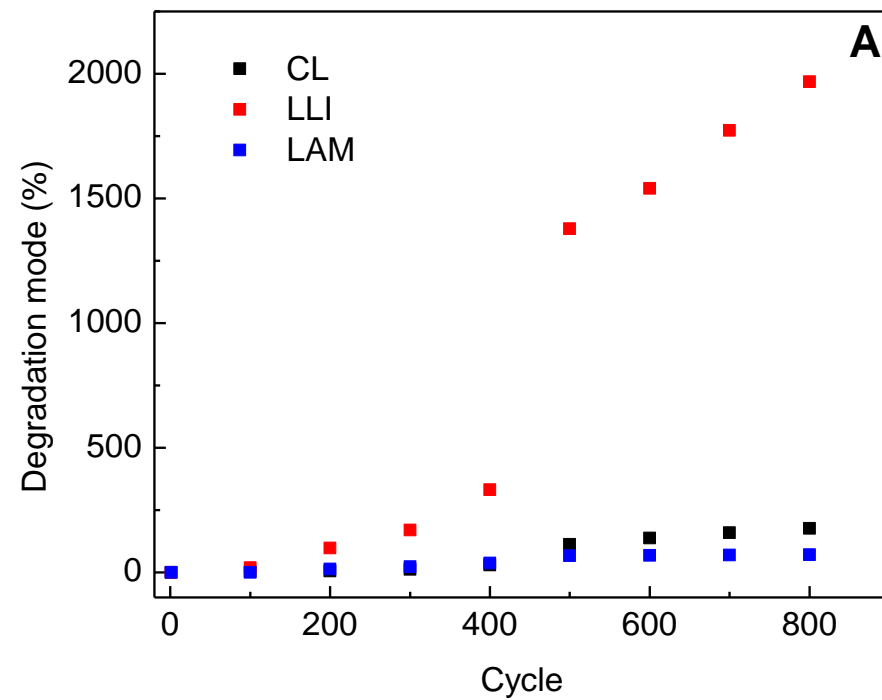


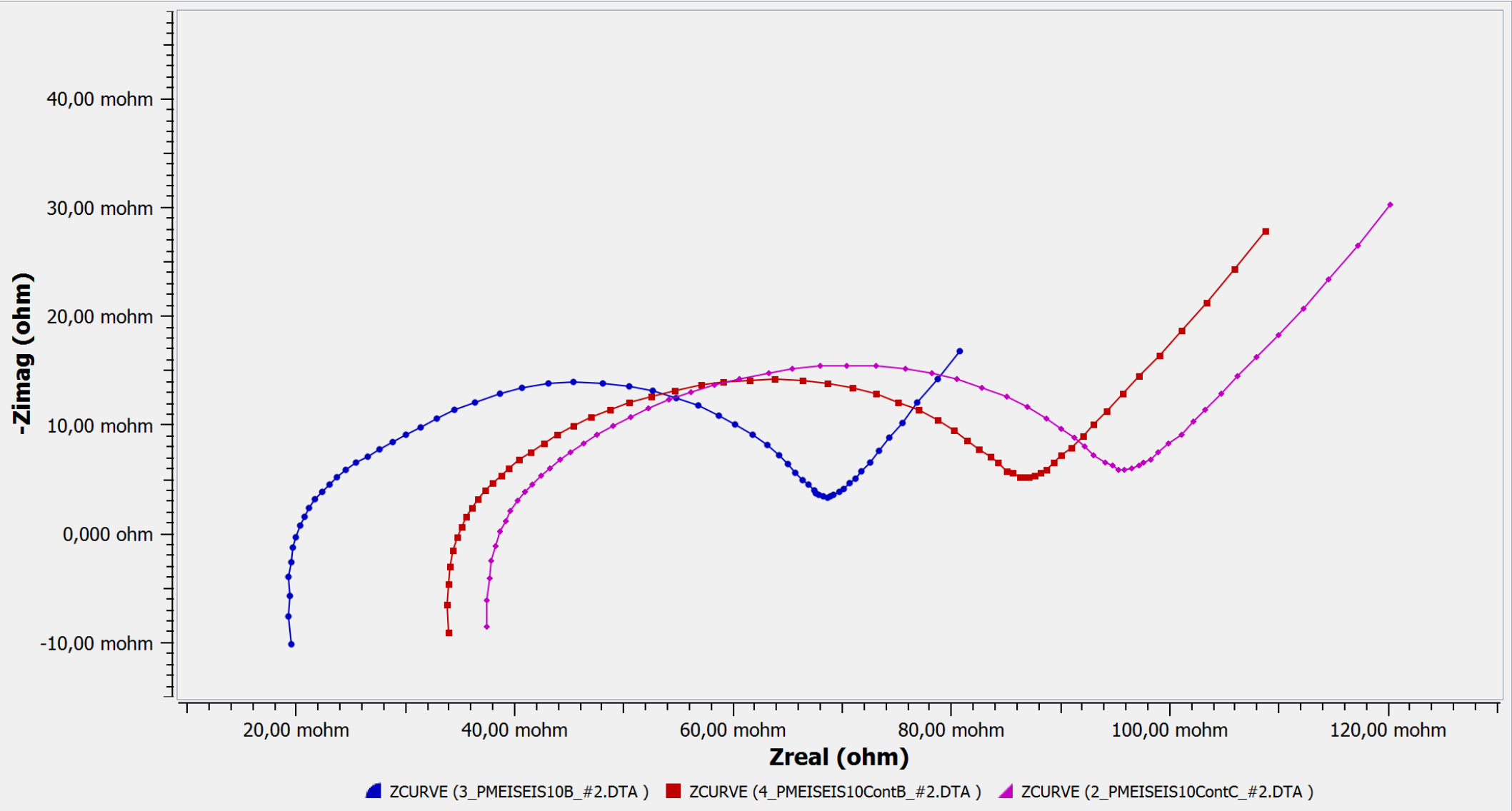


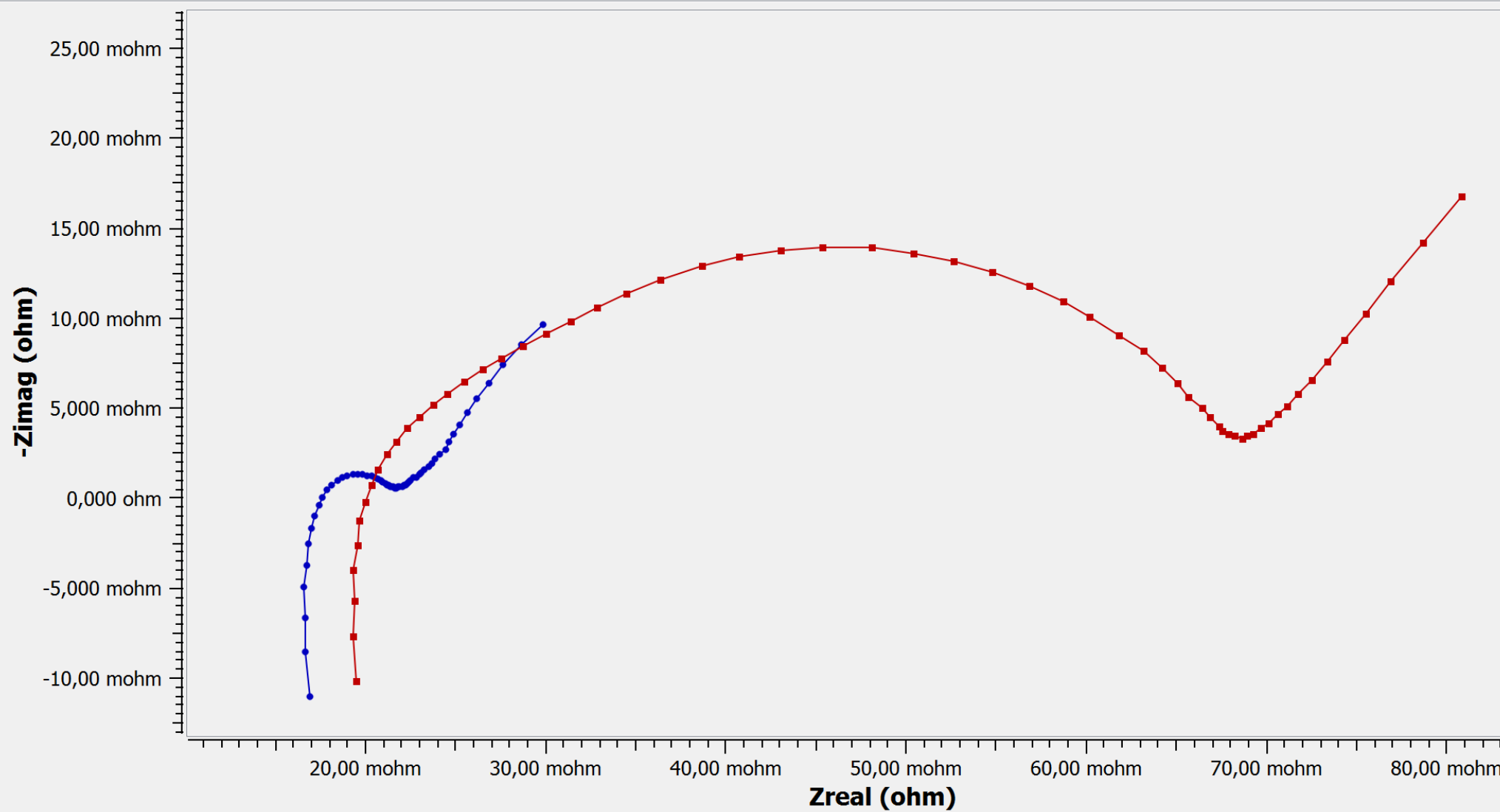
$$CL = 100 \frac{(R_{ohm,n} - R_{ohm,1})}{R_{ohm,1}}$$

$$LLI = 100 \frac{(R_{SEI,n} + R_{ct,n}) - (R_{SEI,1} + R_{ct,1})}{R_{SEI,1} + R_{ct,1}}$$

$$LAM = 100 \frac{(Y_{0,1} - Y_{0,n})}{Y_{0,1}}$$



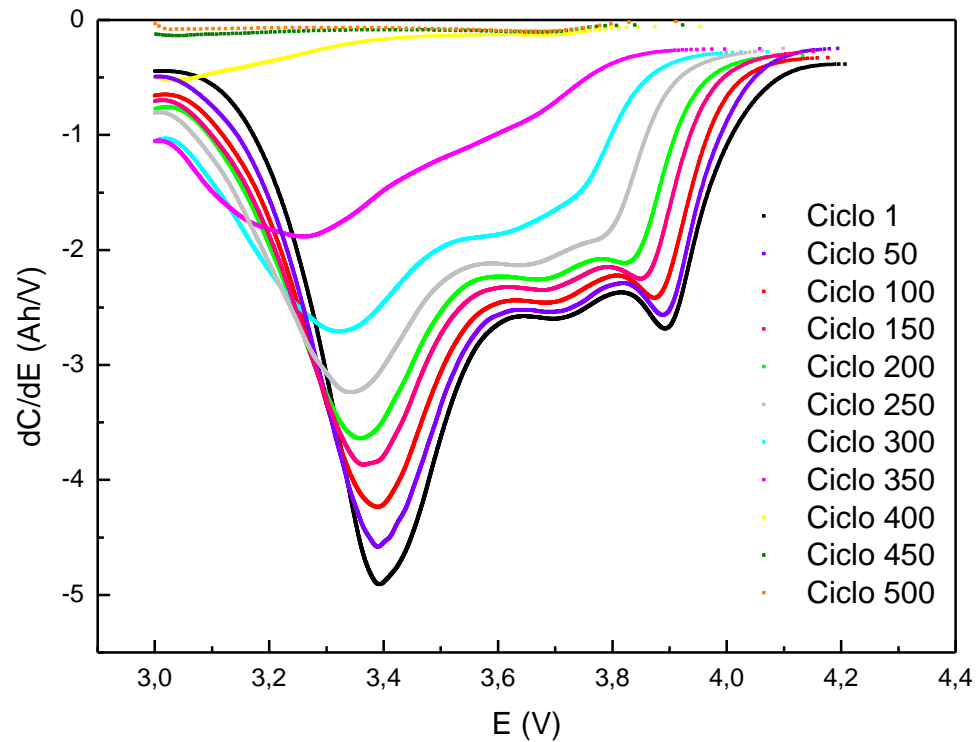




ZCURVE (2_PMEISEIS45_#6.DTA) ZCURVE (3_PMEISEIS10B_#2.DTA)

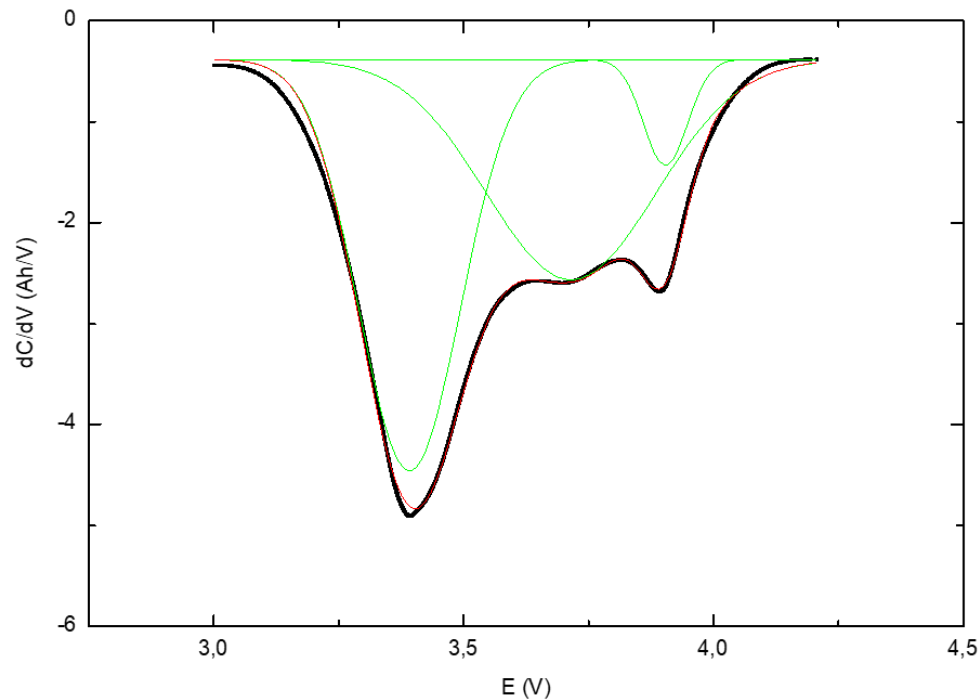
Resultados, curvas de capacidad incremental dC/dE (Ah/V) vs E(V)

Las curvas de capacidad incremental se obtienen graficando el valor de la derivada de la curva anterior en función del voltaje.



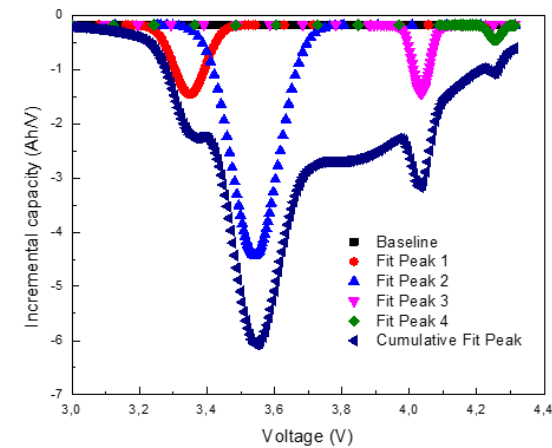
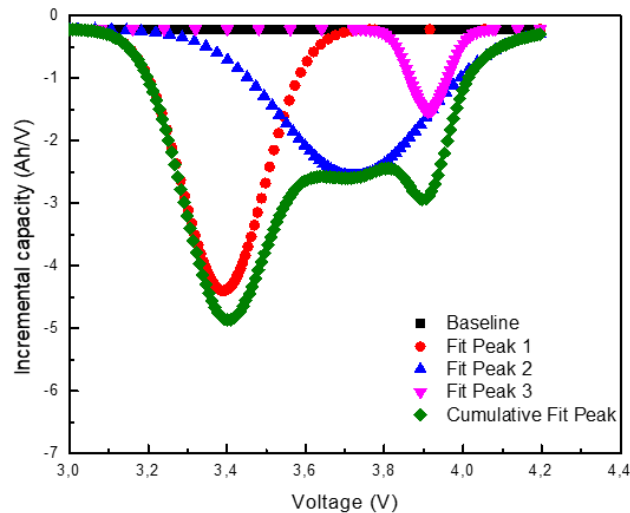
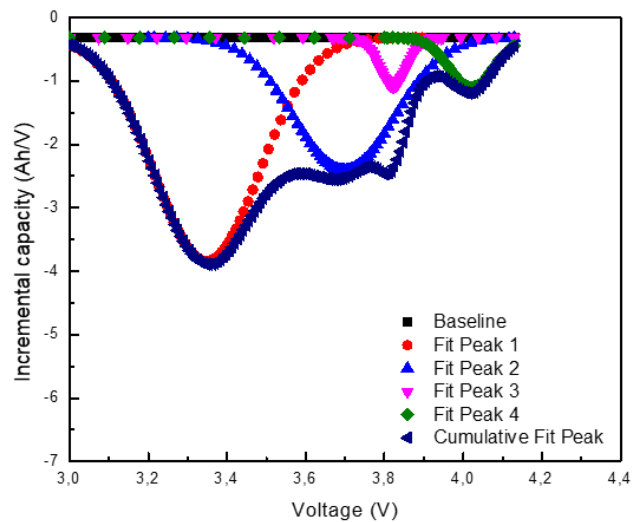
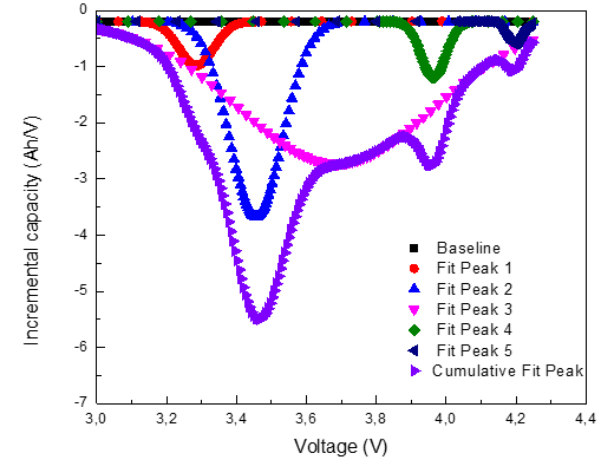
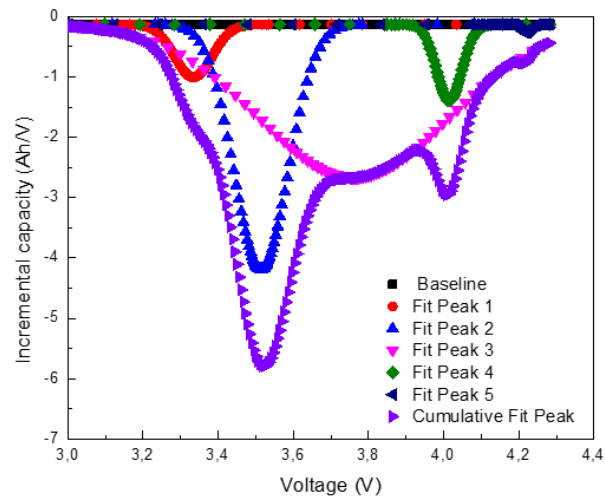
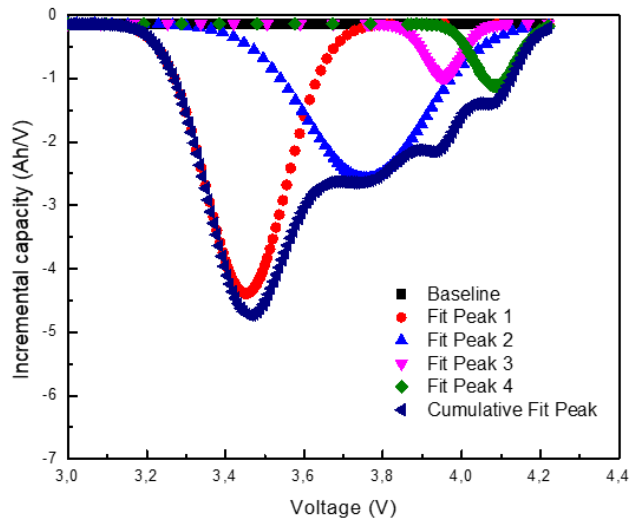
Resultados, deconvolución de las curvas IC

Se realizó el ajuste de picos de las curvas IC, con el fin de identificar parámetros que permitan cuantificar los modos de degradación y con ello el envejecimiento de las baterías

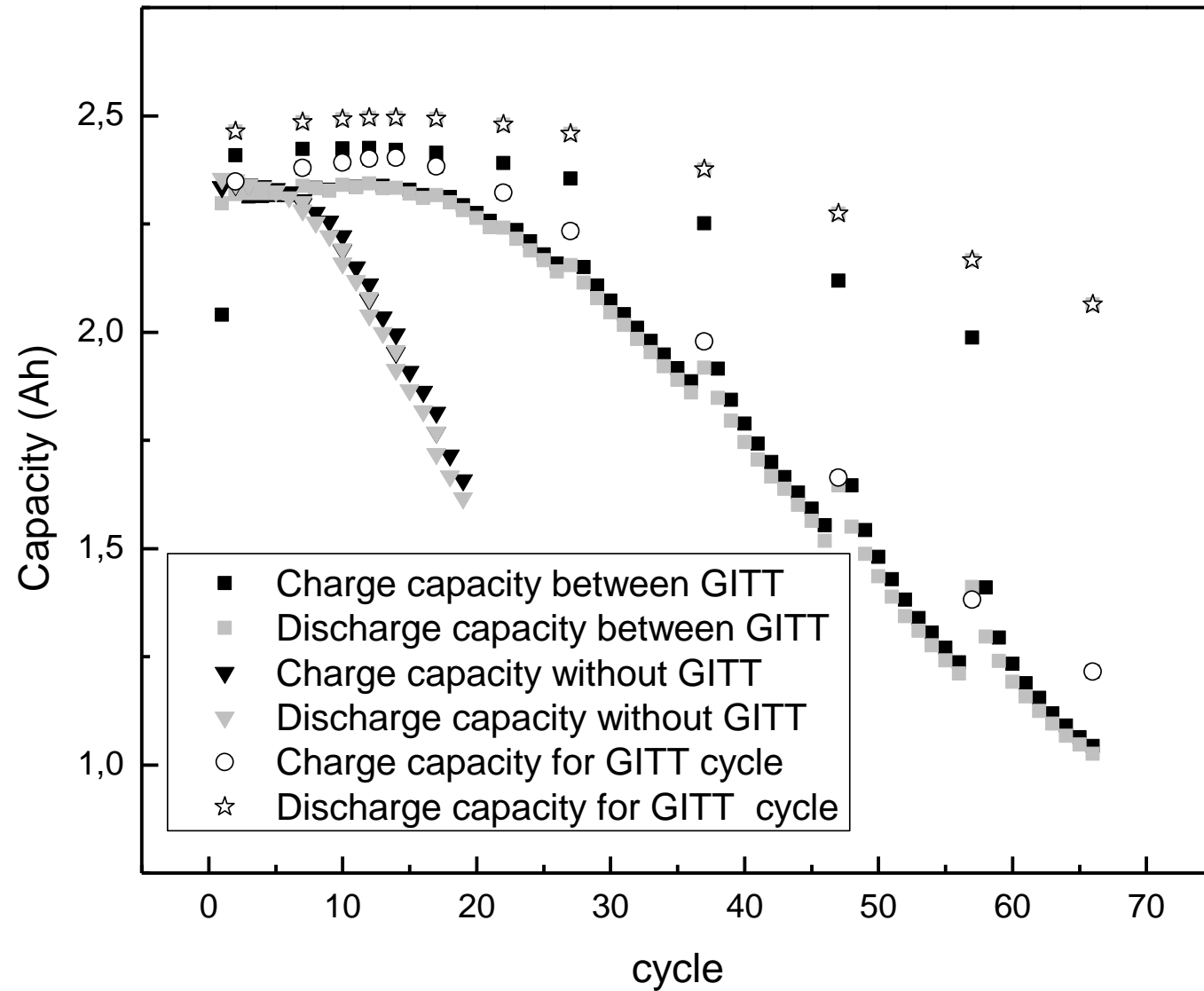


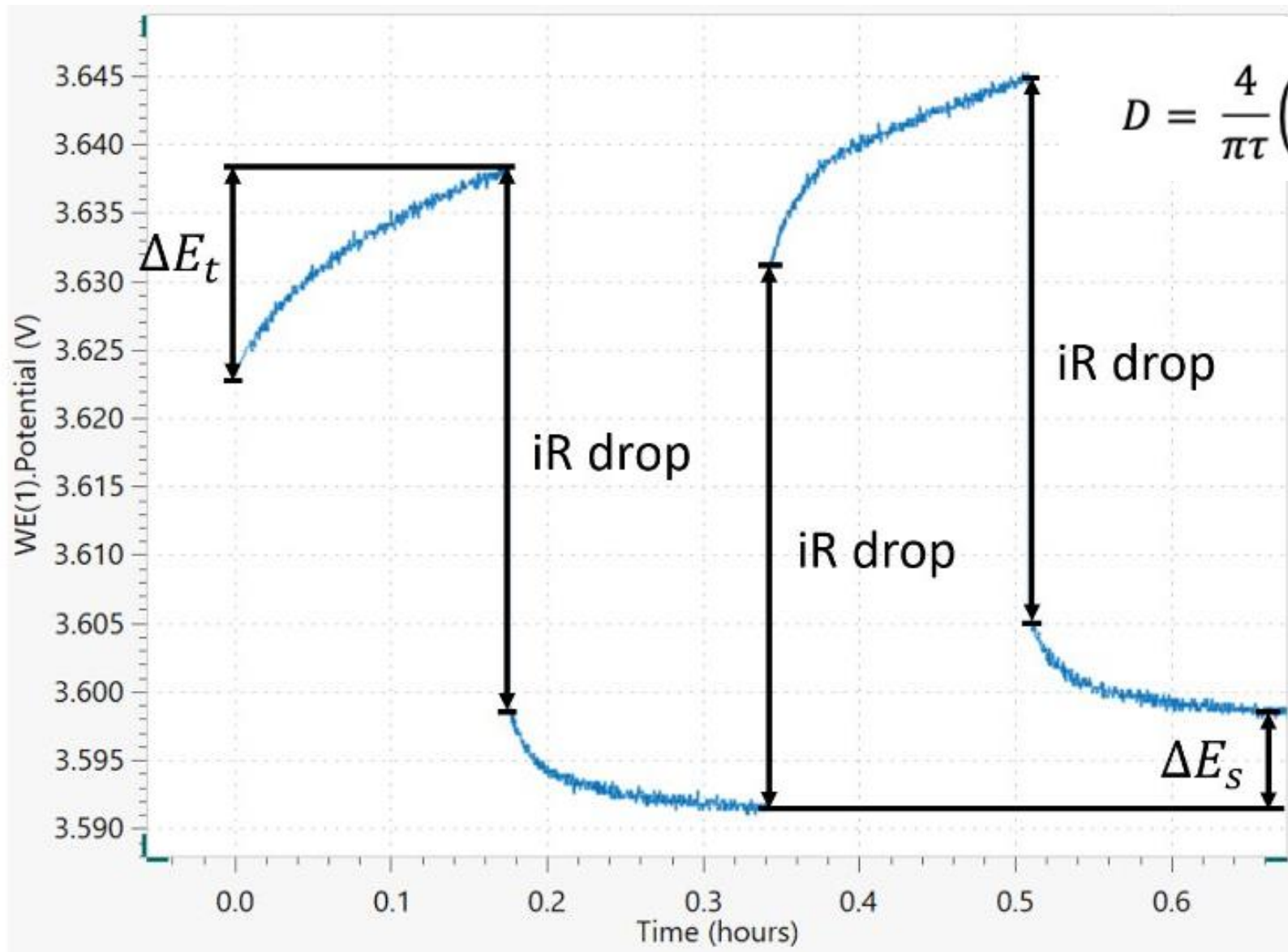
	Pico 1	Pico 1	Pico 1
Ciclo	Área (Ah)	Altura (Ah/V)	Centro (V)
1	1,03753	4,07264	3,39186

Efecto de la Temperatura y la velocidad de descarga

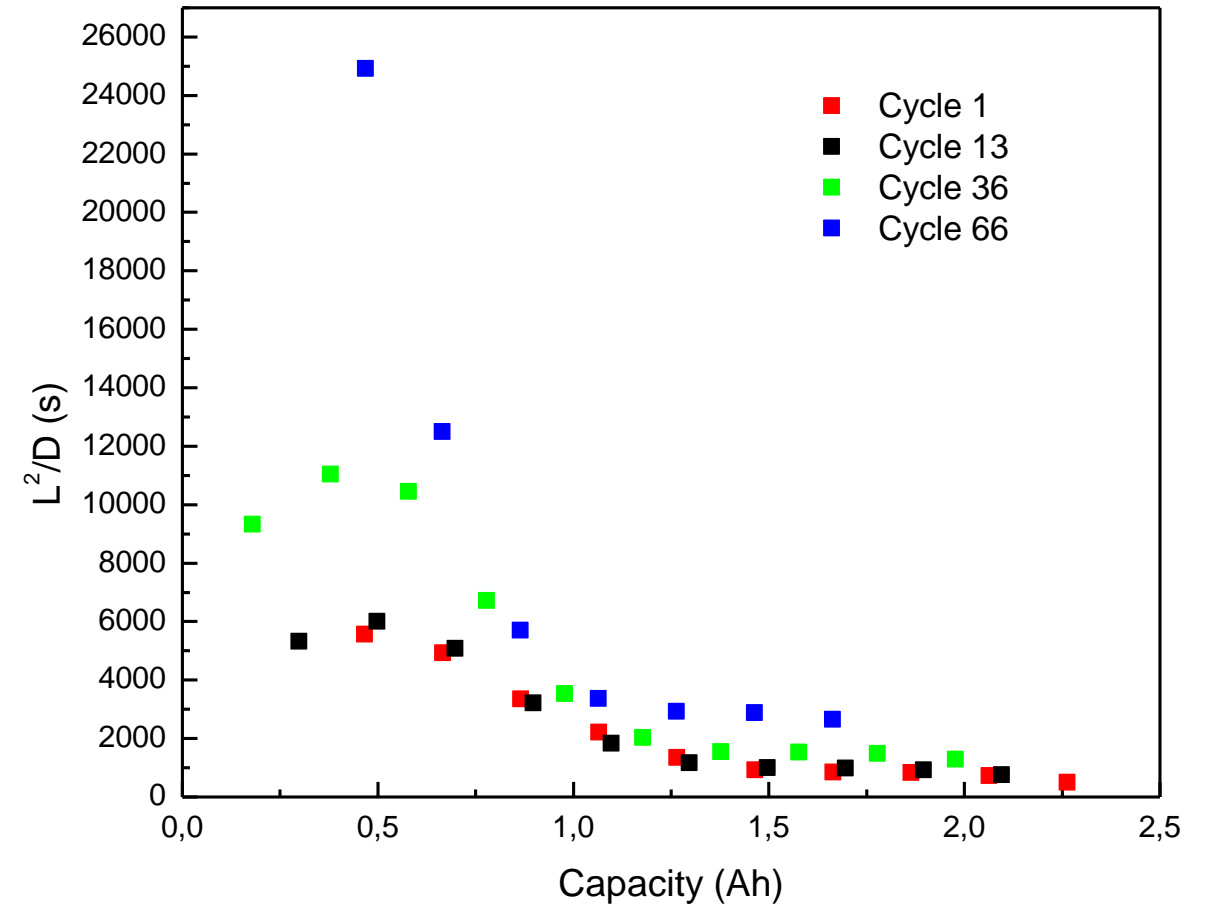
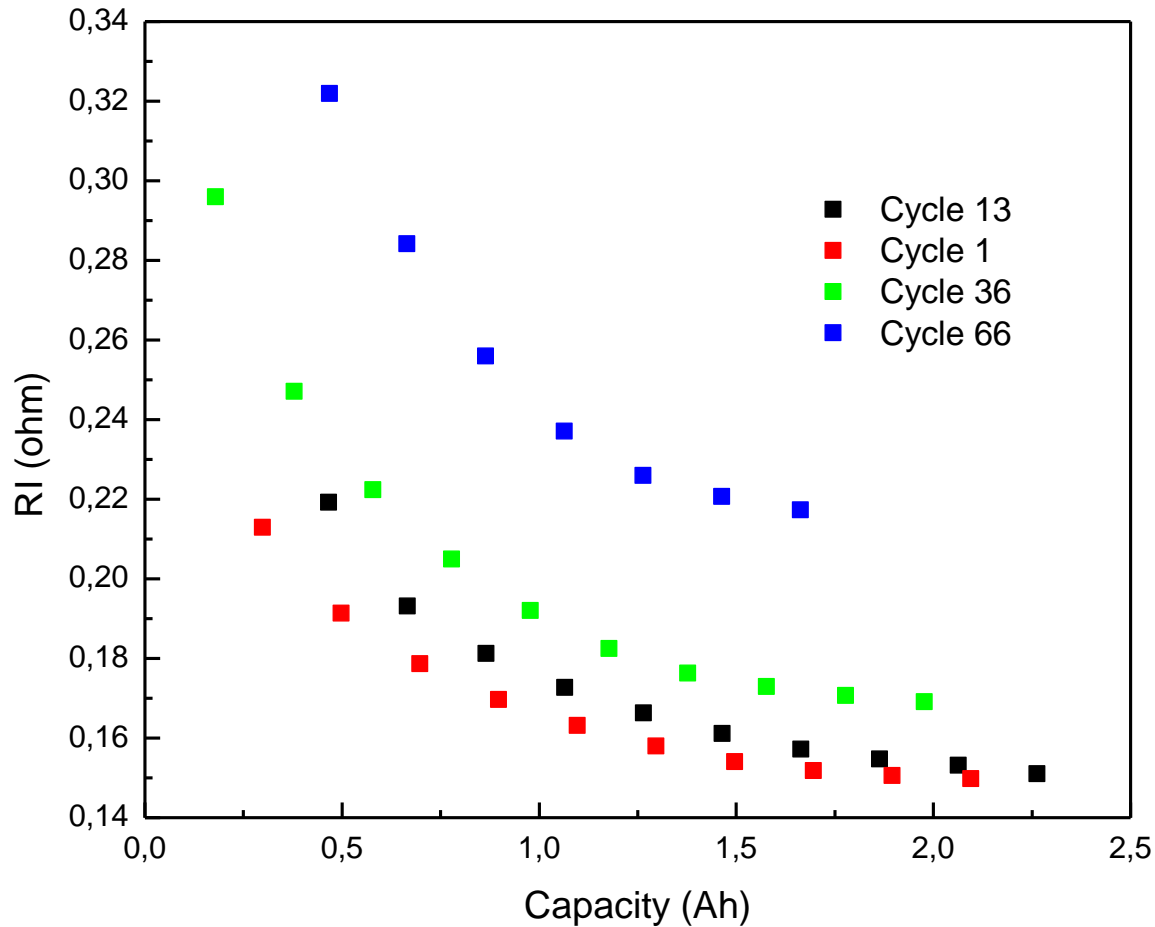


Curvas de Carga y descarga/GITT





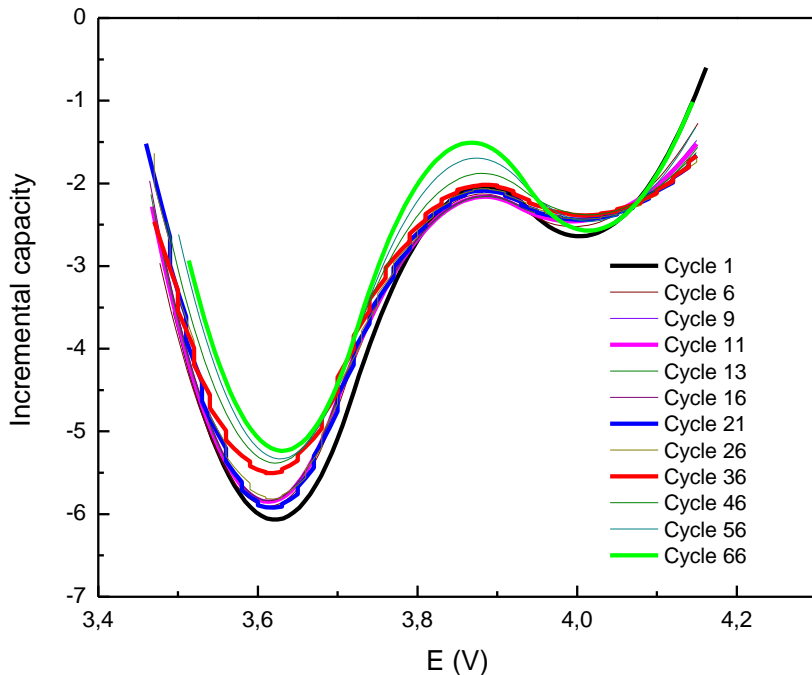
Sobrepotencial de caída óhmica y constante de tiempo difusional



Curvas de capacidad incremental

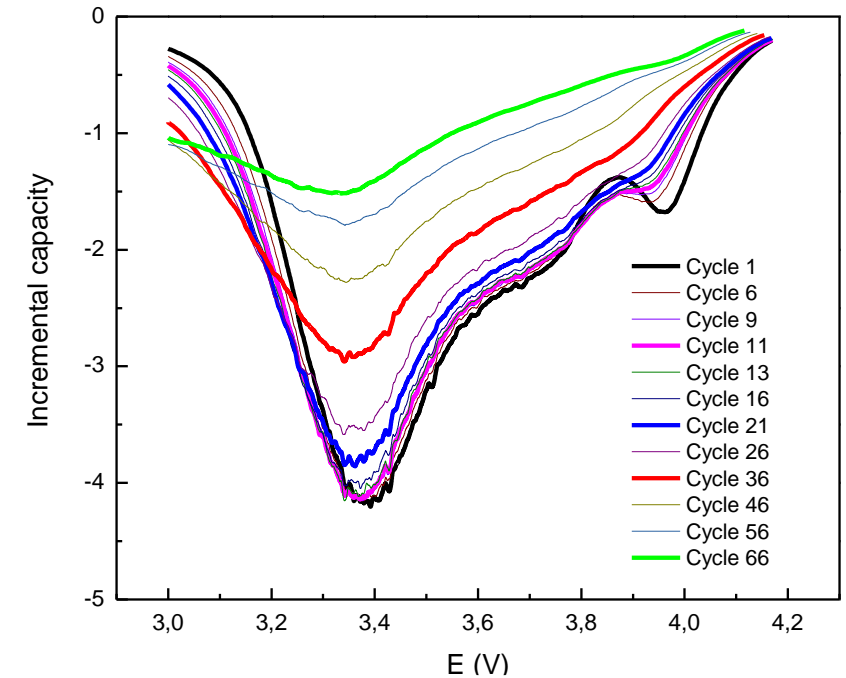
Para responder esta pregunta, realizamos las curvas de capacidad incremental para las descargas con y sin GITT con el fin de analizar los cambios en el perfil a diferentes estados de salud

IC curves for GITT discharge



Se observa claramente que el proceso faradaico es el causante de la degradación, pero es necesario conocer cuál es el proceso más relevante

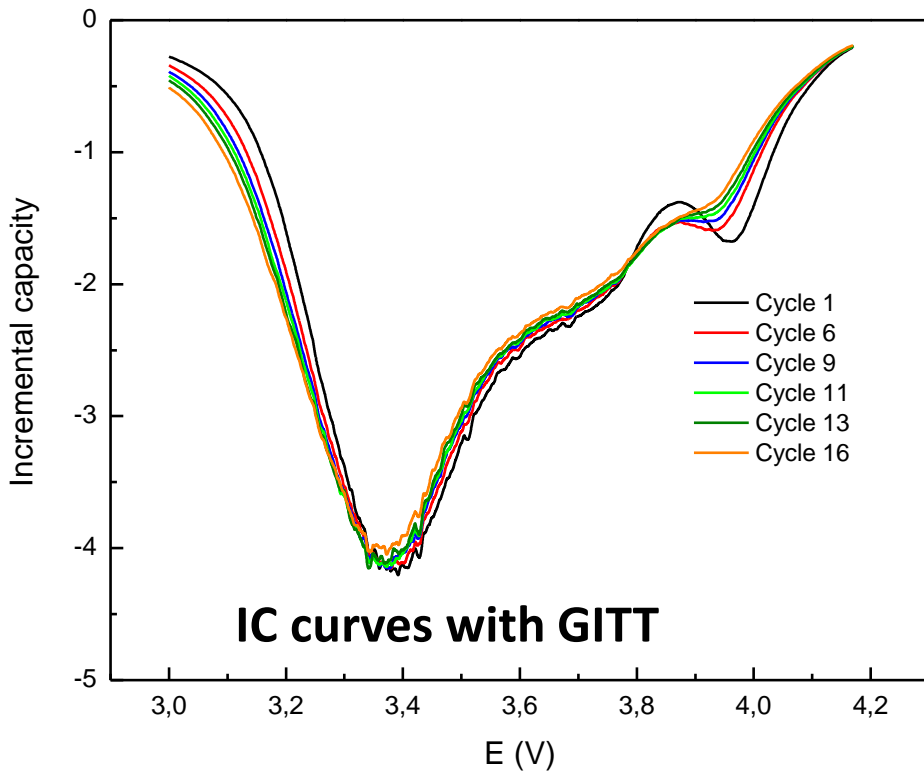
IC curves with GITT discharge



Los picos y los valles de las curvas IC se asocian a transformaciones de fase como consecuencia del proceso de envejecimiento, y la posición, ancho y área se asocian a diferentes mecanismos de degradación. Las curvas IC para las descargas a 3A y OCP fueron analizadas para estudiar el efecto **termodinámico y faradaico por separado**

Curvas de capacidad incremental

Para este propósito, comparamos las curvas IC bajo las mismas condiciones **con y sin GITT**, para observar la diferencia en la evolución de picos y de valles



Para las curvas con GITT, podemos observar que luego del primer ciclo, el perfil no cambia de manera significativa. Por lo que concluimos que el proceso que ocurre es reversible y que tiene como consecuencia una reducción en el proceso de envejecimiento de la batería. Concluimos que este proceso es el de **stripping de litio**.

