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The development of high power Li-ion batteries is of great relevance for hybrid electric vehicles (HEVs) technology. Electrochemical performance of high voltage graphite/LiNi_{0.4}Mn_{1.6}O₄ cells operating with electrode formulation and mass-loading suitable for scale-up assembled with new reinforced polyvinylidene fluoride macroporous membrane (PVdF-NCC) and ethylene carbonate - dimethyl carbonate 1M LiPF₆ (LP30) electrolyte with additives (monofluoroethylene carbonate, F₁EC, and succinic anhydride, SA) was evaluated according to the DOE Battery Test Protocol to simulate the dynamic functioning of batteries in plug-in HEVs. The results compared to those of cells with commercial polypropylene monolayer separator (Celgard®2400) evidence the beneficial impact of the new fluorinated separators.

DOE Battery Test Protocol for plug-in Hybrid Electric Vehicles (PHEVs) at 30°C

Laboratory high-voltage graphite/LiNi_{0.4}Mn_{1.6}O₄ cells Electrode formulation

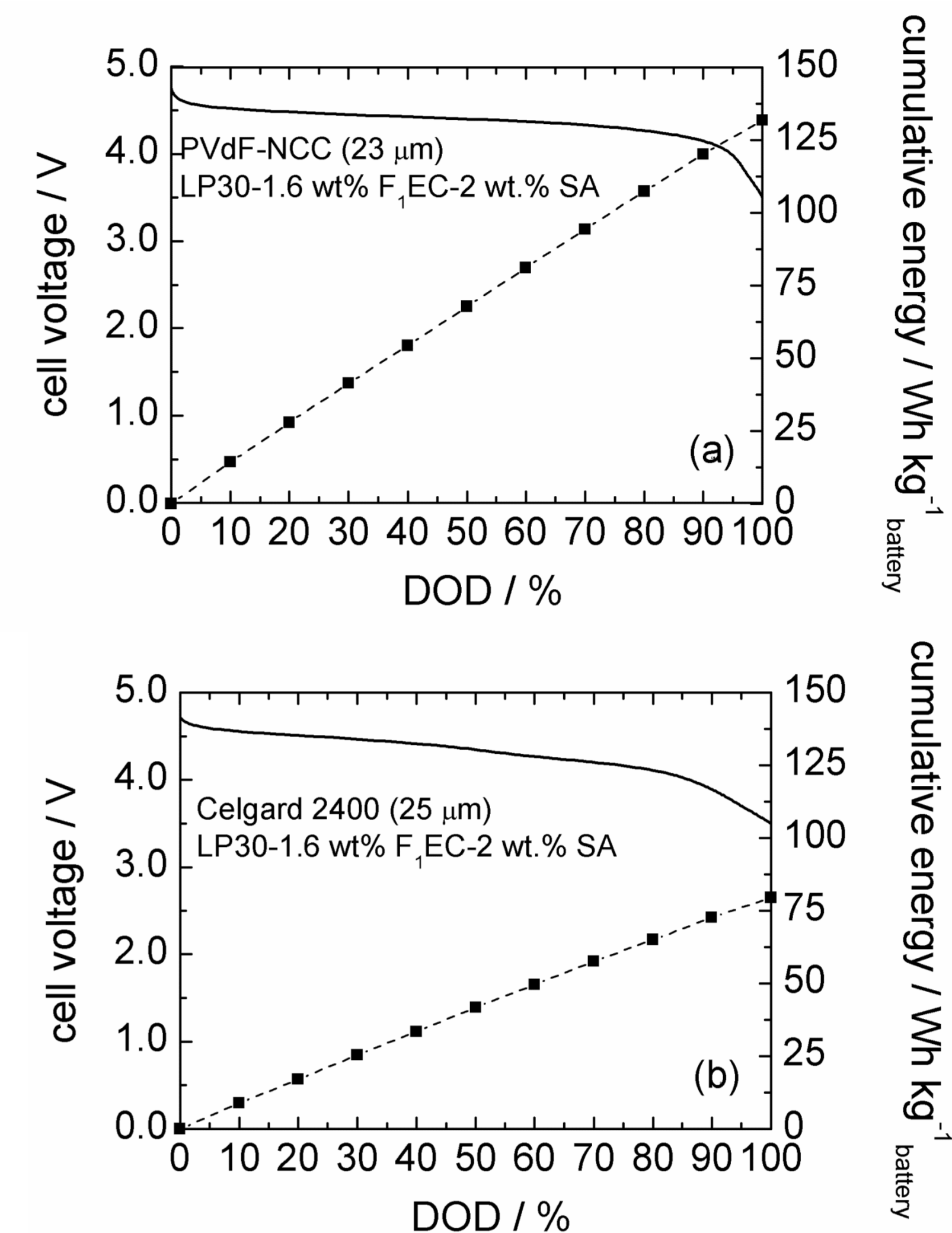
Graphite electrode	LiNi _{0.4} Mn _{1.6} O ₄ electrode
91 wt.% SLA-1025 (8.7 mg cm ⁻²)	92 wt.% LNMO (21.3 mg cm ⁻²)
3 wt.% Pureblack	4 wt.% Super C65
6 wt.% PVdF Solef 5130	4 wt.% PVdF Solef 5130

Energy storage system performance targets for plug-in HEVs

Characteristics at EOL (End-of-Life)	Unit	Minimum PHEV	Medium PHEV	Maximum PHEV
	miles	10	20	40
Peak Discharge Pulse Power (10 s)	kW	45	37	38
	W kg ⁻¹	750	529	317
Peak Regen Pulse Power (10 s)	kW	30	25	25
	W kg ⁻¹	500	357	208
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	5.8	11.6
	Wh kg ⁻¹	56.7	82.9	96.7
Available Energy for CS (Charge Sustaining) Mode, 10 kW Rate	kWh	0.5	0.3	0.3
	Wh kg ⁻¹	8.3	4.3	2.5
Maximum System Weight	kg	60	70	120

Static capacity tests (SCT) at 2C effective discharge rate

specific parameters refer to total battery weight, i.e. twice the composite weight of both electrodes

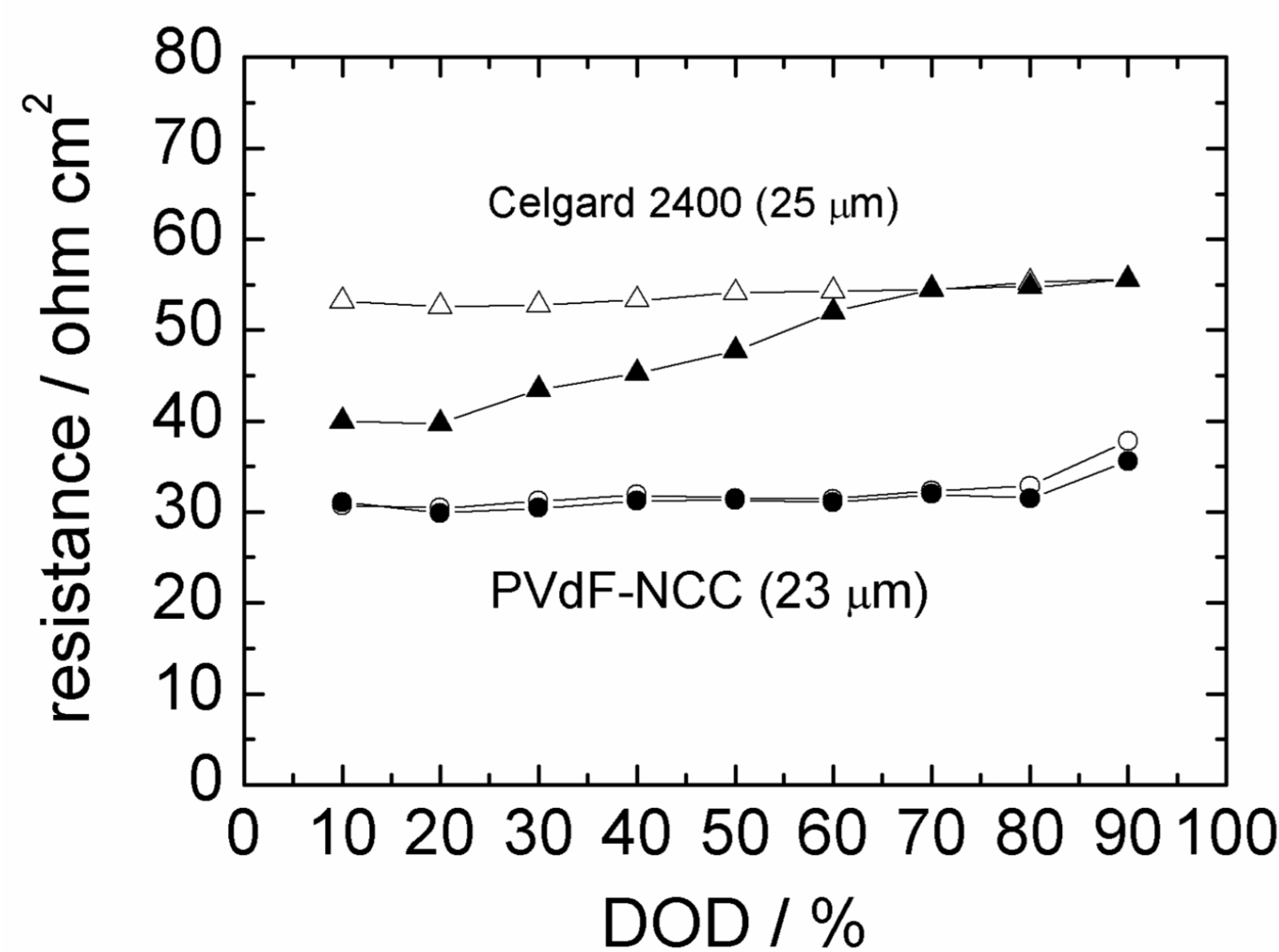
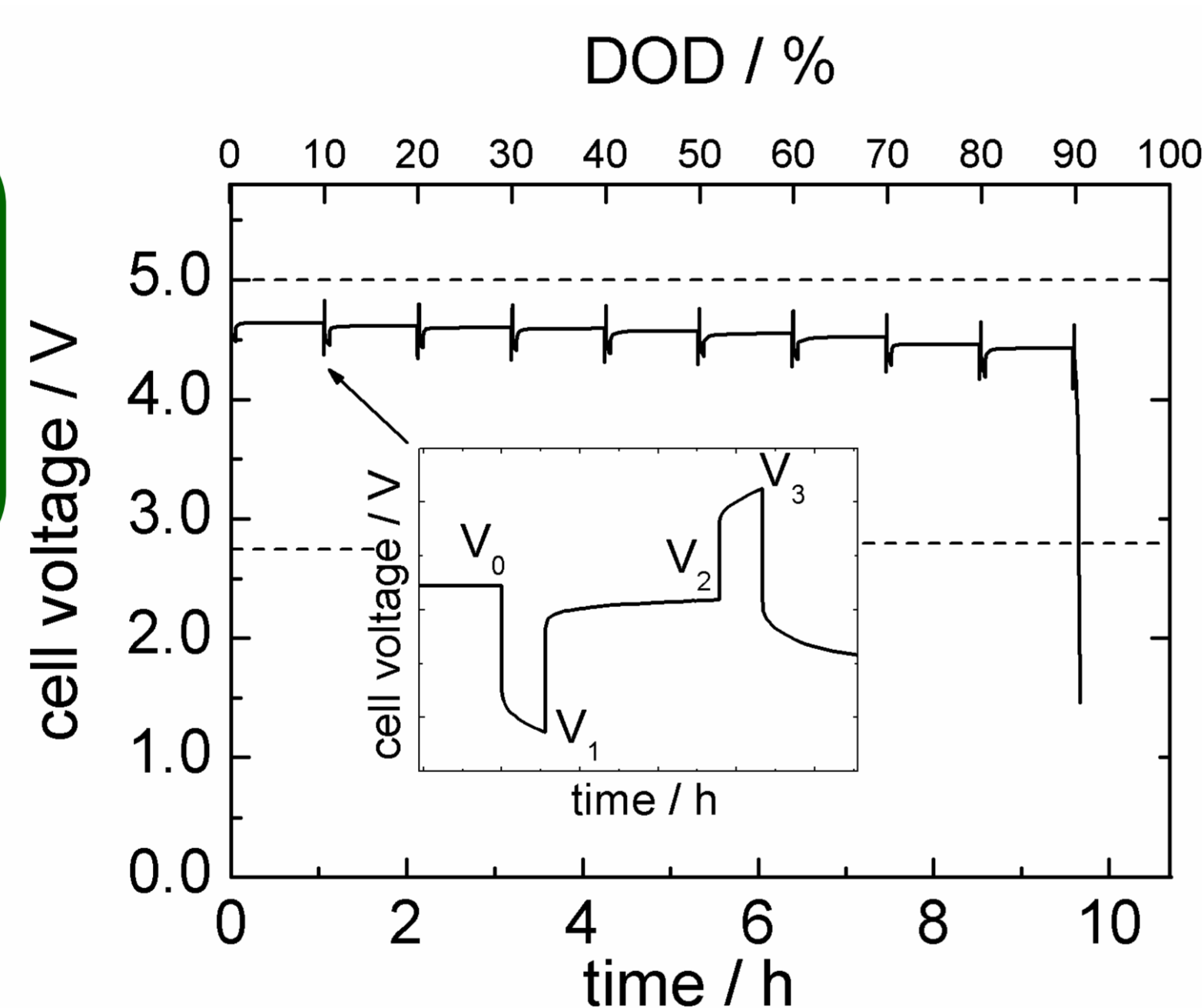
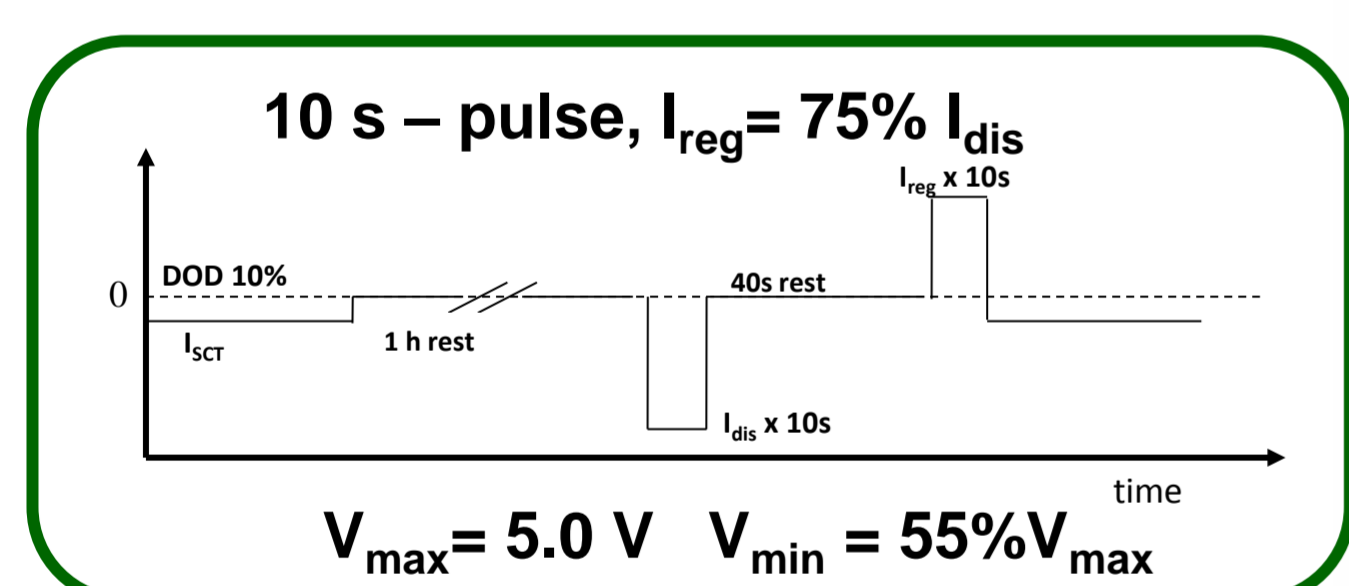


Discharge voltage profile (solid line) and cumulative specific energy (dashed line) at 2C effective rate at different DOD of the cells with (a) PVdF-NCC, 3.55 mA cm⁻² and (b) Celgard, 2.12 mA cm⁻².

Hybrid Pulse Power Characterization tests at 5C

Full cell with PVdF-NCC separator

Cell voltage profile over HPPC at 5C



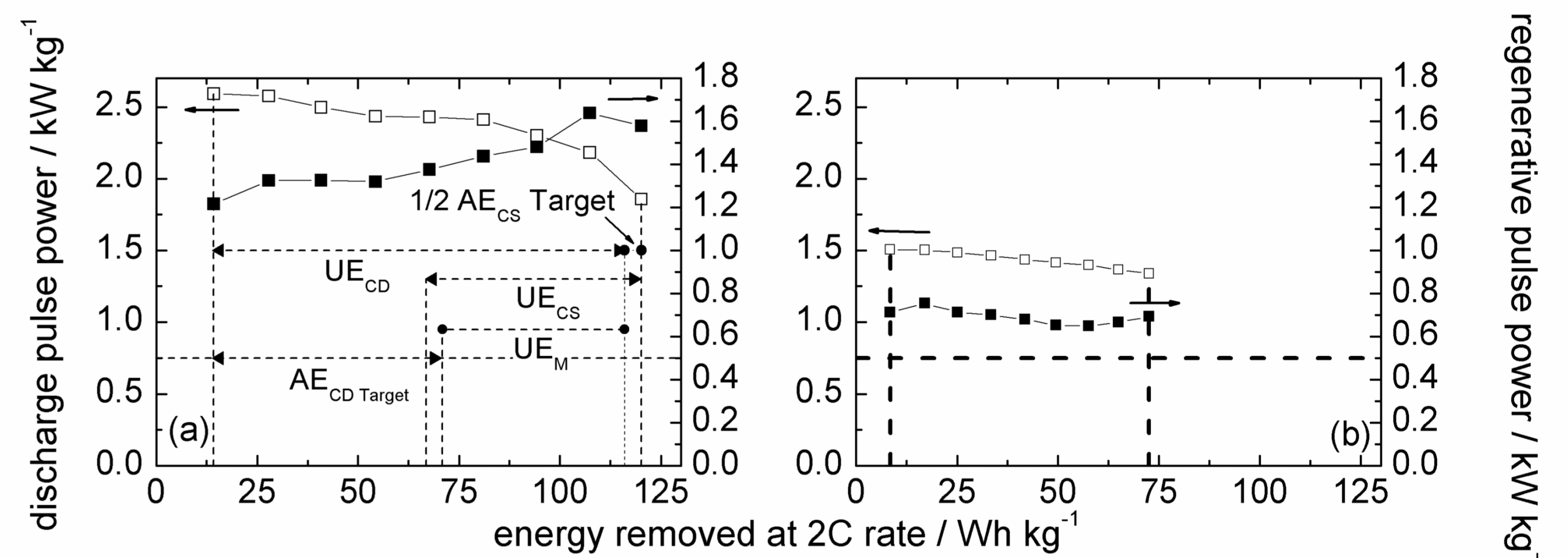
Discharge (empty symbol) and regenerative (full symbol) pulse resistances vs. DOD% from 5C HPPC on cells with PVdF-NCC and Celgard®2400 separators.

$$R_{dis} = (V_1 - V_0) / I_{dis}$$

$$R_{reg} = (V_3 - V_2) / I_{reg}$$

$$P_{dis} = V_{min} (V_0 - V_{min}) / (R_{dis} W_{battery})$$

$$P_{reg} = V_{max} (V_{max} - V_2) / (R_{reg} W_{battery})$$



Discharge (empty symbol) and regenerative (full symbol) pulse power from 5C HPPC tests on cells with PVdF-NCC (a) and Celgard®2400 (b) separator

Useable energies for CS and CD modes (UE_{CS} and UE_{CD}) and energy margin (UE_M)

$$UE_{CS} = (E_{90\%DOD} - E_{10\%DOD}) - (AE_{CD Target} - \frac{1}{2} AE_{CS Target})$$

$$UE_{CD} = (E_{90\%DOD} - E_{10\%DOD}) - \frac{1}{2} AE_{CS Target}$$

$$UE_M = (UE_{CD} - AE_{CD Target}) = (UE_{CS} - AE_{CS Target})$$

Experimental E_{SCT}, UE_{CD}, UE_{CS} and UE_M values of full cells with different separators, and the DOE energy targets AE_{CS Target} and AE_{CD Target} for different PHEV types.

Plug-in SCT&HPPC tests	E _{SCT} Wh kg ⁻¹	Minimum PHEV				Medium PHEV				Maximum PHEV						
		UE _{CD}	UE _{CS}	UE _M	AE _{CD Target}	AE _{CS Target}	UE _{CD}	UE _{CS}	UE _M	AE _{CD Target}	AE _{CS Target}	UE _{CD}	UE _{CS}	UE _M	AE _{CD Target}	AE _{CS Target}
LP30 - 1.6% F ₁ EC - 2% SA																
PVdF-NCC (23 μm)	132	102	53	45	57	8	104	25	21	83	4	105	10	8	97	3
Celgard®2400 (25 μm)	79	60	12	3	-	-	62	-	-	-	-	63	-	-	-	-

Conclusions

The results of the electrochemical tests on high-voltage laboratory graphite/LiNi_{0.4}Mn_{1.6}O₄ cells with optimized electrode formulation and high-mass electrode loading for the high-energy demanding plug-in applications show the strong effect of the separator on cell performance. Unlike cells with Celgard®2400, which not displayed usable energy values with satisfactory energy margin, cells with PVdF-NCC macroporous membrane displayed usable energy values exceeding the targets even for Medium PHEVs.

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