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# Rheological and electrochemical characterization of biopolymer binders in lithium-ion batteries

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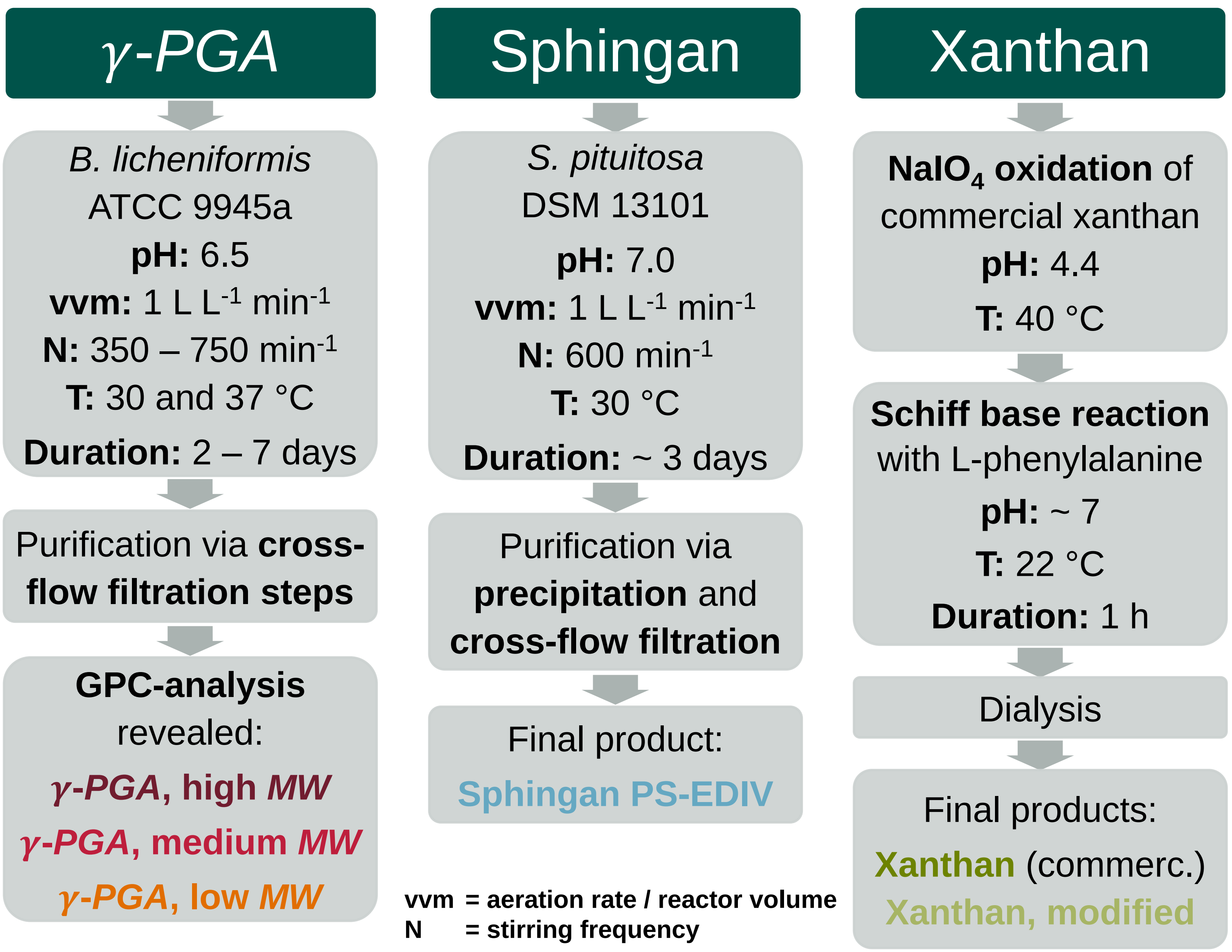
## Motivation & approach

- Improvement of sustainability, capacity and security of lithium-ion batteries (*LIBs*)
- Water-soluble $\gamma$-polyglutamic acid, branched sphingan and xanthan biopolymers are used as binder for anode active material
- Effect of polymer molecular weight (*MW*) and functional groups on electrode integrity, rheological properties and cycling performance

## Biopolymer production & modification



**$\gamma$-PGA**

*B. licheniformis*
ATCC 9945a
**pH:** 6.5
**vvm:** 1 L L$^{-1}$ min$^{-1}$
**N:** 350 – 750 min$^{-1}$
**T:** 30 and 37 °C
**Duration:** 2 – 7 days

Purification via **cross-flow filtration steps**

**GPC-analysis** revealed:
**$\gamma$-PGA, high *MW***
**$\gamma$-PGA, medium *MW***
**$\gamma$-PGA, low *MW***

**Sphingan**

*S. pituitosa*
DSM 13101
**pH:** 7.0
**vvm:** 1 L L$^{-1}$ min$^{-1}$
**N:** 600 min$^{-1}$
**T:** 30 °C
**Duration:** ~ 3 days

Purification via **precipitation** and **cross-flow filtration**

Final product:
**Sphingan PS-EDIV**

**Xanthan**

**$NaIO_4$ oxidation** of commercial xanthan
**pH:** 4.4
**T:** 40 °C

**Schiff base reaction** with L-phenylalanine
**pH:** ~ 7
**T:** 22 °C
**Duration:** 1 h

Dialysis

Final products:
**Xanthan** (commerc.)
**Xanthan, modified**

**vvm** = aeration rate / reactor volume
**N** = stirring frequency

## Biopolymer suitability as anode binder

- Structural and chemical properties of polymeric binders significantly affect structural electrode integrity before and during cell cycling
- Coating adhesion strength is a critical property for electrode quality
- High *MW* $\gamma$-*PGA* an xanthan and can compete with common polyvinylidene difluoride (*PVDF*) electrode binder
- Higher electrode stability due to polymeric network formation and more contacts to the active material and current collector
- Low *MW* polymers result in lower adhesion strength of the active material

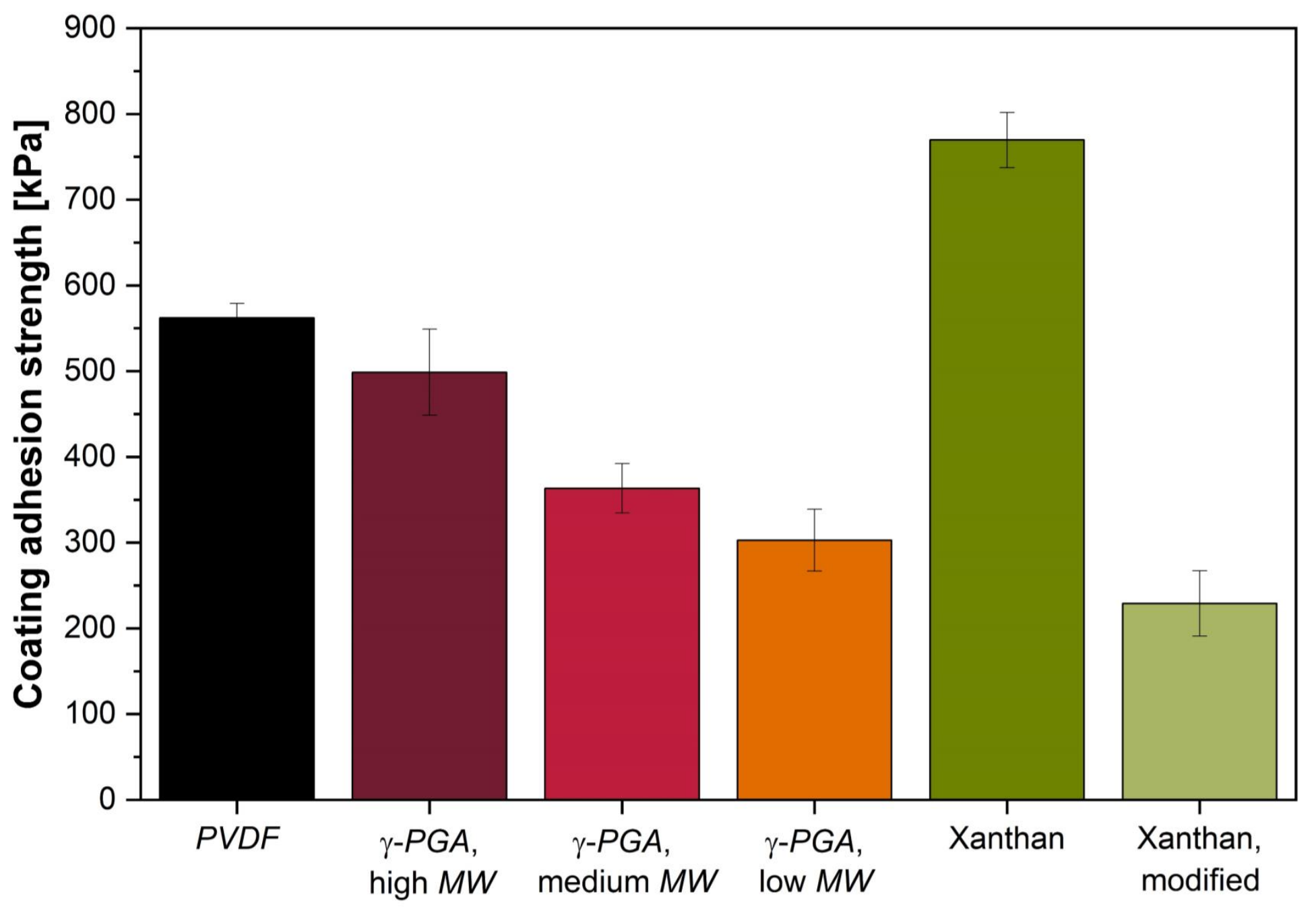
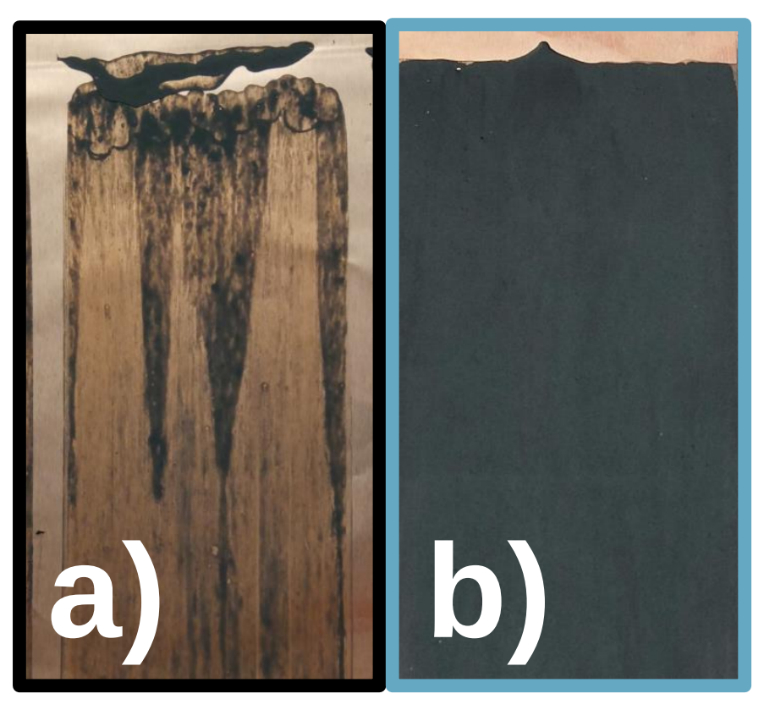


*Fig. 1: Effect of different biopolymers on coating adhesion strength of LIB graphite anodes using pull-of tests; electrode slurry consisted of 90 % graphite, 5 % carbon black and 5 % biopolymer binder; n = 5.*

## Rheological binder solution properties

- Anodes with sphingan as single binder not successful (*Fig*. 2 a))
→ dominating storage modulus G' (solid) over loss modulus G'' (viscous) of the binder solution indicated by a phase shift $\delta$ < 45 °
- Combination with carboxymethylcellulose (*CMC*) results in a xanthan-like flow point $\boldsymbol{\tau_f}$ and processability (*Fig*. 2 b))

*Fig. 2: Anodes with 100 % sphingan (a) or 45:55 % sphingan:CMC (b) binder solution.*



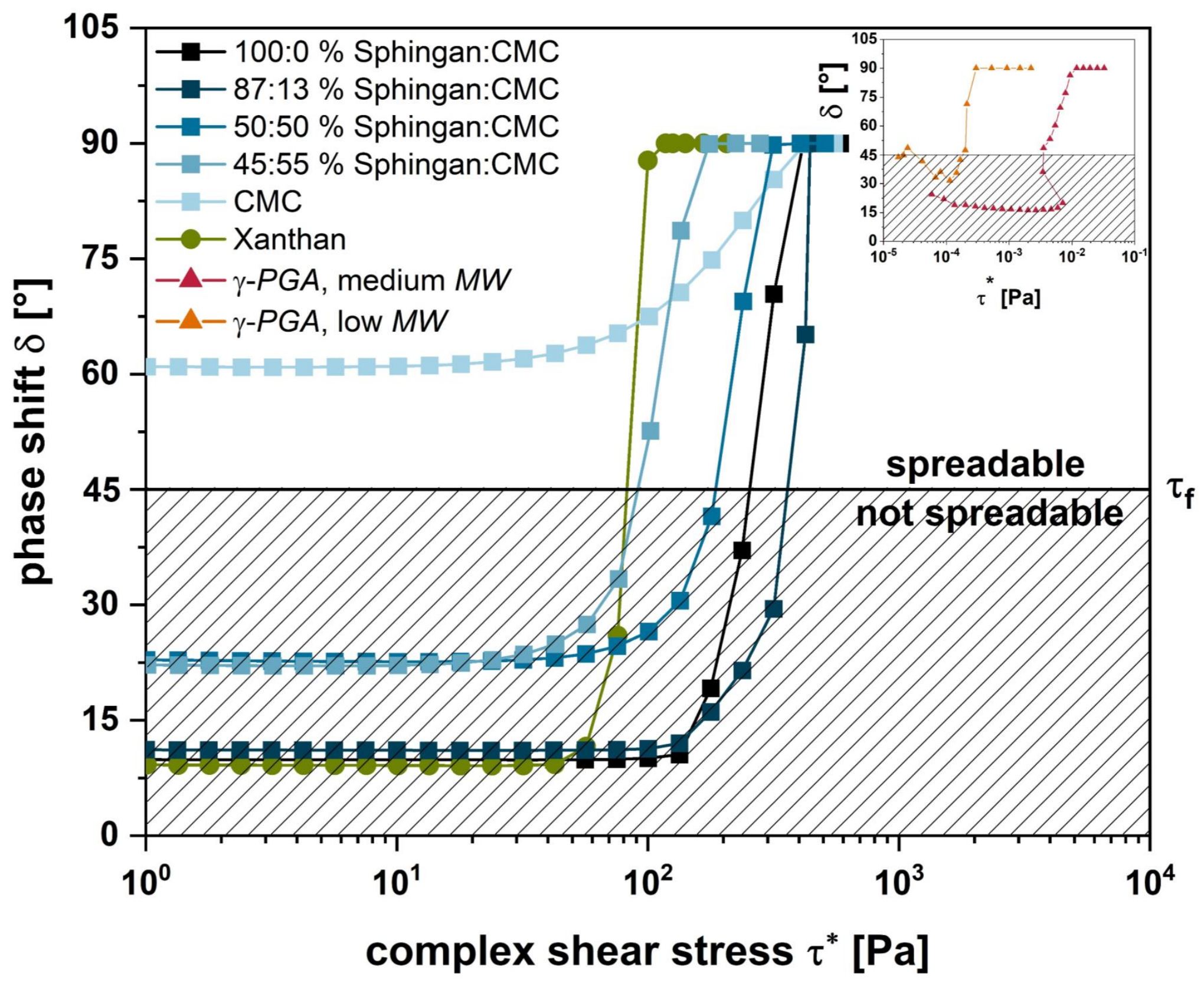


*Fig. 3: Oscillatory shear stress amplitude sweep of 50 g L$^{-1}$ binder solutions at f = 1.6 s$^{-1}$ (≈ ω = 10 rad s$^{-1}$) and 25 °C using parallel plate geometry with 1 mm gap distance. $\boldsymbol{\tau_f}$ indicates the flow point of the solution at a phase shift 45 °.*

## Cycling of anodes in *LIB* full cells

- Highest capacities but with lower state of health ($SoH_{100}$) after 100 charge/discharge cycles for biopolymers with lower *MW* (low *MV* $\gamma$-*PGA* and modified xanthan)
- Highest $SoH_{100}$ for $\gamma$-*PGA* (high *MW*), *PVDF* and xanthan
- Higher $SoH_{100}$ correlates with adhesion strength (*Fig*. 1)

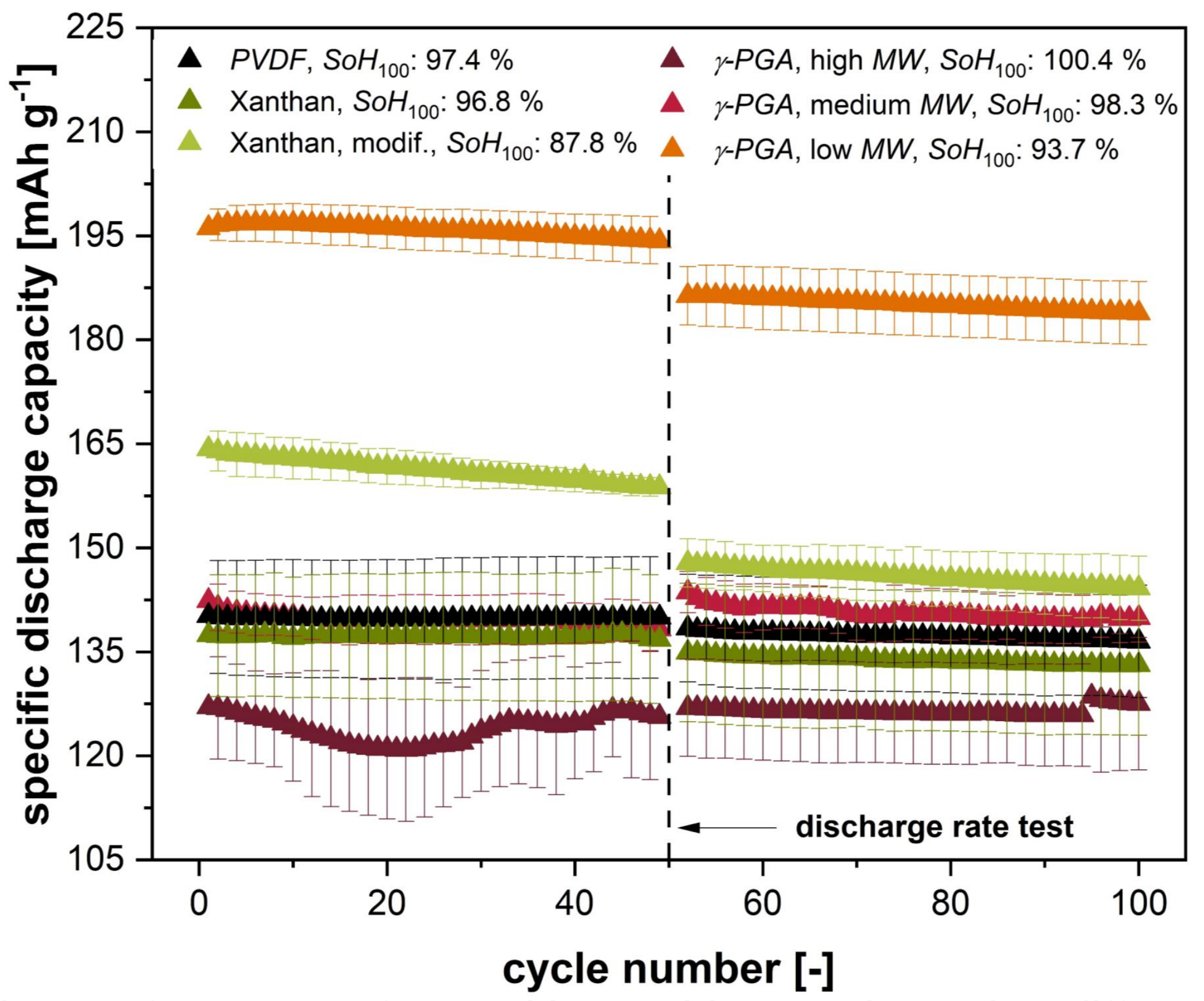


*Fig. 4: Cycling performance of LIB with graphite anodes using different binders vs. lithium nickel manganese cobalt oxide (NMC 622) cathodes at 20 °C and charge/discharge rate of 2 C between 2.9 and 4.2 V, n = 3.*

## Conclusion & outlook

- Combinations with *CMC* make sphingan rheologically accessible as binder polymer for *LIB* anodes
- Possible trade-off between *LIB* capacity and cycle life/adhesion strength depending on biopolymer and its respective *MW*

➢ Cycling and adhesion strength analysis of sphingan:CMC anodes

➢ Applying polymers with high $SoH_{100}$ to more demanding but powerful silicon anodes