Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2023

Enzymatically demethylated pectins: from a fruit waste to an outstanding polymer binder for silicon-based anodes of Li-ion batteries

Mariama NDOUR^{a,b}, Jean-Pierre BONNET^b, Sébastien CAVALAGLIO^b, Tristan LOMBARD^b, Josip Safran^c, Corinne Pau-Roblot^c, Véronique BONNET^a*

^{a.} Laboratoire de Glycochimie, des Antimicrobiens et des Agroressources, (UR 7378), Université de Picardie Jules Verne, 33 Rue Saint Leu, 80039 Amiens Cedex, France.

^{b.} Laboratoire de Réactivité et Chimie des Solides (CNRS UMR 7314), Université de Picardie Jules Verne, 33 Rue Saint Leu, 80039 Amiens Cedex, France.

^{c.} UMRT INRAE 1158 BioEcoAgro - BIOPI Biologie des Plantes et Innovation, SFR Condorcet FR CNRS 3417, Université de Picardie Jules Verne, 33 Rue Saint Leu, 80039 Amiens Cedex, France.

* corresponding author: veronique.bonnet@u-picardie.fr.

Supporting Information

Figure S1 FTIR of high methylated citrus pectin (DM = 76%, Mw = 50 kg/mol) (CP1), low methylated citrus pectin (DM = 50%, Mw = 98 kg/mol) (CP2) and apple pectin (DM = 55%, Mw = 262 kg/mol) (AP)	2
Figure S2 TGA curves of of high methylated citrus pectin (DM = 76%, Mw = 50 kg/mol) (CP1), low methylated citrus pectin (DM = 50%, Mw = 98 kg/mol) (CP2) and apple pectin (DM = 55%, Mw = 262 kg/mol) (AP)	2
Figure S3 ¹³ C CPMAS NMR spectra of chemically demethylated citrus pectin (CDCP1) compared to commercial pectin CP1	3
Figure S4 FTIR spectra of chemically demethylated citrus pectin (CDCP1) and chemically demethylated apple pectin (CDAP)	3
Figure S5: Normalized SEC-RI molar mass distribution profiles of CP1, CDCP1, AP and CDAP (by shomical demotivation) oluted in H.O.(NaNO. (NaN	3
Figure S6 Normalized SEC-RI molar mass distribution profiles of CP1 and EDCP1 (by enzymatic demethylation) eluted in $H_2O/NaNO_3/NaN_3$	4
Figure S7 FTIR of EDCP1-2, DM = 8%), EDCP1-3, DM = 3% compared to CP1	4
Figure S8 SEM images of silicon-based electrodes CP1 as binder from formulation 1 (Spex + magnetic stirring) and 2 Turbula [®] + magnetic stirring	4
Table S1 Summary of the physico-chemical characteristics of the different pectins and electrodes formulated	5
Figure S9 SEM images of silicon-based electrodes with (a) CP1, (b) CP2 and (c) CDCP1 as binder from formulation 1 (Spex + magnetic stirring)	5
Figure S10 Electrochemical tests, (a) Galvanostatic curve of the 1 st capacity loss of a Si/Li half- cell with CP1 as a polymer binder at loading of 1, 1.5 and 1.6 mg/cm ² , Comparison of silicon capacity retention of (b) CP1 based anodes after 25 cycles at loading of 1, 1.5 and 1.6 mg/cm ² and (c) CP2 based anodes after 20 cycles at loading of 1 and 1.6 mg/cm ²	6
Figure S11 : Electrochemical galvanostatic curves of the 1 st and 2 nd losses of capacity of Si / Li cell of silicon composite-based electrodes for A) commercial apple pectin (AP purple) B)24%	7

enzymatically demethylated citrus pectin (EDCP1-Pink), C) 28% chemically demethylated apple pectin (CDAP- Orange), D) 24% chemically demethylated) citrus pectin (CDCP1- green), E) commercial 50% methylated citrus pectin (CP2 - blue), F) commercial 76% methylated citrus pectin (CP1 - black), G) sodium carboxymethylcellulose (CMC90 - black), and H) sodium polygalacturonic acid (PGANa - red).



Figure S1 FTIR of high methylated citrus pectin (DM = 76%, Mw = 50 kg/mol) (CP1), low methylated citrus pectin (DM = 50%, Mw = 98 kg/mol) (CP2) and apple pectin (DM = 55%, Mw = 262 kg/mol) (AP)



Figure S2 TGA curves of of high methylated citrus pectin (DM = 76%, Mw = 50 kg/mol) (CP1), low methylated citrus pectin (DM = 50%, Mw = 98 kg/mol) (CP2) and apple pectin (DM = 55%, Mw = 262 kg/mol) (AP)



Figure S3: 13C CPMAS NMR spectra of chemically demethylated citrus pectin (CDCP1) compared to commercial pectin CP1



Figure S4 FTIR spectra of chemically demethylated citrus pectin (CDCP1) and chemically demethylated apple pectin (CDAP)



Figure S5 Normalized SEC-RI molar mass distribution profiles of CP1, CDCP1, AP and CDAP (by chemical demethylation) eluted in $H_2O/NaNO_3/NaN_3$



Figure S6 Normalized SEC-RI molar mass distribution profiles of CP1 and EDCP1 (by enzymatic demethylation) eluted in $H_2O/NaNO_3/NaN_3$



Figure S7 FTIR spectra of EDCP1-2 (DM = 8%), EDCP1-3 (DM = 3% compared to CP1

(b)

(a)





Figure S8 SEM images of silicon-based electrodes CP1 as binder from formulation 1 (Spex + magnetic stirring) and 2 Turbula[®] + magnetic stirring

Table S1. Physico-chemical characteristics of the formulations with the different pectins and loading, porosity, adhesion measured.

Pectins	DM (%)	Mw (kg/mol)	Buffer solution (mL)	Slurry pH	Loading (mg/cm ²)	Porosity %	Adhesion
CP1	76	50.2	0.5	3.25	1.6	69	3B
CP2	50	9.7	0.7	3.25		75	3B
AP	55	262	0.6	3.25		75	3B
CDCP1	24	26	0.5	3.05		65	3B
CDAP	28	18.2	0.5	3.05		65	3B
EDCP1	24	49.5	0.6	3.05		65	3B

(a)

(b)





(c)



Figure S9 SEM images of silicon-based electrodes with (a) CP1, (b) CP2 and (c) CDCP1 as binder from formulation 1 (Spex + magnetic stirring)



Figure S10 Electrochemical tests, (a) Galvanostatic curve of the 1st capacity loss of a Si/Li half-cell with CP1 as a polymer binder at loading of 1, 1.5 and 1.6 mg/cm², Comparison of silicon capacity retention of (b) CP1-based anodes after 25 cycles at loading of 1, 1.5 and 1.6 mg/cm² and (c) CP2-based anodes after 20 cycles at loading of 1 and 1.6 mg/cm²



Capacity (mAh/g)

В

А





Capacity (mAh/g)





Ε



D



Figure S11 : Electrochemical galvanostatic curves of the 1st and 2nd losses of capacity of Si / Li cell of silicon composite-based electrodes for A) commercial apple pectin (AP purple) B)24% enzymatically demethylated citrus pectin (EDCP1-Pink), C) 28% chemically demethylated apple pectin (CDAP- Orange), D) 24% chemically demethylated) citrus pectin (CDCP1- green), E) commercial 50% methylated citrus pectin (CP2 - blue), F) commercial 76% methylated citrus pectin (CP1 - black), G) sodium carboxymethylcellulose (CMC90 - black), and H) sodium polygalacturonic acid (PGANa - red).