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β -cyclodextrin and adamantane polyacrylic acid copolymers as supramolecular binder for silicon anodes: N-methylpyrrolidone or water for preparing the slurries?

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Abstract:

Silicon is a promising material for anodes in future generations of LIBs. However, its volume changes during the lithiation/delithiation process that degrades battery performance, making it an impractical alternative. To mitigate this issue, we have found a viable alternate solution, which is the preparation of adamantane-polyacrylic acid (AdEN-AA) and β -cyclodextrin-polyacrylic acid (β CD6A-AA) polymers as supramolecular binders. The advantage of these binders is that polymers leverage host-guest interactions. To carry out this research, we prepared the anode materials in water and in NMP, and then we studied their capacity to crosslink and gel. Additionally, we examined the extent of the supramolecular interaction vs. hydrogen bond. Thermogravimetric analysis showed that the thermal stability of the mixture of complementary polymer increased in the following order: AdEN-AA/ β CD6A-AA in NMP < β CD6A-AA/PAA < AdEN-AA/ β CD6A-AA, with the latter two in water. Accordingly, the anode material prepared in water shows the highest

stability, retaining capacities of over 1000 mAhg⁻¹ after 90 cycles vs. 279 mAhg⁻¹ of the electrode prepared in NMP. The results agreed with the SEM micrographs of the anode material, in which the slurry prepared in water showed better integrity of the silicon nanoparticles and of solid electrolyte interphase than the slurry prepared in NMP.

Keywords: carbohydrate-containing polymer binders, supramolecular crosslinking, silicon anodes, energy storage

1. Introduction.

It is impossible to conceive of modern life without the use of portable electronic devices (smart phones, tablets, laptops, e-books, PADs, etc.) along with the satellites that connect them to the internet. (Borthomieu, 2014) In this era of portability, lithium-ion batteries (LIBs) are responsible for powering the devices which must not only function daily, but also with enough power to run all the applications required of them. In parallel, humanity is seeking out a long-term plan for successful technological integration, but this comes with a high environmental cost that threatens its own sustainability. In this regard, it is fundamental to use environmentally-friendly power sources and the energy storage devices they require to achieve these environmental goals. The limited oil resources and the environmental impact from the CO₂ emissions of vehicles driven by internal combustion engines has driven us toward electromobility. Once again, LIBs represent the heart of this new era. (Bajolle, Lagadic, & Louvet, 2022; Frith, Lacey, & Ulissi, 2023)

Sales of electric vehicles (EVs) doubled in 2021 from the previous year (6.6 millions) and it is expected that by 2030, 30% of vehicles sold will be electric. The demand for high-capacity LIBs to power the future of EVs is imminent. In LIBs, the anode material is composed of carbon graphite with a maximum theoretical gravimetric capacity of 372 mAh g⁻¹ (LiC₆). (Timur, Pales, & Elizabeth Connelly, 2023)

Silicon has a high theoretical capacity, both at its partial (Li₁₅Si₄, 3580 mAh g⁻¹) or complete (Li₂₂Si₅, 4200 mAhg⁻¹) lithiation. Additionally, silicon has a low lithiation/delithiation potential (0.5 V vs. Li⁺/Li), and it has the advantage of being both the

second most abundant element on the Earth's crust and environmentally friendly (not toxic). (Ramdhiny & Jeon, 2023; Warner, 2019)

A critical drawback of Si-based anodes is its volume expansion-contraction (~300%) upon full lithiation/delithiation ($22\text{Li} + 5\text{Si} \rightleftharpoons \text{Li}_{22}\text{Si}_5$). This volume change yields to fading mechanisms, such as comminution of large active material particles, slackened film contacts between Si and carbon conductive agents, delamination of the current collector, and destabilization of solid-electrolyte interphase (SEI) over extended cycles. This undesirable behavior can be partially mitigated by controlling the size and morphology of silicon particles and by designing polymer binders with self-healing properties to release the stress created by the continuous volume expansion/contraction. (Bétermier et al., 2023)

Current LIBs use polyvinylidene difluoride (PVDF) as polymer binders to hold the active materials together and to attach them to the anode and current cathode collectors. However, due to the weak Van der Waals interaction, PVDF inefficiently binds the Si anode materials and does not contribute to the self-healing of cracked particles caused by its large volume expansion. This leads to a rapid capacity fading. (Ramdhiny & Jeon, 2023)

Natural bioinspired materials, like mussel and millipede adhesion which uses covalent cross-linking; hyper-branched, conductive, and self-healable polymers, are some of the approaches to enhancing the performance of Si anodes. Ideally, for achieving a long cycle life of LIBs, it is desirable that the lithiation and delithiation processes, along with the respective volume expansion and contraction of Si anode, be reversible. Therefore, the interactions between the polymer chains of the binder must also be reversible, as is the case in supramolecular interactions. (Tae woo Kwon, Choi, & Coskun, 2019) Sodium carboxymethylcellulose (Na-CMC), sodium alginate, and polyacrylic acid (PAA) are some of the most commonly used commercial binders for silicon anodes. (Lim et al., 2023; Lin, Wang, & Hong, 2022; Liu, Yang, Wu, Chiao, & Wu, 2005; Magasinski et al., 2010; Schlemmer, Selinger, Hobisch, & Spirk, 2021) The carboxylic acid groups in their structure interacts, via H-bonds, with the silanol groups (Si-OH) on the silicon surface and between polymer chains.

Previous research has pointed out that combining different types of interactions (supramolecular Host-Guest, π - π stacking, H-bond, electrostatic, etc.) in an all-in-one system improves the binder's properties and the performance of silicon anodes. (Sudhakaran & Bijoy, 2023) Jeong *et al.* prepared an effective multidimensional binder based on a blend of β -cyclodextrin epichlorohydrin crosslinked (β CDp) polymer and linear alginate polymer. In this approach, the hydroxyl groups, from hyperbranched β CDp, bind the Si surface via multiple hydrogen bond interactions, and the alginate controls the aggregations of β CDp units through repulsive electrostatic interactions between the carboxylate and hydroxyl groups. After 100 cycles, the anode showed a gravimetric capacity of 1400 mAhg⁻¹ at 1C, for a polymer blend containing 13% of alginate and 87% β CDp. (Jeong *et al.*, 2014) Recently, Zheng *et al.* prepared a 3D polymer binders' network using thermal-induced covalent crosslinking of β -CD-1,4-butanediol diglycidyl ether polymer with PAA and partially neutralized sodium polyacrylate (PAAS) at different ratios. Under these conditions, covalent, ionic, and H-bond interaction were considered to drive the properties of the whole system. Thus, the electrode prepared with the PAAS₆- β -CDp₁-PAA₃ composition, and cycled at C/20 c-rate, exhibited a discharge-specific capacity of 3869 mAhg⁻¹ and 2513 mAhg⁻¹, for the first and 100th cycle, respectively. (Zheng *et al.*, 2023) In another report Lin *et al.* prepared a similar system but with a previously crosslinked β CD using epichlorohydrin instead of 1,4-butanediol diglycidyl ether as crosslinking agent. The 3D polymer binder networks were obtained by thermal-induced crosslinking with PAA. After 100 cycles the electrode with the best performance (PAA-20 β -CDp) showed a specific capacity of 1488 mAg⁻¹, 35.4% lower than the initial value. (Lin *et al.*, 2022). None of these works explore the capacity of cyclodextrins to form inclusion complexes with a wide variety of guests as supramolecular interaction for preparing polymer binders.

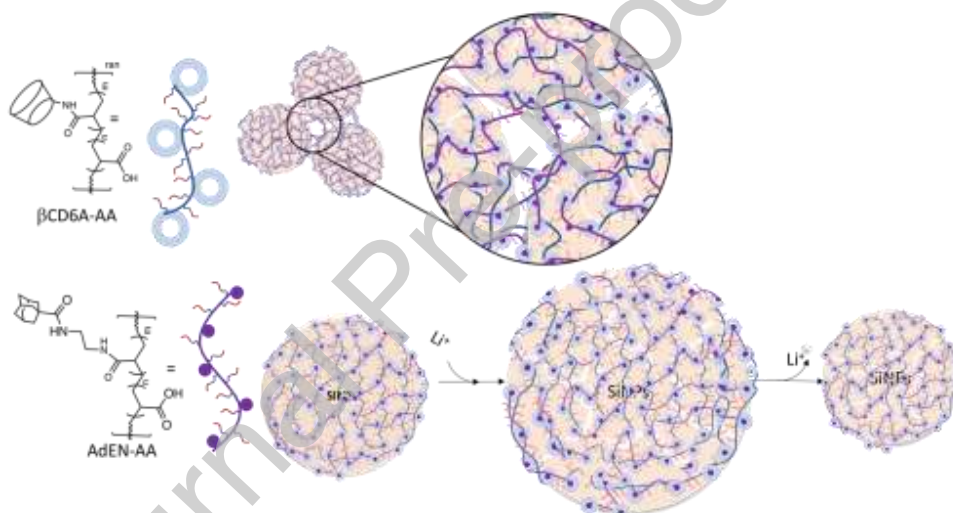
Based on this approach, Kwon *et al.* used β CDp as a host and prepared a compound with six adamantane pendant moieties as a multi-guest. The system resulted in a dynamic crosslinker in a supramolecular fashion. This anode showed a gravimetric capacity of 1800 mAhg⁻¹ after 100 cycles at 0.5 C. (Tae-woo Kwon *et al.*, 2015) An outstanding result of

silicon microparticle-composed anodes was obtained by *Choi et al.*, in which the principle of a dual polymer binder in a pulley fashion was applied. The molecular pulley consists of an α -cyclodextrin-PEG polyrotaxanes, with some of the sliding units of α -CD linked to a polyacrylic acid polymer (PAA). This binder combination allowed for the pulverized silicon particles to remain joined, leading to a stable cycle life of silicon anodes with real capacities similar to those of commercial LIBs.(Choi, Kwon, Coskun, & Choi, 2017b) Moreover, Bétermier et al. recently synthesized a series of polyrotaxanes using α -CDs linked to PAA, with polyethylene oxide sliding within the cyclodextrin cavity. By varying the doping ratio of polyrotaxanes, the cross-linking density, as well as the polymer molecular weight and the ring coverage, the authors studied the effects of the structure/composition of the mechanically interlocked system and their performance as a binder for silicon anodes. Values of specific initial capacity higher than 3000 mAhg^{-1} with 82% of capacity retention after 100 cycles were achieved.(Bétermier et al., 2023)

The study of binary association via inclusion complexes of polyacrylic acid polymers (PAA) with pendant cyclodextrin (β CD) and hydrophobic moieties such as adamantane (Adm), was first addressed by Prud'Homme et al.(Guo et al., 2005, 2010; Li et al., 2008; Wang et al., 2010) β CD and Adm were grafted onto a PAA polymers at different ratios via amide linkages. Ethylenediamine, 1,6-hexamethylenediamine and 1,12-dodecylmethylenediamine were used as tethers of different lengths. The rheological studies showed that the extent of polymer interaction was maximized at stoichiometric amounts of β CD and Adm.(Li et al., 2008) Competition between methylene groups in tethers and Adm for the β CD cavity was observed for the longest tethers (1,6-hexamethylenediamine and 1,12-dodecylmethylenediamine). The binary interaction between β CD and Adm resulted in supramolecular crosslinked polymer networks.(Wang et al., 2010) Self-healing properties of host-guest supramolecular complementary linear co-polymers, using β -cyclodextrin and adamantane have already been addressed.(Cai, Huo, Wang, Sun, & Tong, 2018)

Guided by the hypothesis: *"In polymers containing carbohydrates, the reinforcement of the hydrogen bond by host-guest supramolecular interactions enhances the binder properties of these polymers in preparing silicon anodes"*, in this work we prepared two

PAA copolymers carrying Adm and β CD, as depicted in Scheme. 1a). The polymers were designed according to the concept of host-guest supramolecular binders. The dynamic binder properties arise from the interaction of the carboxylic acid group in the PAA backbone with hydroxyl groups on the silicon surface via hydrogen bonds (red traces in Scheme 1), whereas the pendant β CD and Adm interact via host-guest ($K_{incl}=10^4$). As will be demonstrated, the slurries prepared in N-methylpyrrolidone (NMP), a common solvent used in the preparation of commercial electrodes, showed lower charge-discharge performance (gravimetric capacity value) than those prepared in water; an environmentally-friendly formulation. Additionally, we established that host-guest supramolecular interaction is mandatory for a good performance by the electrode.



Scheme 1: a) Representation of the copolymers and their host-guest effects as supramolecular binders for silicon anodes. Red lines represent the carboxylic acid groups from PAA, which interacts with the silicon surface via H-bond. **Reversible, H-bond and host-guest interaction should reestablish the silicon structure upon going through lithiation/delithiation processes.**

2. Experimental.

2.1. Chemicals

6-monodeoxy-6-monoamino- β -cyclodextrin (NH_2 - β CD, >95%) was purchased from Cyclolab Hungary. Anhydrous dimethylformamide (DMF), adamantane-1-carbonyl chloride (AdCOCl, >95%), triethylamine (Et_3N , >99%), benzoyl chloride (BzCOCl, >99%), Acrylic acid ($\geq 99\%$), thionyl chloride ($\geq 98\%$) and Silicon nanoparticles (SiNPs, $d_{\text{average}}=100$ nm, $\geq 98\%$) were purchased from Sigma-Aldrich. N-Boc-ethylenediamine (N-Boc-Et, >98%) was purchased from Aksci.Inc. Ammonium persulfate (>98%), sodium chloride (>99%) and sulfuric acid ($\geq 98\%$) were purchased from Merck. Acrylyl chloride was freshly prepared according to Ref. (Stempel, Cross, & Mariella, 1950) Super P conductive carbon black was purchased from MTI Corp.

2.2. Preparation of monomers.

2.2.1. Preparation of N-(2-acrylamidoethyl)adamantane-1-carboxamide (AdENAc)
N-Boc-ethylenediamine (3.52 g, 22 mmol) and triethylamine (2.22 g, 22 mmol) were added to a round-bottom flask with dichloromethane (50 mL). The solution was cooled to 0 °C in an ice bath through constant stirring. Adamantane-1-carbonyl chloride (4.00 g, 20 mmol), previously dissolved in dichloromethane (10 mL), was dropwised over 30 min and the resulted mixture was stirred at r.t. The formation of amide was followed by ATR-FTIR, by comparing the band intensity of carbonyl stretching ($-\text{C}=\text{O}$) from the carbamate and carbamoyl groups at 1687 and 1626 cm^{-1} , respectively. The reaction mixture was poured into a separatory funnel and washed exhaustively with saturated NaHCO_3 , brine and water. The organic phase was dried over anhydrous Na_2SO_4 , and the solvent removed to dryness. The white precipitated corresponding to tert-butyl (2-(adamantane-1-carboxamido)ethyl)carbamate, was dried overnight in a vacuum oven at 60 °C. N-Boc deprotection was carried out using the solvent-free method described by Borggraeve et al. (Verschueren, Gilles, Van Mileghem, & De Borggraeve, 2021) The vanishing of the carbonyl group from carbamate at 1687 cm^{-1} indicates the full conversion of the reaction. The ammonium salt of adamantane derivative (2-(adamantane-1-carboxamido)ethan-1-aminium) was dissolved in chloroform (20 mL) and stirred for 2 hours, with Na_2CO_3 . The

solution was filtered through a piece of cotton wool and the solvent evaporated, becoming completely dry, to obtain the amine derivative N-(2-aminoethyl)adamantane-1-carboxamide, as a white solid.

N-(2-aminoethyl)adamantane-1-carboxamide (1.00 g, 4.5 mmol) and triethylamine (0.45 g, 4.45 mmol) were dissolved, through constant stirring, in DCM and the solution was cooled at 0 °C in an ice bath. A solution of DCM (10 mL) containing freshly prepared acryloyl chloride (0.61 g, 6.72 mmol, 1.5 eq.) was added dropwise and the mixture was stirred at r.t, overnight. The reaction mixture was poured into a separatory funnel and washed thoroughly with saturated NaHCO₃, brine and water. The organic phase was dried over anhydrous Na₂SO₄, and the solvent was removed to dry. The solid was dried in a vacuum oven overnight to obtain corresponding 1.05 g (81%) of AdENAc. IR (ATR-FTIR): ν , cm⁻¹ 3274 (m, NH), 3071, 3066 (w, Csp²-H), 2924 (m, CH), 2847 (w, CH), 1658 (s, C=O), 1625 (s, C=O), 1550 (s, NH bending), 1436 (w, δ (CH₂)). ¹H-NMR (200 MHz, CDCl₃): δ , ppm 7.10 (s, 1H, amida), 6.57 (s, 1H, amida), 6.21 (m, 2H, vinyl), 5.62 (dt, 1H, vinyl), 3.43 (q, 4H, -CH₂-), 2.09-1.57 (adamantane, 15H).

2.2.2. Preparation of 6-monodeoxy-6-monoamidoacrylyl- β -cyclodextrin (β CD6Acr)
 β CD6Acr was prepared according to the procedure reported by Pu et al. (Pu, Yang, Wei, & Yuan, 2016) To briefly summarize, in a round bottom flask, 6-monodeoxy-6-amino- β -cyclodextrin (β CD6-NH₂) (1.0 g, 0.9 mmol) and triethylamine (0.1 g, 0.99 mmol) were dissolved, and added through constant stirring, in anhydrous DMF (15 mL) at 0 °C. Afterward, acryloyl chloride (0.1 g, 0.99 mmol) dissolved in DMF (5 mL), was added dropwise for over 30 min and the mixture was set to react overnight. The reaction was poured in acetone (20 mL) and a white precipitate was obtained. The solid was filtered, washed with copious acetone, and set to dry in a vacuum oven overnight to obtain 0.98 g of β CD6Acr (88%) as a white solid IR (ATR-FTIR): ν , cm⁻¹ 3323 (m, broad, -OH), 2924 (m, CH), 1660 (s, -C=O), 1154, 1079, 1029 (stretching and bending vibration modes of α -glucopyranoside in β CD). ¹H-NMR (200 MHz, D₂O): δ , ppm 7.87 (s, 1H), 6.39 – 6.09 (m, 2H), 5.72 (dt, 1H), 5.04 (dtd, 7H), 4.11 – 3.68 (m, 25H), 3.65 – 3.27 (m, 18H).

2.3. Preparation of polyacrylic acid co-polymers containing β CD6Acr and AdENAc.

2.3.1. Preparation of β CD6A-AA

β CD6Acr (0.2 mmol) was dissolved in 1.5 mL of water in a Schlenk flask, and the solution was gently fluxed with N_2 for 30 min. Afterward, acrylic acid (2 mmol, 10 eq.) was added to the solution and $(NH_4)_2S_2O_8$ (0.01 mmol) was poured into the mixture. The mixture was set to react for 45 min at 65 °C (longer times should be avoided since the mixture gels). The resulted viscous mixture was poured into acetone to precipitate the copolymer β CD6A-AA. The polymer was purified by filtering through a 10 kDa cellulose membrane (Merck) in an Amicon cell, for 48 h in a steady-state flux.

2.3.2. Preparation of AdEN-AA

AdENAc (0.2 mmol) was dissolved in 2.0 mL of DMF in a Schlenk flask, and the solution was gently fluxed with N_2 for 30 min. Afterward, acrylic acid (2 mmol, 10 eq.) was added to the solution and benzoyl peroxide (0.01 mmol) was poured into the flask. The mixture was set to react for 2 hours at 65 °C, and the resulted viscous polymer solution precipitated in acetone. The precipitate was washed with acetone to remove the unreacted monomers. The polymer was purified by filtering through a 10 kDa cellulose membrane (Merck) in an Amicon cell, for 48 h in a steady-state flux.

2.4. Preparation of silicon anodes and electrochemical characterization.

Slurries of silicon anodes were prepared in N-methyl pyrrolidone (NMP) or water for comparison purposes. To briefly summarize, commercial SiNPS, carbon super P and polymer binder (β CD6A-AA and AdEN-AA) were dispersed in NMP or water at a weight ratio of 50:20:15:15. The slurry was cast onto copper foil using a Dr. Blade settled at 60 μ m height. The electrode was dried at 80 °C for 24 hours under vacuum before calendaring 40 μ m. For Cyclic Voltammetry measurements, a three electrode Swagelok T-cell, with lithium as a counter and reference electrode, and silicon anode previously prepared as a working electrode, were used. The electrolyte solution consisted of lithium hexafluorophosphate (1.0 M) in 1:1 (w/w) ethylene carbonate (EC)/dimethyl carbonate (DMC) containing 5 wt.% fluoroethylenecarbonate (FEC).

Cyclic voltammograms were recorded on a Gamry Interface 1000 Potentiostat/Galvanostat, between 0.01 and 1.5 V, at 0.1 mV/s. The galvanostatic battery test was performed using a LANDT Inst. Battery Test System, by assembling CR2032 coin-type half-cells using a Celgard-2400 polyethylene separator and lithium metal as a counter electrode. The CR2032 coin cells were pre-cycled (three cycles) at C/20 (210 mAhg^{-1}) to form and stabilize the SEI, and then cycled at C/10 in the potential range of 0.01 and 1.5 V. Both the Swagelok T-Cell and CR2032 coin cell were assembled in an Ar-filled glovebox.

2.5. Equipment.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum-Two spectrometer (Perkin-Elmer, Waltham, MA, US) with a UATR coupled unit. The sample was directly pressed on the diamond until reaching 30% of the total pressure and scanned in the range of 4000 to 500 cm^{-1} with a resolution of 1 cm^{-1} .

The $^1\text{H-NMR}$ spectra were recorded at 300 K, on a 200 MHz instrument (BRUKER AVANCE 200), using D_2O or CDCl_3 as solvents. All chemical shifts were referred to TMS lock signal.

Thermogravimetric analysis (TGA) was performed on a Star System 1 (Mettler Toledo, USA). The samples were heated in an aluminum pan, from 40 to $500 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C}/\text{min}$, in an inert atmosphere (N_2 gas).

The high-resolution surface images were generated using a Zeiss GeminiSEM 360 field-emission scanning electron microscope (FE-SEM). In particular, the operated detector is a scintillator-type for secondary electrons, and it is coupled with a photomultiplier tube with annular geometry, arranged concentrically to the electron beam, mounted inside the objective lens of the electro-optical column. In all cases, electrons were accelerated with voltages of 5 kV in a high vacuum sample chamber (2×10^{-6} mbar) without applying any coating on the samples.

3. Results and Discussion.

3.1. Polymer synthesis and properties of mixed (Interaction)

Host (βCD6Acr) and guest (AdENAc) monomers were prepared by reacting acryloyl chloride with $\beta\text{CD6-NH}_2$ in anhydrous DMF, and with N-(2-aminoethyl)adamantane-1-carboxamide in dry DCM, respectively. In both cases, the corresponding substituted vinyl

compounds were obtained, as confirmed by ATR-FTIR (Figure 1) and the $^1\text{H-NMR}$ spectra (Figures S1 and S2 in Supplementary Data). The host, $\beta\text{CD6A-AA}$ polymer, was obtained by free radical polymerization of βCD6Acr and acrylic acid at a ratio of 1:10 wt.%, in water. The ATR-FTIR spectrum of $\beta\text{CD6A-AA}$ (Figure 1.a) shows a strong and wide band at 1034 cm^{-1} (enclosed in a rectangle), which is assigned to the superposition of the stretching and bending vibration modes of the α -glucopyranoside rings of the βCD in $\beta\text{CD6A-AA}$. (Egyed, 1990) Additionally, a shoulder at 1660 cm^{-1} , also present as an intense and narrow band in the spectrum of the βCD6Acr , was assigned to the stretching of carbonyl from the amide. These bands indicate the presence of βCD units in the polymer backbone. An additional band at 1703 cm^{-1} was assigned to the stretching of the carbonyl group from acrylic acid in the PAA backbone. It is worth noting the widening and shift in ca. 100 cm^{-1} to lower wavenumbers in the $-\text{OH}$ stretching of the polymer (3240 cm^{-1}), compared to the monomer (3335 cm^{-1}). Both features are attributed to the intermolecular hydrogen bond interaction between any of the carrying $-\text{OH}$ groups (βCD or $-\text{COOH}$) in the polymer backbone. According to the colorimetric Dubois method, the estimated content of βCD in $\beta\text{CD6A-AA}$ was 1:14 wt.%. (DuBois, Gilles, Hamilton, Rebers, & Smith, 1956)

The guest polymer (AdEN-AA) was obtained by free radical polymerization of AdENAc with the same wt.% as in the guest polymer but in dry DMF. The ATR-FTIR spectrum of AdEN-AA (Figure 1.b), shows two intense bands at 1705 cm^{-1} and 1634 cm^{-1} . These bands correspond to the stretching of carbonyl from acrylic acid and amide, respectively. In addition to the latter, in the AdENAc spectrum, a second amide band was recorded at 1657 cm^{-1} (according to the ethylenediamine tether linking adamantane with the acryloyl moiety amide linkage). Nevertheless, this is not noticeable in the spectrum of AdEN-AA, probably due to its overlapping with the other two aforementioned bands. The two intense bands recorded at 2845 cm^{-1} and 2903 cm^{-1} , correspond to the $\nu^s(\text{C}-\text{H})$ and $\nu^{as}(\text{C}-\text{H})$, stretching respectively, of methylene in both the polymer and the adamantane moiety. A broad and asymmetrically shaped band covering the high frequency range of the spectrum was recorded in AdEN-AA. This band corresponds to the $-\text{OH}$ stretching of carboxylic acids in PAA and the $-\text{NH}$ stretching of the secondary amide.

The superimposition of these modes, along with the interactions between the polymer backbones, could have propitiated the observed broadening.

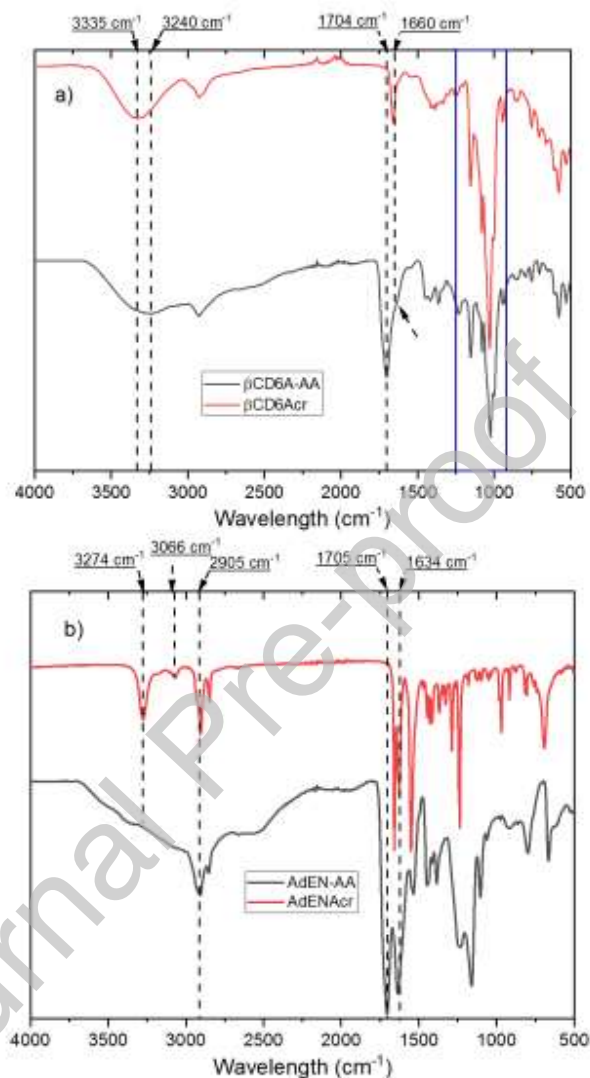


Figure 1. ATR-FTIR spectra of a) β CD6A-AA and b) AdEN-AA (b). Red and black lines correspond to monomers and polymers, respectively. Adamantane and β -cyclodextrin form a host-guest inclusion complex with $K_{inc} \sim 10^4 M^{-1}$. (Rekharsky & Inoue, 1998) According to other reports, due to the supramolecular crosslinking, a gel formation was observed by one of the following possibilities: incorporating both host-guest moieties in the same polymer backbone (Kakuta et al., 2013; Pu et al., 2016), or by preparing complementary units grafted onto polyacrylic acid (Wang et al., 2010), or by in-situ crosslinking of acryloyl adamantane in the presence of

linear or crosslinked homopolymer of β CD.(Cai et al., 2018) Therefore, the adamantane moiety in AdEN-AA and the β CD in β CD6A-AA should interact as supramolecular crosslinkers, as depicted in Figure 2.

First, we studied the solvent effects on the supramolecular crosslinking of polymers by mixing 0.5 mL of solutions with an equal amount (20 mg) of β CD6A-AA and AdENAA polymers in NMP as the solvent (Figure 2, a). No gel formation was observed when we mixed the solutions with the complementary polymers. It is well-known that the interaction of polar aprotic solvents with the cyclodextrin cavity is thermodynamically more favorable than with water. Therefore, in NMP a competition for the CD's cavity between solvent and adamantane takes place and the supramolecular crosslinking effect decreases. When using water as the solvent under the same experimental conditions, a gel formation was observed (Figure 2.b). In this case, an inclusion complex takes place, since the presence of water inside the β CD cavity is thermodynamically unfavorable.(Rekharsky & Inoue, 1998)

It is important to note that, in addition to the host-guest interaction, hydrogen bonds are also present between carboxylic acid groups and hydroxyl groups in the polymer backbones. To establish the contribution of both interactions in gel formation, an equal amount of β CD6A-AA and PAA (20 mg) were mixed in a vial with 0.5 mL of water. β CD6A-AA was selected instead of AdEN-AA, since the -OH groups from cyclodextrins extend the H-bond interaction. As can be noted, the mixture doesn't gel in the absence of a guest (Figure 2.c). These results concluded that the host-guest complementarity is mandatory for an efficient interaction between the polymers and the formation of a crosslinked network.

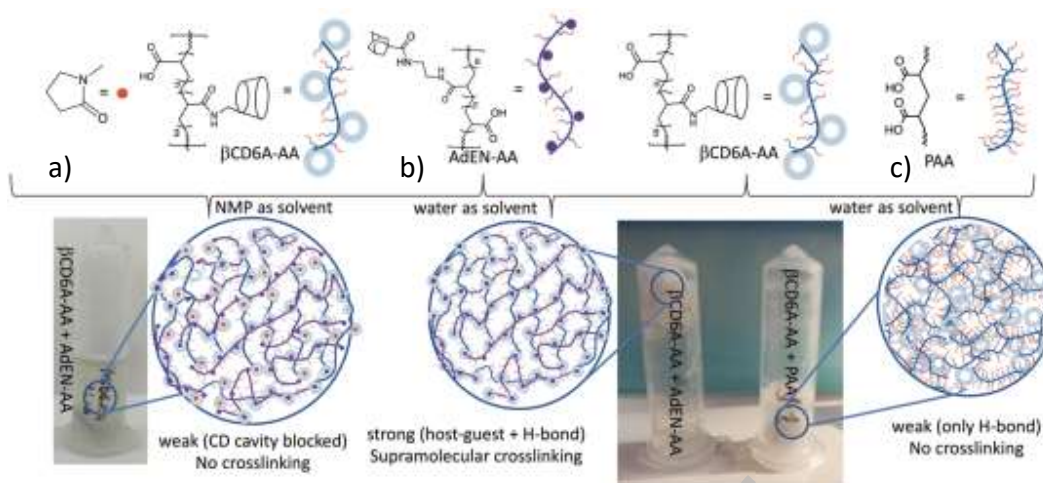


Figure 2. a) Representation of the supramolecular crosslinking effect of β CD6A-AA and AdEN-AA and photo of results when β CD6A-AA and AdEN-AA are mixed in a) NMP, b) in water) and c) result of mixing β CD6A-AA and PAA.

3.2. Thermogravimetric analysis

The thermal stability of polymers is, among other factors, dependent on the interaction between the corresponding backbones. Therefore, to confirm the host-guest interaction in gel formation, thermal analysis of the β CD6A-AA and AdEN-AA mixture in NMP and in water, and of β CD6A-AA and PAA in water, was carried out (Figure 3).

As can be noted, the thermograms of β CD6A-AA and AdEN-AA in NMP, as well as β CD6A-AA and PAA, have similar profiles with three defined stages, although the latter appears to have shifted to higher temperatures (ca. 30 °C, taken the 50% weight loss as a comparison point). The first stage of the mixture in NMP, between 40 and 190 °C, shows a weight loss of 11.6%, whereas the mixture with PAA lost only the 8.6% in the range of 40 to 204 °C. This first stage is attributed to the loss of the water absorbed by the polymers and from the dehydration due to the partial anhydride formation between the -COOH groups in PAA segments. (Maurer, Eustace, & Ratcliffe, 1987; Moharram & Allam, 2007) A second stage, with a higher decomposition rate, occurs between 190 and 450 °C, and between 204 and 433 °C for β CD6A-AA/AdEN-AA in NMP and β CD6A-AA/PAA, respectively. In this stage, the former lost 69% of its weight, a 19% higher loss than that of β CD6A-AA/PAA. This weight loss is due to degradation of anhydride, previously formed, with the decomposition of adamantane and cyclodextrin pendant moieties. (Maurer et al., 1987; Moharram & Allam,

2007) The slightly higher stability of β CD6A-AA/PAA over β CD6A-AA/AdEN-AA in NMP could be attributed to the hydrogen bond interaction of the β CD units and carboxylic acid in the polymer backbone, which exert a thermal stabilization effect. The final stage, beyond 450 °C, corresponds to the thermal degradation of the polymer backbone.

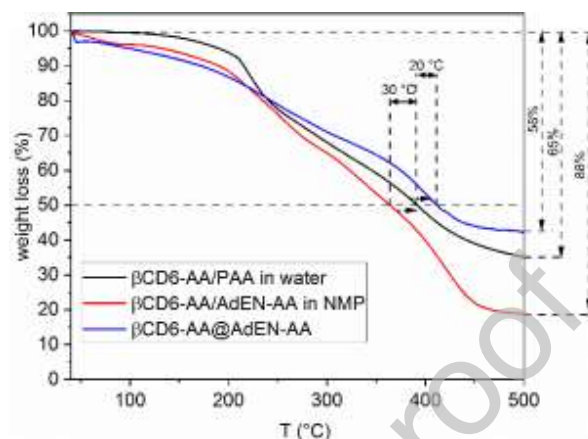


Figure 3. Thermogravimetric analysis of the mixture of β CD6A-AA and AdENAA in NMP and in water and β CD6A-AA/PAA in water.

Compared to the observations, the mixture of AdEN-AA and β CD-AA in water results in a completely different outcome. From the beginning, a constant weight loss is observed, reaching over 400 °C, with a lower decomposition rate compared to the two first stages of the thermograms of samples prepared in NMP and the sample β CD6A-AA/PAA. Additionally, in the final stage, the mixture of AdEN-AA and β CD-AA in water loses only 58% of the total weight compared to the 65% lost in β CD6A-AA/PAA and the 88% lost in β CD6A-AA/AdEN-AA in NMP.

Accordingly, the following order of thermal stability was found: AdEN-AA/ β CD-AA in NMP < AdEN-AA/PAA < AdEN-AA/ β CD-AA, both the latter in water. This order seems to agree with the extent of respective interaction of systems according to the weak hydrogen bond interaction in NMP < the hydrogen bond interaction occurring in β CD6A-AA/PAA and < both, the hydrogen bond interaction, and the formation of the inclusion complex in β CD6A-AA/AdEN-AA in water.

3.3. Electrochemical Characterization

As noted before, the host-guest interaction between AdEN-AA and β CD6A-AA polymers is favored when water is used as a solvent instead of NMP. Therefore, the slurries prepared in the different solvent should directly influence the electrochemical properties of the electrodes. To check the electrochemical response and stability of the prepared electrodes in NMP and in water, the corresponding electrochemical characterization was carried out. Silicon electrodes with AdENAA@ β CD6AA as binders were first characterized by cyclic voltammetry (C.V) in a three-electrode Swagelok cell. Cycle life was assessed by assembling a CR2032 half-cell using lithium as the counter and reference electrode, and silicon as the working electrode.

3.3.1. Cyclic Voltammetry

Figure 4 shows the voltammograms of the first three cycles of silicon electrode prepared in water (Figure 4.a) and in NMP (Figure 4.b). In both voltammograms, during the first reduction sweep in which the lithiation was promoted, no reduction peaks were observed until the potential reached 10 mV. At this point, an amorphous phase ($a\text{-Li}_x\text{Si}$) was formed through the lithiation of cristaline Si. (Jerliu et al., 2018; Obrovac & Krause, 2007; Xu, Zhang, & Cheng, 2016)

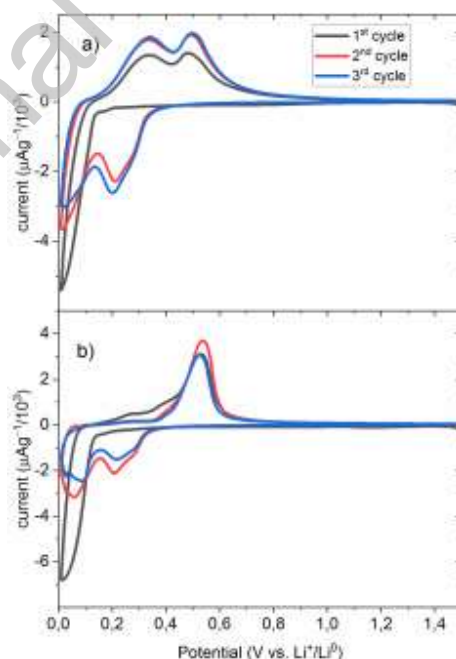


Figure 4. Cyclic Voltammogram of cells with anode prepared using AdmAA@ β CD6AA as binder in: (a) water and (b) NMP.

In the reverse scan, delithiation occurs and two peaks around 0.34 V and 0.50 V are recorded in the C.V of the electrode material prepared from water. In the C.V of the electrode prepared in NMP, the former peak is scarcely noted at 0.26 V during the first cycle and disappears in further cycles. The later peak appears well-defined at 0.53 V. According to the literature, these signals correspond to the delithiation process from different phases of silicon: α -Li_xSi and α -Li_(x+x')Si, respectively. (Jerliu et al., 2018; Obrovac & Krause, 2007)

In further cycles, the electrode with a binder prepared from water shows anodic peaks with the same intensity and shape, indicating a stabilization of the electrode interphase. In the case of the cathodic peaks, the intensity slightly increases from the first to the second and third cycles. The electrode prepared in NMP exhibits a different behavior, with an increase and subsequent decrease of these peaks from the first to the third cycle, respectively. The value of integral voltammetric area of the discharging/charging branches is higher for water-based electrodes than in NMP for the three C.V cycles. These results indicate that lithium intercalation is favored when water is used as the solvent.

The first three galvanostatic charge-discharge profiles of electrodes prepared in both solvents were recorded by assembling the corresponding coin-type half-cells. Accordingly, the characteristic plateaus of Si at 0.1 V and 0.45 V, are observed for the lithiation and delithiation process, respectively (Figure. 5). Both cells show a stable potential during lithiation of the electrodes. Nevertheless, the capacity achieved for the first three cycles have notable differences when comparing both electrodes. The electrode prepared in water (Figure 5.a) increases its capacity from 2226 mAhg⁻¹ to 2474 mAhg⁻¹ between the first and second cycles and this capacity is retained during the third cycle. These capacity increases are attributed to the formation of the solid electrolyte interphase (SEI) and the stabilization of both the SEI and the entire electrode. It is worth noting that this result is consistent with the behavior observed in the voltammograms. On the other hand, the capacity of the electrode prepared in NMP (Figure 5.b) is lower (1200 mAhg⁻¹) than that of

the one prepared in water and decreases by 50% from the first to the third cycle, indicating a lower initial performance than the electrode prepared in water.

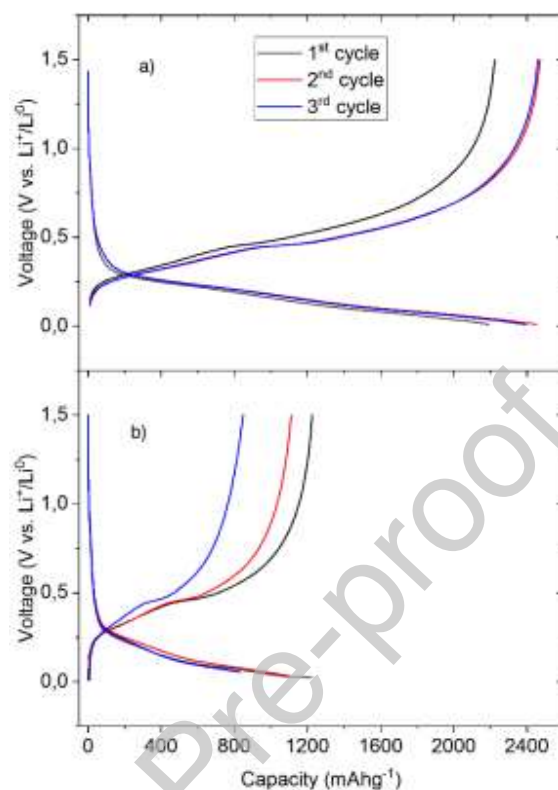


Figure 5. Galvanostatic profile at 0.1C of the first three cycles of a cell with a Si anode prepared using AdmAA@ β CD6AA as binder in: (a) water and (b) NMP

3.3.2. Electrode charge-discharge performance

Considering the previously obtained results, it is expected that the electrodes prepared in water show a better response and stability during the cycle life compared to those prepared in NMP. Therefore, the cycling performance of the electrodes was studied in the range of 0.01-1.50 V at C/10 (Figure 6).

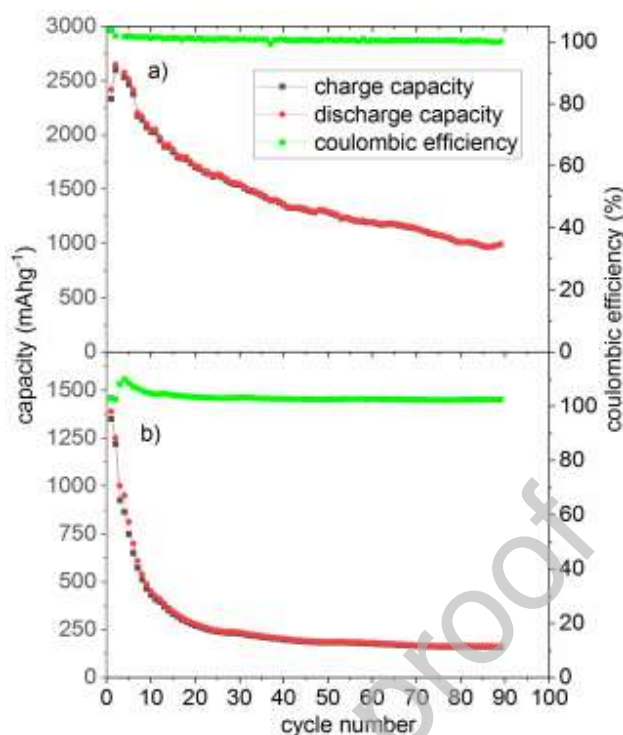


Figure 6. Charge-discharge cyclic performance of electrode material prepared with a) water and b) with NMP.

Regardless of the solvent, both electrodes show coulombic efficiencies near to 100% in all cycles, which indicates an efficient exchange of lithium in the anode and the electrochemical stability of the binder. Nevertheless, the electrodes exhibit marked differences in their initial capacities and in the percentage of retention of the specific charge/discharge capacity during cycling. The anode prepared with water starts with a specific discharge capacity of 2415 mAhg^{-1} ; which is approximately twice the value of the anode prepared in NMP (1348 mAhg^{-1}). After the first cycle, the electrode in water increases its capacity to 2648 mAhg^{-1} , but it subsequently decreases by 28% in the 20th cycle and by 60% (1035 mAhg^{-1}) after 90 cycles. Within the first 20 cycles, the electrode prepared in NMP shows an abrupt decrease by 80% (279 mAhg^{-1}) of its initial capacity. Considering the extent of interactions studied earlier, it is possible to state that the higher capacity retention of the electrode prepared in water indicates the effectiveness of host-guest supramolecular interaction in reestablishing the anode's performance throughout successive cycles.

Some recent works in which polymer binders containing cyclodextrin have been prepared are shown in Table 1. From these results, two main approaches can be considered. The first approach involves the preparation of hyperbranched β -cyclodextrin polymers to be used with three different purposes: a) to facilitate multiple hydrogen bonds between hydroxyl groups, arising from glucopyranoside units or the crosslinker and alginate and/or PAA (Jeong et al., 2014), b) to covalent crosslinking with PAA, partially neutralized PAA or Alginate, by thermal-induced esterification reaction (Lin et al., 2022; Zheng et al., 2023) or c) to serve as host of adamantane in a short range host-guest supramolecular interaction.(Tae-woo Kwon et al., 2015) The second approach is grounded in the pulley principle, employing α -CD to create polyrotaxanes where polyethylene oxide slides within the cyclodextrin cavity, releasing the stress resulting from the volume expansion of silicon.(Bétermier et al., 2023; Choi, Kwon, Coskun, & Choi, 2017a)

Table 1. Different chemistries of polymer binders containing β -CD.

Binder (solvent)	Binder interactions	C.P(mAhg ⁻¹) ^a (C.P.R, %, C-	Ref.
AdEN-AA@ β CD-6AA (water)	H-bond, host-guest	1035(60, C/10, 30%)	This work
Alg- β CDp (water)	H-bond, electrostatic	1435 (70, 1C, 20%)	(Jeong et al., 2014)
PAAS ₆ - β -CDp ₁ -PAA ₃ (water)	3D covalent crosslinking	2513 (71, C/20, N.I.*)	(Zheng et al., 2023)
PAA-20 β -CDp (water)		1468 (65, C/5, N.I.*)	(Lin et al., 2022)
β CDp-6AD (water/EtOH)	H-bond, host-guest	1800 (90, C/2, 20%)	(Tae-woo Kwon et al., 2015)
PR-PAA(DMSO)	Polyrotaxanes	2270 (91, C/5, 10%)	(Choi et al., 2017a)
PR-PAA (EtOH)		3000 (82, C/10, 20)	(Bétermier et al., 2023)

N.I.: not informed. a) C.P.: Capacity at cycle 90th (C.P.R: % of Capacity retention).

As can be noted from Table 1, capacities higher than 2200 mAhg⁻¹ are reported for binders prepared with polyrotaxanes. Although this is an amazing approach, it has several drawbacks. Multiple reaction steps, several purification procedures, and control in the formation of rotaxane are issues that hamper a future commercialization. Additionally, both related reports use organic solvent for preparing the anodes, which is environmentally inadequate.

Concerning 3D covalent crosslinked binders, which allow the preparation of anode material in water, PAAS₆-β-CDp₁-PAA₃ and PAA-20β-CDp distinguished themselves with capacities of 2513 mAhg⁻¹ and 1468 mAhg⁻¹, respectively. The differences between PAAS₆-β-CDp₁-PAA₃ and PAA-20β-CDp are the crosslinker used to prepare the hyperbranched β-CDp, and the use of partially neutralized sodium polyacrylate polymer (PAAS). As can be noted, an increase in C-rate from C/20 in PAAS₆-β-CDp₁-PAA₃ to C/5 in PAA-20β-CDp decreases the capacity by half. Although PAAS₆-β-CDp₁-PAA₃ showed an outstanding capacity, this value is achieved at a very low C-rate (C/20), probably due to the straitjacket effect of the 3D covalent crosslinked network. None of these reports mentioned the percentage of binders used to prepare the anodes.

The binder effects of Alg-βCDp and βCDp-6AD (Table 1), rely on a mere supramolecular interaction. Both binders show capacities of 1435 mAhg⁻¹ and 1800 mAhg⁻¹, respectively. While in the former H-bond and electrostatic interactions are in charge of releases the stress from volume changes the latter has, additionally to H-bond, host-guest supramolecular interaction. The higher capacity of βCDp-6AD could be attributed to the formation of an inclusion complex between adamantane and βCD cavity, although the different C-rates should also be considered. As previously mentioned, AdEN-AA@βCD-6AA is also based on the host-guest supramolecular interaction, but in our case long-range interactions are encouraged, given that lineal rather than hyperbranched βCD polymer binder was prepared. Although this binder showed a 40% lower capacity than βCDp-6AD, the latter uses methanol as solvent for preparing the slurries. We consider that this is a starting point in the study of linear supramolecular complementary polymers as potential binders for silicon anodes. Different β-CD-PAA and adamantane-PAA ratios are currently under study in order to improve these results. According to the SEM results discussed in the next section, the effectiveness of the AdEN-AA@βCD-6AA as a binder, is well-founded when the slurry is prepared in water.

3.4. SEM Characterization

The topographical characterization of the anode material prepared in water and in NMP was studied using Scanning Electron Microscopy (Figure 7). SEM images were recorded before and after cycling the electrodes, as well as after removing the formed solid electrolyte interphase (SEI). As can be noted in Figure 7.a-b), both fresh electrodes consist of round-shaped silicon particles. The electrode prepared in water (Figure 7.a) shows a homogenous rough surface covered by uniformly spread Si nanoparticles. On the other hand, in the electrode prepared in NMP (Figure 7.b), the Si nanoparticles appear like an island, spilled across the entire surface. These differences of the Si distribution have a direct impact on the SEI formation, as shown in the corresponding SEM micrographs of the surfaces after the 90th cycle. (Figure 7.c-f)). A smooth and compact SEI is observed in the electrode prepared in water, whereas the SEI of the electrode prepared in NMP appears rough, with certain spike and scale-like morphologies. This indicates a weaker stability of this interphase, which has the potential to isolate the Si particles and result in rapid capacity fade, as depicted in Figure 6.

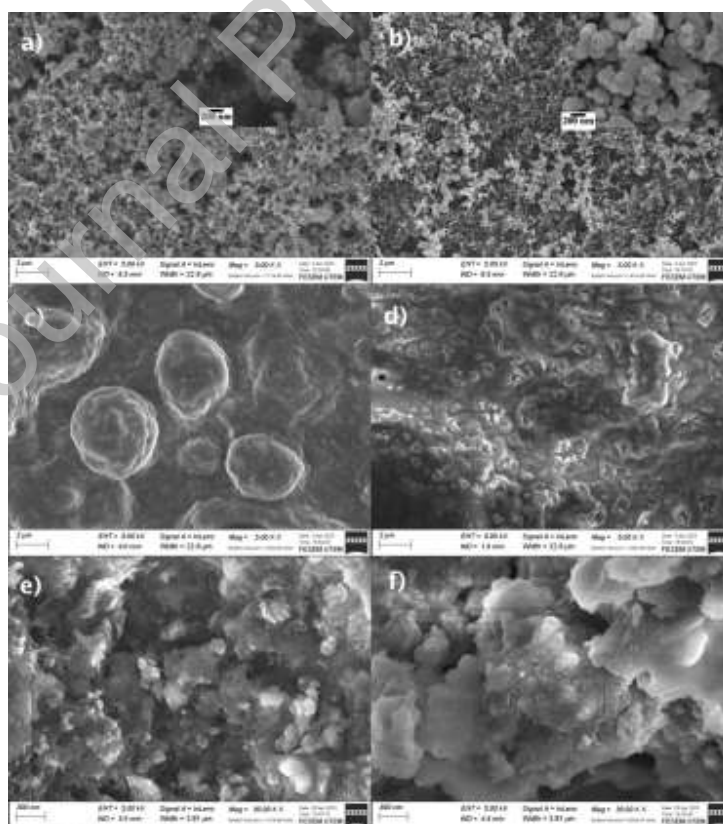


Figure 7. SEM of electrodes prepared in water (left column) and in NMP (right column), before (a-b) and after (c-d) of 90 cycles. Figures c-f correspond to the electrode before (c-d) and after (e-f) the SEI was removed.

In the electrode prepared from water, after the SEI removal (Figure 7.e), Si nanoparticles are observed on the surface, indicating the integrity of the anode material after cycling. In contrast, the surface of the electrode prepared in NMP scarcely shows nanoparticles and instead has an appearance of aggregated pulverized material. From these results it is possible to confirm the efficient self-healing properties of the supramolecular binder assembled in water. The stable SEI in electrodes with a binder in a water solvent ensures a strong electrical connection between particles during cycling, resulting in improved cyclability.

4. Conclusions.

Host-guest supramolecular binders were prepared through the co-polymerization of acrylic acid (AA) with 6-monodeoxy-6-monoamidoacrylyl- β -cyclodextrin (β CD6A-AA) and with N-(2-acrylamidoethyl)adamantane-1-carboxamide (AdEN-AA). The mixture of copolymers in water forms gel due to their supramolecular crosslinking, a condition that doesn't occur when mixing them in NMP nor when mixing β CD6A-AA with PAA in water. The highest thermal stability was achieved by the mixture of β CD6A-AA/AdEN-AA in water. This electrode showed the best performance when compared to the electrode prepared in NMP. The battery prepared with the former showed the highest initial capacity (2415 mAhg^{-1}), which decreases after the 90th cycle to 1035 mAhg^{-1} .

These results indicate that using an aqueous binder is the most suitable option for Si anodes. The binder prepared in a water solvent is more effective than one prepared in an NMP solvent at mitigating the volume expansions of silicon at the nanoscale while maintaining anode integrity and stable electrochemical performance. Therefore, this polymer binder offers significant improvements when water is used as the solvent instead of NMP. This finding provides a new opportunity to positively influence the development of emerging electrode materials in rechargeable batteries.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: