

Mechanochemical Synthesis of PEDOT:PSS Hydrogels for Aqueous Formulation of Li-Ion Battery Electrodes

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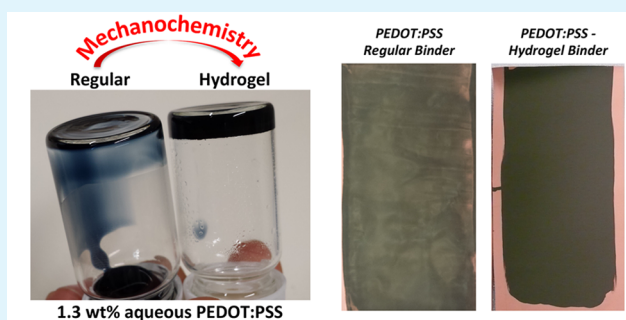
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S Supporting Information

ABSTRACT: Water-soluble binders can enable greener and cost-effective Li-ion battery manufacturing by eliminating the standard fluorine-based formulations and associated organic solvents. The issue with water-based dispersions, however, remains the difficulty in stabilizing them, requiring additional processing complexity. Herein, we show that mechanochemical conversion of a regular poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) water-based dispersion produces a hydrogel that meets all the requirements as binder for lithium-ion battery electrode manufacture. We particularly highlight the suitable slurry rheology, improved adhesion, intrinsic electrical conductivity, large potential stability window and limited corrosion of metal current collectors and active electrode materials, compared to standard binder or regular PEDOT:PSS solution-based processing. When incorporating the active materials, conductive carbon and additives with PEDOT:PSS, the mechanochemical processing induces simultaneous binder gelation and fine mixing of the components. The formed slurries are stable, show no phase segregation when stored for months, and produce highly uniform thin (25 μm) to very thick (500 μm) films in a single coating step, with no material segregation even upon slow drying. In conjunction with PEDOT:PSS hydrogels, technologically relevant materials including silicon, tin, and graphite negative electrodes as well as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , and carbon-sulfur positive electrodes show superior cycling stability and power-rate performances compared to standard binder formulation, while significantly simplifying the aqueous-based electrode assembly.

KEYWORDS: lithium-ion battery, water-soluble binder, aqueous electrode formulation, hydrogel, mechanochemical synthesis



Efficient Aqueous Processing for High Performance Batteries

INTRODUCTION

Our progressively fossil-fuel-constrained society has a huge incentive on the development of energy storage systems encompassing the entire battery life cycle, from materials to manufacturing procedures including battery recycling and final disposal.^{1,2} The development of innovative processes leading to reduced electrode production cost and environmental pollution yet with higher performances is thus timely needed to enable lithium ion batteries for automotive and other large-scale applications. Aqueous processing of battery electrodes is particularly attractive in this context as the environmental and economic benefits cannot be overstated. The conventional electrode fabrication process relies on casting slurries composed

of active materials and inactive constituents such as carbon-based conducting additives and dissolved polymer binders, onto a metal current collector.^{3–5} Water-soluble binders can thus orient the Li-ion battery manufacturing toward an environmentally friendlier, safer and economic direction, eliminating the use of volatile and carcinogenic organic solvents associated with the conventional fluorine-based electrode assembly.⁶

Fluorinated binders such as polyvinylidene difluoride (PVDF) are not suitable for conversion electrode materials,

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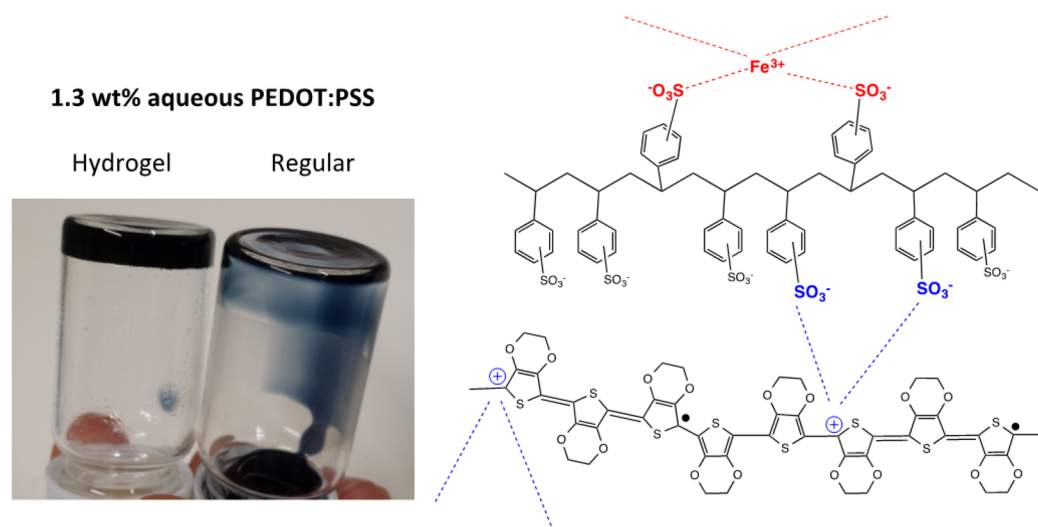


Figure 1. PEDOT:PSS hydrogels. Photographs of the PEDOT:PSS hydrogel (left) and regular (right) formulations at 1.3 wt % PEDOT:PSS content. Schematic representation of the hydrogel structure. The coordination of Fe^{3+} by the SO_3^- is considered as the main process in the gel formation and polymer–metal framework stabilization.

as metallic and alloy-type electroactive materials undergo large structural changes.⁷ As a matter of fact, limited binder swelling by the electrolyte is desired to prevent the electrolyte decomposition that subsequently diminishes the binder-particle cohesion. In an effort to promote passivation and the mechanical integrity of the electrode, several binder concepts have been tested in recent years including conductive, self-healing and shape-memory polymers.^{8,9} Water-based suspensions of PEDOT:PSS have been particularly employed as conductive agent additives showing reliable cycling with some anode as well as cathode electrode materials.^{10–14} The physicochemical properties of the used aqueous polymer suspensions and associated battery electrode slurries were, however, poorly detailed. In particular, the use of viscous polymer solutions will inevitably lead to inferior quality coatings since the rheological properties are expected to impact the slurry stability through particle segregation, as will be detailed in the following.

Albeit applied to negative lithium battery electrodes, aqueous processing for cathode materials remains troublesome as these are found to exhibit loss of Li^+ , oxidation of transition metal center, and corrosion of the Al current collector.¹⁵ Moreover, water-based dispersions are difficult to stabilize, being susceptible to phase segregation when hydrophobic or dissimilar volumetric mass materials are used, requiring additives, additional processing complexity as well as texturing control agents to stabilize the slurry. Although these can be controlled to a certain extent, the ultimate challenge is to avoid particle sedimentation or aggregation upon battery electrode slurry handling as well as drying. For instance, electrically conductive carbon additives tend to flocculate in dense electrode slurries^{16,17} leading to nonhomogeneous coatings affecting the electrochemical performances. In addition, the flow behavior of the slurry closely impacts the electrode fabrication processes such as casting, pressing and slitting. Finding solutions to these drawbacks is thus required to widely adopt aqueous binder processing as a general route for lower costs and environmental processing of battery electrodes.

Herein, we show that the mechanochemical conversion of a regular (commercial) PEDOT:PSS aqueous dispersion produces a hydrogel with promising binder characteristics for lithium-

ion battery electrode manufacturing. We particularly focus on: (i) the simplicity and reproducibility of the mechanochemical conversion approach; (ii) the physicochemical properties (adhesion, electrical conductivity); (iii) the rheological properties and suitability for electrode manufacture (viscosity and slurry stability); (iv) the anodic and cathodic electrochemical stability; and crucially, (v) the improved performances of technologically relevant battery materials such as silicon, tin, graphite, and aluminum negative battery electrodes as well as LiCoO_2 , LiMn_2O_4 , LiFePO_4 , and carbon–sulfur positive electrodes. Additionally, given the electrically conductive nature of the PEDOT:PSS hydrogel binder and its miscibility with other aqueous formulations, hybrid binder compositions and carbon-free electrodes can be manufactured and tested. Overall, the mechanochemically synthesized PEDOT:PSS hydrogels, when applied as binder for lithium-ion battery electrode processing, show major advantages given the simple aqueous procedures, excellent dispersion stability, preserved electrical conductivity, enhanced structural integrity and adhesion of the prepared electrodes as well as improved power and cycling stability performances.

MECHANOCHEMICAL SYNTHESIS OF PEDOT:PSS HYDROGELS

The mechanochemical conversion was performed by ball milling in the presence of metallic iron. Milling emerges as a promising tool to induce chemical and physicochemical transformations of compounds enabling the access to new materials phases and properties.¹⁸ Here, the acidity of the regular PEDOT:PSS solution (pH of 2–3) promotes the dissolution of the metallic iron (Fe^0), with the released iron ions being subsequently coordinated by sulfonate groups of the PSS chain (Figure 1, refer to Supporting Information, Section 1, for detailed discussion and analysis). This results in a stable coordination network that freezes the structures and produces a homogeneous polymer–metal framework incorporating all the initially present water (of up to 99% by mass).

The PEDOT:PSS hydrogels are found to behave as typical plastic fluids since they retain the dimensional integrity of a solid material (Figure 1) and are stable for months (see the

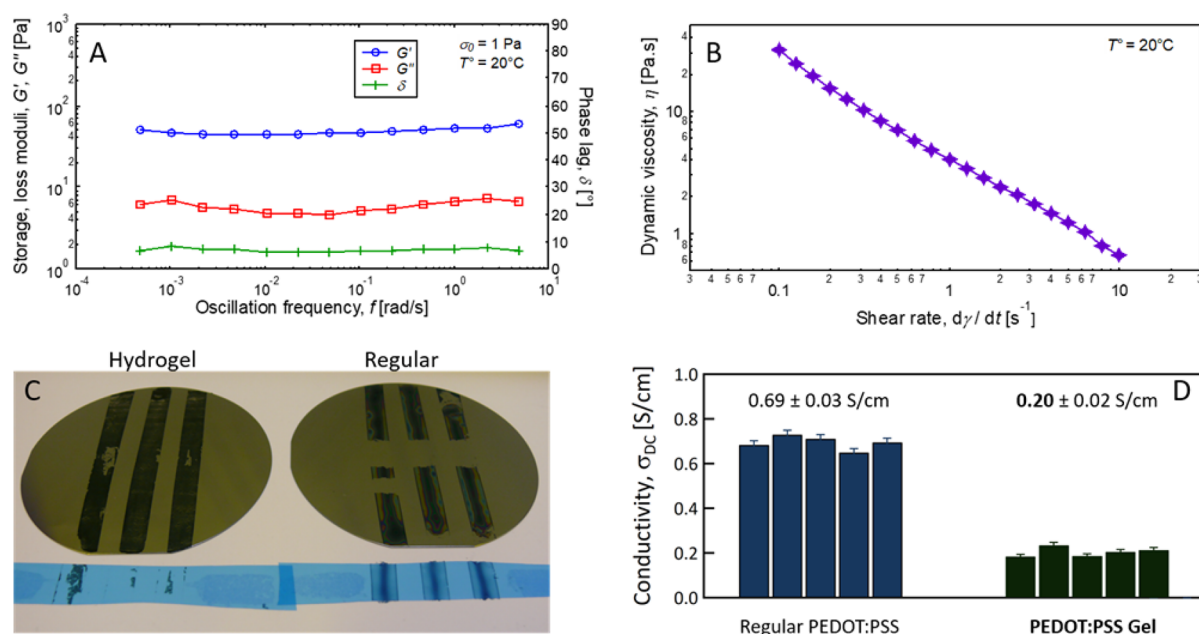


Figure 2. Physicochemical characterization. (A) Frequency dependence of the dynamic storage, loss moduli, and stress–strain phase lag. (B) Steady-shear viscosity as a function of the shear rate for PEDOT:PSS hydrogels. (C) Adhesion test on silicon wafers: left—hydrogel, right—regular PEDOT:PSS coatings. (D) Electrical conductivity change upon gelation.

Supporting Information) but reversibly flow when mechanically stressed, which allows them to be processed and formulated as thixotropic viscous fluids, as detailed next.

There are several clear advantages of the here disclosed mechanochemical synthesis of PEDOT:PSS hydrogels with respect to other reported methods. Those approaches address the synthesis of cross-linked conducting polymer formulations or high-viscosity solutions mediated by transition metal complexes.^{19,20} Such methods have been performed either by the in situ oxidative polymerization followed by polymer chain cross-linking in the presence of the oxidant metallic species (e.g., Fe^{3+} , Ce^{4+}) or by direct interaction of the conducting polymer with metal salts in aqueous solution.^{21–24} To assess their relevance, we also tested these protocols and briefly discuss them in the following (further details are provided in the Supporting Information).

Oxidative polymerization of EDOT was found not suitable when performed in the presence of cathode electrode materials, due to corrosion and oxidation, resulting in active material degradation. Also, the dispersion homogeneity was difficult to maintain, with the formed PEDOT:PSS composite behaving like a viscous fluid rather than a gel. Similarly, direct addition of transition metal salts to the PEDOT:PSS solution resulted in rapid precipitate particle formation and agglomeration. Even under milling conditions, uniform gels could not be obtained out of the formed precipitates, pointing toward the importance of gradual incorporation (as a result here of slow dissolution) of iron ions and slow kinetics of the gel formation. The mechanochemical conversion proposed here overcomes these drawbacks. This process is particularly suitable for preparing electrode slurries, as the gel generation accompanies fine particle mixing with permanently frozen constituent distribution and absence of phase segregation, thus preventing the sedimentation of the active material particles.

PHYSICOCHEMICAL CHARACTERIZATION OF PEDOT:PSS HYDROGELS

The synthesized PEDOT:PSS hydrogels have been extensively characterized using a number of analytical techniques to assess the composition, as well as structural and chemical changes accompanying the gelation process. Energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy and elemental analysis confirm the presence of iron, amounting to 4% atomic concentration in dry gels (Figures S1 and S2). According to thermogravimetric analysis, regular PEDOT:PSS preserves a burning residue of around 9%, while the hydrogels maintain about 18% by mass, the difference being assigned to iron residuals (Figure S3). Moreover, changes in the thermal stability are considerable. For the regular PEDOT:PSS, the PSS counterion starts to decompose at temperatures higher than 300°C , followed by the degradation of PEDOT at about 450°C , in agreement with previous reports indicating the good thermal stability of the poly ionic PEDOT:PSS complex.¹² In the gel, however, the onset of the PSS decomposition is shifted to higher temperatures and overlaps with the decomposition of PEDOT, consistent with the presence of an additional metal-coordinated network with improved strength. The gel formation is also accompanied by a color change of the PEDOT:PSS, from blue to green quantified by UV–vis spectroscopy (Figure S4). The absorption spectra indicates partial reduction of PEDOT:PSS²⁵ consistent with the proposed chemistry of the gel formation process (i.e., oxidation of iron accompanying partial reduction of PEDOT:PSS).

Next, we focus on the rheological properties of the obtained hydrogels and electrode slurries. The rheological properties are of utmost importance for electrode processing as they largely control the coating speed, current collector metal surface wetting and adhesion, ultimately affecting the defect density, electrode coating quality and electrochemical properties. The dynamic and steady-state mechanical properties of the PEDOT:PSS hydrogels were evaluated by rotational shear rheometry.

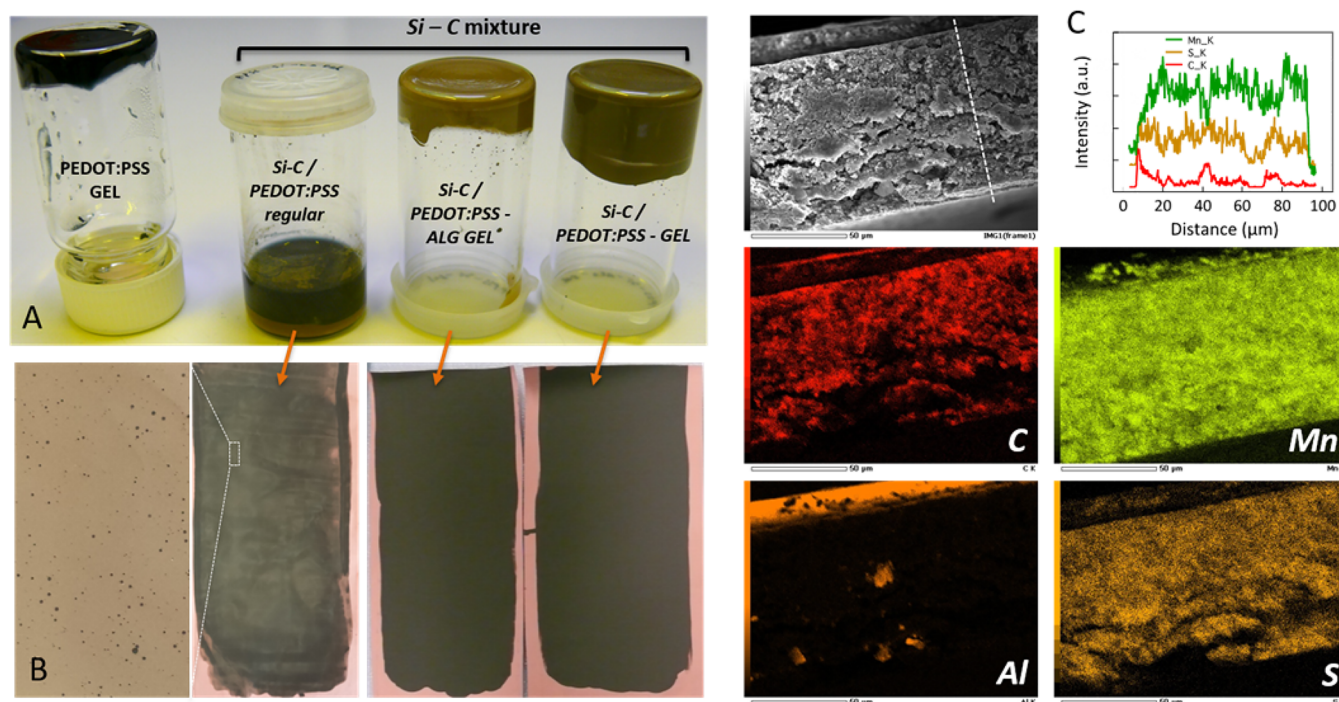


Figure 3. Battery electrode slurry processing. (A) Optical photographs of various PEDOT:PSS formulations used for battery electrode fabrication. (B) Associated coatings using hydrogel and regular PEDOT:PSS formulations. (C) SEM and EDX elemental mapping of thick electrode coatings employing $\text{LiMn}_2\text{O}_4/\text{C}$ composite and PEDOT:PSS hydrogel binder on Al foil current collector.

At first, the linear viscoelastic response of the hydrogels was investigated by performing frequency sweeps under low stress control. As shown in Figure 2A, the viscoelastic response of the material is expressed by nearly frequency-independent plateaus in moduli, which is the trademark of self-standing gels. The absence of a dynamic relaxation is expected for pseudoplastic fluid that preserves by definition its integrity until a critical stress is exceeded. Here, the oscillatory shear frequency sweep measurement was performed at very low stress amplitude of 1 Pa, which is below the yield stress of the structured hydrogel. Therefore, the absence of relaxation simply indicates that the material acts well as a rigid body in this regime due to the cohesion of the network. In addition, the elastic response is 1 order of magnitude higher than the viscous contribution in the investigated frequency range. Accordingly, the phase lag between the applied stress and the resulting strain remains close to 0° , which attests a solid-like behavior. The stability of the viscoelastic response was surveyed by repeating frequency sweeps over a period of 5 days. Only a parallel frequency scaling of the moduli was observed, indicative of slight water evaporation rather than material aging.

In parallel, steady-shear experiments were carried out by measuring the evolution of the viscosity when subjected to an increasing shear rate. In this rheological test, the network structure is forced to flow by the steady-shear stress. Under these conditions, the PEDOT:PSS hydrogel exhibits a pronounced shear-thinning behavior usually encountered for well-dispersed suspension of interacting particles.²⁶ Precisely, the apparent shear viscosity of the material decreases by 2 orders of magnitude when the shear rate is varied in the range of 0.1 to 10 s^{-1} (Figure 2B).

Practically, this pseudoplastic behavior is beneficial to the slurry casting step because it allows the films to thin and wet out the surface evenly, facilitating the formation of thin to thick

coatings. Once applied, the material regains its higher viscosity due to restructuring, therefore avoiding drips and runs. The estimated viscosity is 2000 to 5000 mPa.s (for regular hydrogels at 1.3 wt % PEDOT:PSS by mass as well as for electrode slurries with 5 to 20% content in PEDOT:PSS), considered as adequate for standard laboratory-scale and industrial coating tools.⁴ The PEDOT:PSS hydrogels produce uniform films even when applied on hydrophobic surfaces (Figure 2C). This is another important characteristic considering that the electrode slurry components are typically hydrophobic with low surface tension.

The adhesive properties of the material are essential for the application as binder in the Li-ion battery electrodes. Therefore, a qualitative adhesive tape test was performed on regular and hydrogel PEDOT:PSS films cast on a silicon wafer. As it can be noticed in Figure 2C, the PEDOT:PSS hydrogel exhibits improved adhesion to the Si substrate in comparison to the regular one. It was already reported that LiFePO_4 cathodes deposited on Al, with regular PEDOT:PSS as a binder, exhibit already an adhesion strength of $55\text{--}65 \text{ N}\cdot\text{cm}^{-2}$, which is higher than the values measured for conventional PVDF-based LiFePO_4 cathodes ($35\text{--}40 \text{ N}\cdot\text{cm}^{-2}$).²⁷ Therefore, the improved adhesion strength provided by the PEDOT:PSS hydrogels is further beneficial for the application as a binder in the electrodes for the Li-ion battery technology.

Contrary to the currently preferred range of highly insulating polymeric binders such as PVDF with an electrical resistivity exceeding $1 \times 10^{14} \Omega\cdot\text{cm}$, PEDOT:PSS is intrinsically conducting. Four-probe current–voltage measurements were carried out to evaluate the sheet resistance of dried films of regular PEDOT:PSS and hydrogel. The average thickness of the dried films was evaluated to access the DC conductivity, σ_{DC} (Figure 2D, refer to Supporting Information, Section 1, for details). For regular PEDOT:PSS films, the conductivity is 0.69

± 0.03 S/cm without any secondary doping or post-treatments to enhance the electrical conductivity. Similarly, for dried films of PEDOT:PSS hydrogel the conductivity is evaluated at 0.20 ± 0.02 S/cm. This clearly shows that the charge transport is hardly affected by the mechanochemical conversion of the PEDOT:PSS, the hydrogel being a good electrical conductor. However, since the charge transfer in PEDOT:PSS occurs via a hopping mechanism between π -conjugated segments along and between the PEDOT chains, the conductivity in PEDOT:PSS films thus depends on the supramolecular organization of the PEDOT chains in the insulating PSS anionic matrix.²⁸ The slight decrease in the electrical conductivity value probably stems from a reorganization of PEDOT within the PSS matrix induced by the high mechanical stress during ball milling. In addition the partial reduction of PEDOT, as confirmed by UV-vis, is also impacting negatively the intrinsic conductivity, due to the decrease number of charge carriers within the polymer structure. Moreover the reduction of PEDOT and also the coordination of iron could lead to decrease in the PEDOT:PSS electrostatic pairing events, which would also impact the chain ordering and subsequently the electrical conductivity.²⁹ In any case, the material remains a good electrical conductor, a factor that further opens the possibility of building battery electrodes solely with aqueous PEDOT:PSS hydrogel binders and active battery materials.

■ AQUEOUS FORMULATION OF ELECTRODES WITH PEDOT:PSS HYDROGELS

The original aspects we particularly highlight in this work are the simplicity, stability, and electrode coating uniformity when using PEDOT:PSS hydrogel binder formulations (Figure 3). Because of high solvent content, the physical mixing of regular PEDOT:PSS solutions with electrode active components and additives results in nonstable dispersions, with sedimentation taking place on a time-scale of few minutes (note the silicon nanoparticle sedimentation and carbon flocculation in Figure 3A). Because the viscosity is too low to avoid dewetting from the metal foil surfaces, coating such slurries for producing uniformly thick films is also troublesome. The constituents further segregate during drying, resulting in electrodes with nonuniform composition and properties (Figure 3B). With the PEDOT:PSS hydrogel processed formulations, the slurries gain in viscosity yet remain fluid enough to be processed. These factors are essential for producing high-quality and defect-free electrodes (Figure 3B). Hybrid binder formulations have also been tested,²² with the rheology dictated by the PEDOT:PSS hydrogel phase, further highlighting the versatility of this process. These hybrid binders can be easily formulated by mixing the PEDOT:PSS solution with CMC (carboxy methyl cellulose), SBR (styrene butadiene rubber) and ALG (alginate) in the aqueous phase followed by mechanochemical conversion.

The corresponding battery slurries are stable, show no phase segregation (over several months, see Figure S5) and produce highly uniform thin ($25 \mu\text{m}$) to very thick ($500 \mu\text{m}$) films in a single coating step, with no material sedimentation even upon slow drying. We have produced thick coatings of different active electrode materials ($\text{LiMn}_2\text{O}_4/\text{C}$ in Figure 3C; LiCO_2/C and Si/C in Figure S6) and let them dry slowly (for about 24 h) at room temperature. Scanning electron microscopy and EDX mapping of the electrode cross sections show no sign of sedimentation, phase segregation or delamination, despite the highly dissimilar volumetric presence of the constituents (LiMn_2O_4 and LiCoO_2 vs carbon). Moreover, no particle

breakdown is observed under these mild milling conditions. These results highlight the importance of the rheological properties of the PEDOT:PSS hydrogels and the corresponding slurry formulations suitable for aqueous formulation of Li-ion battery electrodes.

■ ELECTROCHEMICAL CHARACTERIZATION OF PEDOT:PSS HYDROGELS

With the rheological properties and structural integrity demonstrating clear advantages over the standard aqueous binder-electrode formulations, we have next analyzed the electrochemical properties of the PEDOT:PSS hydrogels and formulated electrodes. The cyclic voltammetry curves of regular and hydrogel PEDOT:PSS thin films have been first recorded in aprotic electrolytes (Figure S7). No pronounced faradaic reactions could be detected for both tested materials in the potential range between 2.8 and 4.2 V vs Li/Li^+ . Cathodic polarization, in turn, reveals an irreversible reduction and continuous current decrease for both formulations. The observed process is attributed to the reduction reaction of PEDOT, expected to occur at potentials below 2.5 V vs Li/Li^+ .³⁰ Overall, the PEDOT:PSS hydrogels show similar electrochemical behavior and stability in comparison to the regular PEDOT:PSS for both anodic and cathodic polarization. The hydrogels are thus suitable for both positive and negative electrode manufacture and operation.

The battery electrode formulation was efficiently achieved by ball milling all the constituents to enable simultaneous fine particle mixing and in situ conversion of the PEDOT:PSS binder into a metal-coordinated network. A large variety of compositions were examined to assess the generality of this approach (see Supporting Information for full experimental details). First, the electrochemical response of negative electrodes was analyzed. While binders are generally regarded as passive elements in the battery performance, the cyclic stability is intimately connected to the properties of the binder.^{31–34} The binder acts as a supporting matrix, promoting the cohesion between the active material particles and the adhesion to the current collector and it has an important contribution to the stability of the solid electrolyte interphase (SEI), in particular when working with negative electrode materials.^{35–37}

Graphite and aluminum particle electrodes are first analyzed. When processed with PEDOT:PSS hydrogel binders, both materials displayed stable electrode slurry processing, together with superior electrochemical cycling stability and power performances as compared to other aqueous and nonaqueous binder formulations (Figures S8, S9). Aluminum electrode processing with aqueous binder formulations was possible only by exploiting PEDOT:PSS hydrogel formulations. The use of CMC and other aqueous binders failed, with fast dissolution of aluminum nanoparticles in neutral to basic ($\text{pH} > 6$) aqueous solutions, whereas the low pH (< 3) of the PEDOT:PSS hydrogel formulation prevented the corrosion. This characteristic also accounts for the better adhesion observed for PEDOT:PSS cathode formulations coated on Al foil current collectors.

The superior electrochemical performances of Sn and Si nanoparticles processed with the PEDOT:PSS hydrogel binder are being considered next (see the Supporting Information for composition, electrode loading, as well as manufacturing and electrochemical testing details, Table S1 and Figure S10). The cycling stability and rate performance of Sn nanoparticle-based

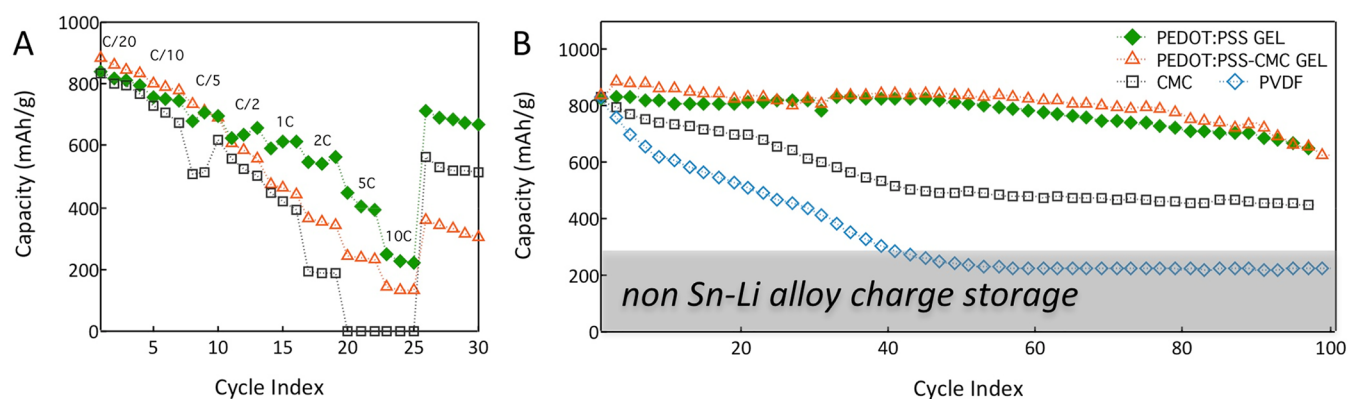


Figure 4. Electrochemical performances of Sn nanoparticle-based electrodes. (A) Power-rate performances with selected binder formulations for Sn nanoparticle-based electrodes and (B) cycling stability at a charge–discharge rate of C/10 (1C corresponds to 950 mA/g).

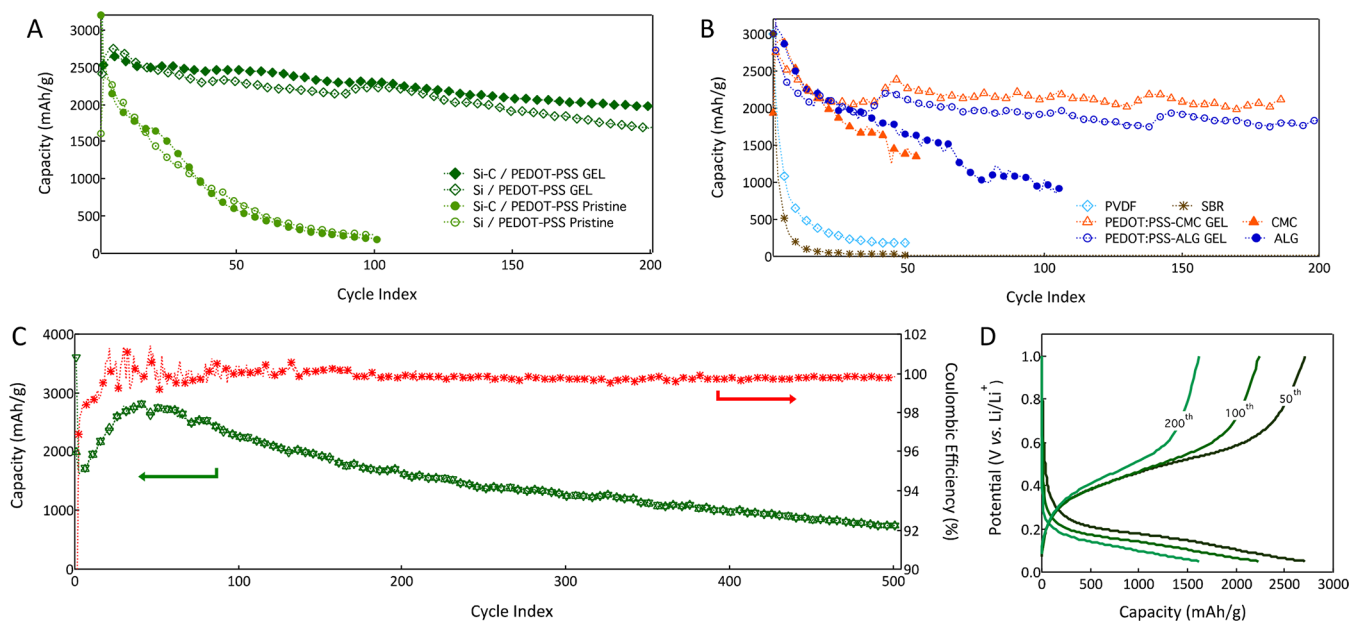


Figure 5. Electrochemical performances of Si nanoparticle-based electrodes. (A, B) Cycling stability of Si nanoparticle-based electrodes with selected binder formulations including hybrid PEDOT:PSS–CMC and alginate formulations. The cycling rate is C/12 (1C corresponds to 3500 mA/g). (C) Extended cycling of Si nanoparticle–PEDOT:PSS hydrogel electrodes with an ionic liquid-based electrolyte (rate of C/6,7). (D) Associated charge–discharge profiles at different cycling extent. See Table S1 for electrode composition and manufacturing details.

electrodes have been found considerably improved when formulated with the PEDOT:PSS hydrogel binder (or hybrid compositions), as compared to standard CMC and PVDF formulations (Figure 4). In particular, the cycling stability with respect to the latter is dramatically enhanced. The PVDF-based electrodes displayed progressive degradation, with the Sn electrochemical de/lithiation features preserved only for 30 cycles. The residual capacity (marked by the gray box in Figure 4B) is attributed to the carbon black additive, PEDOT:PSS and surface charge storage processes.

Si nanoparticle-based electrodes have been extensively analyzed and tested in various formulations, given the appealing properties of Si as negative electrode for Li-ion batteries (Figure 5). A mass loading of 1 mg/cm² and slow cycling conditions (300 mA/g_{Si}) were applied to assess the intrinsic electrochemical properties and avoid measurement artifacts. The PEDOT:PSS hydrogel formulations clearly produce more uniform electrode coatings (Figure 3A, B), which translates into better cycling stability when compared to regular PEDOT:PSS electrode processing (Figure 5A). This is primarily assigned to

limited dewetting of the hydrogel formulation resulting in conformal coating of Si particles during the drying process of the electrodes, which positively differs from other nongel formulations (Figure S11). Although the PEDOT:PSS phase clearly affects the cycling stability, the addition of conductive carbons only slightly enhances the cycling stability (Figure 5A) at low cycling rate, indicating that, despite of the reduction, PEDOT:PSS hydrogel provides sufficient electric conductivity under such operational conditions. Thus, for slow cycling conditions, carbon additives have essentially no effectiveness. Consequently, carbon-free electrodes can be built and, associated with that, an increase in active material content could be considered. Out of the 10 representative configurations presented here (for each type at least 3 samples were measured), the PEDOT:PSS hydrogel formulations clearly stand as the best option. This holds true even when considering hybrid binder formulations.

There are several aspects that can be assigned to support the improvement in the observed electrochemical response. First, as described above, the better adhesion and mechanical

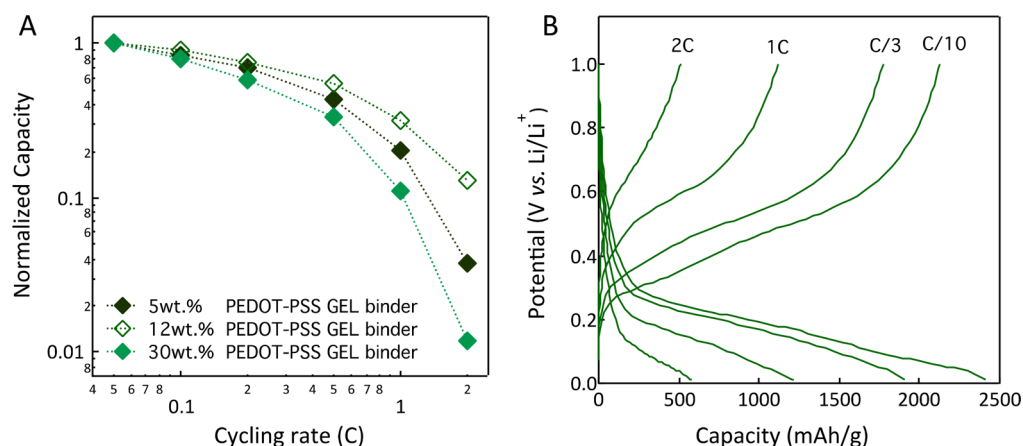


Figure 6. Power performances of Si nanoparticle-based electrodes as a function of the PEDOT:PSS hydrogel binder content. (A) Normalized capacity retention of Si nanoparticle-based electrodes as a function of PEDOT:PSS hydrogel binder content. (B) Potential–capacity plots at different rates for the electrodes with 12 wt % PEDOT:PSS hydrogel binder.

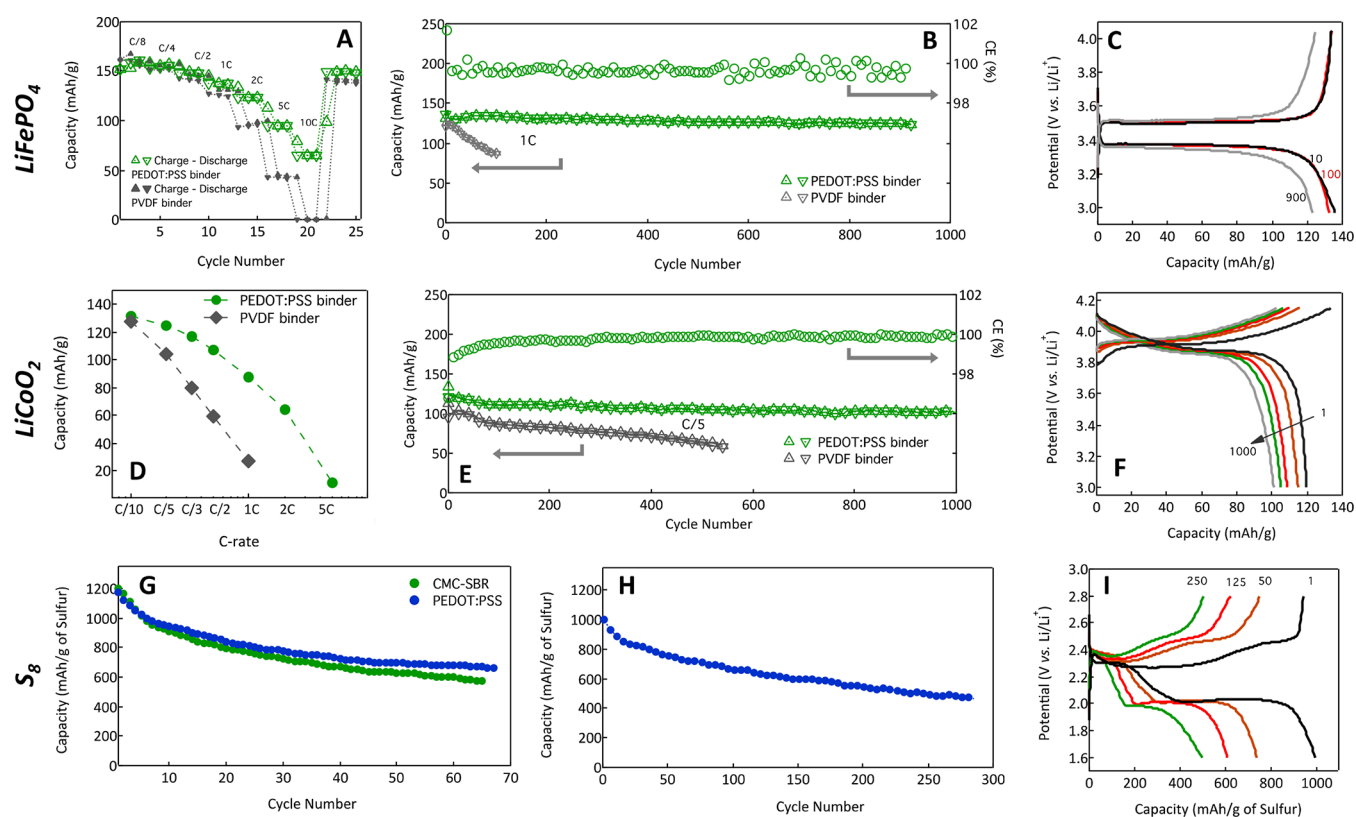


Figure 7. Electrochemical performance of positive electrodes. Power performances–cycling stability–charge–discharge profiles for (A–C) LiFePO₄ and (D–F) LiCoO₂. (G) Cycling stability for S–C composite cathodes for various binder formulations at a cycling rate of C/10. (H) Extended cycling with the PEDOT:PSS hydrogel binder at C/3 rate. (I) The corresponding charge–discharge profiles at different cycles.

strength of the PEDOT:PSS hydrogels are beneficial for accommodating the large stresses accompanying the volume changes in Li-alloying electrode materials.³⁸ This preserves an intimate electrical connection with the current collector and between the particles during volume variations upon cycling. Furthermore, the nonpermeability and very limited swelling of this polymer by the carbonate and other nonaqueous electrolytes effectively prevents direct contact of the electrolyte with the active materials surface (Si, Sn, graphite, etc.). However, further studies are required to access the composition and stability of the SEI with the PEDOT:PSS hydrogel

processed electrode. This is essential for extended cycling of high-capacity alloy materials by building a stable SEI.⁷

The fact that regular PEDOT:PSS-processed electrodes show poor capacity retention highlights the particular necessity of suitable processing conditions and physicochemical properties of the binder. The gelled formulations prevent the migration and segregation of particles during drying, helping thus to maintain the fine particle mixing. These hydrogels also coat more efficiently the low surface tension particles, as dewetting is hampered by the dimensional integrity of the gels (Figures 3 and Figure S11). Noteworthy, after drying, no signs of swelling nor dissolution were observed for PEDOT:PSS hydrogels in

water or aqueous electrolyte solutions (the samples were immersed in 6 M KOH, 1 M LiNO₃, 1 M Li₂SO₄, for more than 1 week), pointing also toward potential applicability in aqueous Li-ion batteries.^{39,40}

Moreover, the PEDOT:PSS hydrogels binders were also found widely compatible with many other electrolyte chemistries and additives. Overall, these electrodes have been tested with different formulations: carbonate-based (ethylene carbonate, diethyl carbonate, dimethyl carbonate, fluoroethylene carbonate, vinyl carbonate, etc.), (poly)ethylene glycol-(ethers), 1,3-dioxolane, dimethylformamide, and ionic liquids (PYR₁₃FSI). No signs of solubility or degradation were observed and no swelling was detected upon extended exposure (more than 1 week), implying that highly efficient surface passivation and protection can be obtained when using PEDOT:PSS hydrogel binders. To highlight the benefic impact, extended cycle-life performance and a Coulombic efficiency of 99.8% in average were obtained for Si nanoparticle-based electrodes associating the PEDOT:PSS hydrogel binder processed electrodes with ionic liquid electrolytes (Figure 5C, D).⁴¹

Because efficient charge collection is also expected to improve the electrochemical stability and, in particular, the power rate performances, we evaluated electrode formulations comprising a different content of PEDOT:PSS hydrogel without any other conductive additive. In addition, in order to maximize the energy density, it is desirable to minimize the content of inactive constituents within the electrode without altering the electrochemical performance. In this context, the polymeric binder and the conductive additive are replaced with the PEDOT:PSS hydrogel. Yet, as discussed in the following, excess of PEDOT:PSS, although enhancing the electrical conductivity of the composite electrodes, was found to induce an adverse effect on the power performances. The PEDOT:PSS hydrogel content-dependent impermeability toward nonaqueous electrolytes has a direct consequence on the power performances. Up to a certain (weight and volumetric) content, the power performances of the electrodes were improved, while above this threshold a detrimental effect is observed. To confirm this, electrodes with a varying amount of PEDOT:PSS hydrogel binder and only Si nanoparticles have been manufactured (with similar Si mass loading) and their power performances were analyzed (Figure 6). The maximum rate performances were attained for approximately 12–15 wt % binder content. The 30 wt % binder content electrode displayed poorer power capacity retention, even lower than the electrode with 5 wt % PEDOT:PSS hydrogel binder, despite its higher electrical conductivity. This is explained by the lower permeability of PEDOT:PSS to carbonate electrolytes, resulting in limited Li⁺-ionic flux and conduction. The optimal PEDOT:PSS hydrogel binder content was found to be different for other active materials; for example, it was found to be about 7 wt % for nano-LiFePO₄ electrodes. Thus, for an optimized electrode formulation, the active particle morphology, the surface area and the conductivity need to be considered together with the ionic and electronic conduction properties of PEDOT:PSS hydrogel binders.

Improved electrode processing as well as enhanced power-rate and cycle stability performances have also been obtained with Li-ion positive electrode materials (LiFePO₄, LiCoO₂, LiMn₂O₄ and Li-S). These results are summarized in Figures 7 and Figure S12. The PVDF-binder processed electrodes show poor cycling capabilities associated with the high-current

density degradation mechanisms such as parasitic phase formation for LiFePO₄ or excessive delithiation in the case of LiCoO₂. These issues are alienated with the PEDOT:PSS hydrogel processed electrode because the intimate electrical connection facilitates the Li ions flow. Similarly to negative electrode materials, enhanced cycling stability, higher Coulombic efficiency and improved power performances were reached with PEDOT:PSS hydrogel processing. The significant increase in the power performance (also content-dependent, as discussed above for negative electrode materials) is assigned to PEDOT, which efficiently maintains the high electrical conduction properties in the operation potential range of the cathode electrode materials. Limited phase segregation during processing (storage, drying), conformal active material coating, improved adhesion (including carbon-coated aluminum foil current collectors), and mechanical strength also account for the clearly enhanced electrochemical performances.

Another particular point to be highlighted here is the chemical stability of the tested positive electrode materials, processed in aqueous conditions. With limited exposure to the aqueous environment (approximately 3 h, including initial premixing, 1 h of milling and gelation followed by subsequent spreading, coating and drying), no differences were found as compared to PVDF binder-processed electrodes (in terms of first cycle capacity and Coulombic efficiency). The long-term stored slurries (more than 3 months, as for example displayed within Figure S5), however, show clear modification, particularly visible at the first cycle. This is attributed to the active material corrosion and metal leaching that can cause structural changes and performance degradation (Figure S13). This well-known process, promoted by water, has precluded the extensive use of aqueous binders for Li-ion cathode materials.⁴² In the case of PEDOT:PSS, the relatively low pH of the solution effectively slows down this process, resulting in improved cycling performances.

Sulfur-carbon composite electrodes have also been combined with PEDOT:PSS hydrogel binder processing, bearing in mind the impermeability to ether and carbonate electrolytes and the effective surface passivation of C/S particle composites. Improved cycling stability is obtained when using the PEDOT:PSS hydrogel binder, implying sufficient surface protection and polysulfide retention (Figure 7G–I, Table S1). The PEDOT:PSS processed electrodes maintain 600 mAh/g for more than 70 cycles, indicative of effective encapsulation and polysulfide shuttle delay. The low polarization under high current density applied load (Figures 7H, I; C/3 rate, 1C corresponds to 1200 mA/g_{Sulfur}) indicates fast electrode kinetics and efficient charge collection, as a result of the electrical conduction properties of PEDOT:PSS.

With the efficient electrode processing routes mastered and enhanced electrochemical properties proved, Li-ion full cells with all PEDOT:PSS hydrogel binder manufactured electrodes were assembled and tested (Figure S14). The assembled LiFePO₄-graphite and LiMn₂O₄-graphite Li-ion cells displayed a stable nominal output voltage of 3.2 and 3.85 V, respectively, and good capacity retention over 50 cycles. Further optimization of the entire manufacturing process and electrochemical cell optimization might be required to reach more competitive performances. Yet, these results show that simple and efficient full aqueous processing of Li-ion battery electrodes is now available through the use of PEDOT:PSS hydrogel binder formulations.

In summary, we show that mechanochemical conversion of PEDOT:PSS aqueous solutions in the presence of metallic iron is a convenient way of producing hydrogels that can retain large amounts of water (up to 99 wt %). In addition, any ball-milling-related safety hazards are minimized due to the mild milling conditions in an aqueous medium. These hydrogels are found to be ideally suited for aqueous formulation of battery electrodes given their combined exceptional rheological properties and dimensional integrity, wide-window electrochemical stability as well as compatibility with battery electrolytes and electrode materials. Overall, the mechanochemically synthesized PEDOT:PSS hydrogels, when applied as binders for lithium-ion batteries, show net advantages given the simple aqueous processing, excellent dispersion stability, preserved electrical conductivity, enhanced structural integrity and adhesion of the prepared electrodes, as well as improved power and cycling stability performances.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b08937.

Experimental details, physicochemical characterization, battery fabrication, and evaluation (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Larcher, D.; Tarascon, J.-M. Towards Greener and More Sustainable Batteries for Electrical Energy Storage. *Nat. Chem.* **2015**, *7*, 19–29.
- (2) Ambrose, H.; Gershenson, D.; Gershenson, A.; Kammen, D. Driving Rural Energy Access: A Second-Life Application for Electric-Vehicle Batteries. *Environ. Res. Lett.* **2014**, *9*, 094004.
- (3) van Schalkwijk, W. A.; Scrosati, B. *Advances in Lithium-Ion Batteries*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2015.

- (4) Park, J.-K. *Principles and Applications of Lithium Secondary Batteries*; Wiley-VCH: Weinheim, Germany, 2013.
- (5) Vlad, A.; Singh, N.; Galande, C.; Ajayan, P. M. Design Considerations for Unconventional Electrochemical Energy Storage Architectures. *Adv. Energy Mater.* **2015**, *5*, 1402115.
- (6) Lux, S. F.; Schappacher, F.; Balducci, A.; Passerini, S.; Winter, M. Low Cost, Environmentally Benign Binders for Lithium-Ion Batteries. *J. Electrochem. Soc.* **2010**, *157*, A320–A325.
- (7) Kovalenko, I.; Zdyrko, B.; Magasinski, A.; Hertzberg, B.; Milicev, Z.; Burtovyy, R.; Luzinov, L.; Yushin, G. A Major Constituent of Brown Algae for Use in High-Capacity Li-Ion Batteries. *Science* **2011**, *334*, 75–79.
- (8) Wang, C.; Wu, H.; Chen, Z.; McDowell, M. T.; Cui, Y.; Bao, Z. Self-Healing Chemistry Enables the Stable Operation of Silicon Microparticle Anodes for High-Energy Lithium-Ion Batteries. *Nat. Chem.* **2013**, *5*, 1042–1048.
- (9) Zhao, H.; Wang, Z.; Lu, P.; Jiang, M.; Shi, F.; Song, X.; Zheng, Z.; Zhou, X.; Fu, Y.; Abdelbast, G.; Xiao, X.; Liu, Z.; Battaglia, V. S.; Zaghbi, K.; Liu, G. Toward Practical Application of Functional Conductive Polymer Binder for a High-Energy Lithium-Ion Battery Design. *Nano Lett.* **2014**, *14*, 6704–6710.
- (10) Higgins, T. M.; Park, S.-H.; King, P. J.; Zhang, C. J.; McEvoy, N.; Berner, N. C.; Daly, D.; Shmeliov, A.; Khan, U.; Duesberg, G.; Nicolosi, V.; Coleman, J. N. A Commercial Conducting Polymer as Both Binder and Conductive Additive for Silicon Nanoparticle-Based Lithium-Ion Battery Negative Electrodes. *ACS Nano* **2016**, *10*, 3702–3713.
- (11) Das, P. R.; Komsysiaka, L.; Osters, O.; Wittstock, G. PEDOT:PSS as a Functional Binder for Cathodes in Lithium Ion Batteries. *J. Electrochem. Soc.* **2015**, *162*, A674–A678.
- (12) Das, P. R.; Gräfenstein, A.; Ledwoch, D.; Osters, O.; Komsysiaka, L.; Wittstock, G. Conducting Polymers as Binder Additives for Cathodes in Li Ion Battery. *ECS Trans.* **2014**, *63*, 31–43.
- (13) Yue, L.; Wang, S.; Zhao, X.; Zhang, L. Nano-Silicon Composites Using poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) as Elastic Polymer Matrix and Carbon Source for Lithium-Ion Battery Anode. *J. Mater. Chem.* **2012**, *22*, 1094–1099.
- (14) Lee, J.; Choi, W. Surface Modification of Over-Lithiated Layered Oxides with PEDOT:PSS Conducting Polymer in Lithium-Ion Batteries. *J. Electrochem. Soc.* **2015**, *162*, A743–A748.
- (15) Myung, S.-T.; Hitoshi, Y.; Sun, Y.-K. Electrochemical Behavior and Passivation of Current Collectors in Lithium-Ion Batteries. *J. Mater. Chem.* **2011**, *21*, 9891–9911.
- (16) Chang, C.-C.; Her, L.-J.; Su, H.-K.; Hsu, S.-H.; Yen, Y. T. Effects of Dispersant on the Conductive Carbon for LiFePO₄ Cathode. *J. Electrochem. Soc.* **2011**, *158*, A481–A486.
- (17) Dreger, H.; Bockholt, H.; Haselrieder, W.; Kwade, A. Discontinuous and Continuous Processing of Low-Solvent Battery Slurries for Lithium Nickel Cobalt Manganese Oxide Electrodes. *J. Electron. Mater.* **2015**, *44*, 4434–4443.
- (18) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. Mechanochemistry: Opportunities for New and Cleaner Synthesis. *Chem. Soc. Rev.* **2012**, *41*, 413–447.
- (19) Shi, Y.; Yu, G. Designing Hierarchically Nanostructured Conductive Polymer Gels for Electrochemical Energy Storage and Conversion. *Chem. Mater.* **2016**, *28*, 2466–2477.
- (20) Lu, Y.; He, W.; Cao, T.; Guo, H.; Zhang, Y.; Li, Q.; Shao, Z.; Cui, Y.; Zhang, X. Elastic, Conductive, Polymeric Hydrogels and Sponges. *Sci. Rep.* **2015**, *4*, 5792.
- (21) Dai, T.; Jiang, X.; Hua, S.; Wang, X.; Lu, Y. Facile Fabrication of Conducting Polymer Hydrogels via Supramolecular Self-Assembly. *Chem. Commun.* **2008**, *36*, 4279–4281.
- (22) Liu, J.; Zhang, Q.; Wu, Z.-Y.; Wu, J.-H.; Li, J.-T.; Huang, L.; Sun, S.-G. A High-Performance Alginate Hydrogel Binder for the Si/C Anode of a Li-Ion Battery. *Chem. Commun.* **2014**, *50*, 6386–6389.

(23) Zhang, X.; Chang, D.; Liu, J.; Luo, Y. Conducting Polymer Aerogels from Supercritical CO₂ Drying PEDOT-PSS Hydrogels. *J. Mater. Chem.* **2010**, *20*, 5080–5085.

(24) Wu, H.; Yu, G.; Pan, L.; Liu, N.; McDowell, M. T.; Bao, Z.; Cui, Y. Stable Li-Ion Battery Anodes by *In-Situ* Polymerization of Conducting Hydrogel to Conformally Coat Silicon Nanoparticles. *Nat. Commun.* **2013**, *4*, 1943.

(25) Correa-Duarte, M. A.; Kosiorek, A.; Kandulski, W.; Giersig, M.; Liz-Marzán, L. M. Layer-by-Layer Assembly of Multiwall Carbon Nanotubes on Spherical Colloids. *Chem. Mater.* **2005**, *17*, 3268–3272.

(26) Weis, C.; Oelschlaeger, C.; Dijkstra, D.; Ranft, M.; Willenbacher, N. Microstructure, Local Dynamics, and Flow Behavior of Colloidal Suspensions with Weak Attractive Interactions. *Sci. Rep.* **2016**, *6*, 33498.

(27) Das, P. R.; Komsiyiska, L.; Osters, O.; Wittstock, G. Effect of Solid Loading on the Processing and Behavior of PEDOT:PSS Binder Based Composite Cathodes for Lithium Ion Batteries. *Synth. Met.* **2016**, *215*, 86–94.

(28) Elschner, A.; Kirchmeyer, S.; Lovenich, W.; Merker, U.; Reuter, K. *PEDOT: Principles and Applications of an Intrinsically Conductive Polymer*; CRC Press: Boca Raton, FL, 2010.

(29) Martin, B. D.; Nikolov, N.; Pollack, S. K.; Saprigin, A.; Shashidhar, R.; Zhang, F.; Heiney, P. A. Hydroxylated Secondary Dopants for Surface Resistance Enhancement in Transparent poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) Thin Films. *Synth. Met.* **2004**, *142*, 187–193.

(30) Kiya, Y.; Iwata, A.; Sarukawa, T.; Henderson, J. C.; Abruña, H. D. Poly[dithio-2,5-(1,3,4-thiadiazole)] (PDMcT)–poly(3,4-ethylenedioxythiophene) (PEDOT) Composite Cathode for High-Energy Lithium/Lithium-Ion Rechargeable Batteries. *J. Power Sources* **2007**, *173*, 522–530.

(31) Chou, S.-L.; Pan, Y.; Wang, J.-Z.; Liu, H.-K.; Dou, S.-X. Small Things Make a Big Difference: Binder Effects on the Performance of Li and Na Batteries. *Phys. Chem. Chem. Phys.* **2014**, *16*, 20347–20359.

(32) Mazouzi, D.; Karkar, Z.; Reale Hernandez, C.; Jimenez Manero, P.; Guyomard, D.; Roué, L.; Lestriez, B. Critical Roles of Binders and Formulation at Multiscales of Silicon-Based Composite Electrodes. *J. Power Sources* **2015**, *280*, 533–549.

(33) Seid, K. A.; Badot, J. C.; Dubrunfaut, O.; Lévassieur, S.; Guyomard, D.; Lestriez, B. Influence of the Carboxymethyl Cellulose Binder on the Multiscale Electronic Transport in carbon–LiFePO₄ Nanocomposites. *J. Mater. Chem.* **2012**, *22*, 24057–24066.

(34) Lacey, M. J.; Jeschull, F.; Edström, K.; Brandell, D. Why PEO as a Binder or Polymer Coating Increases Capacity in the Li–S System. *Chem. Commun.* **2013**, *49*, 8531–8533.

(35) Bülter, H.; Peters, F.; Wittstock, G. Scanning Electrochemical Microscopy for the In Situ Characterization of Solid–Electrolyte Interphases: Highly Oriented Pyrolytic Graphite versus Graphite Composite. *Energy Technol.* **2016**, *4*, 1486–1494.

(36) Courtel, F. M.; Niketic, S.; Duguay, D.; Abu-Lebdeh, Y.; Davidson, I. J. Water-Soluble Binders for MCMB Carbon Anodes for Lithium-Ion Batteries. *J. Power Sources* **2011**, *196*, 2128–2134.

(37) Vogt, L. O.; El Kazzi, M.; Jämstorp Berg, E.; Pérez Villar, S.; Novák, P.; Villevieille, C. Understanding the Interaction of the Carbonates and Binder in Na-Ion Batteries: A Combined Bulk and Surface Study. *Chem. Mater.* **2015**, *27*, 1210–1216.

(38) Sandu, G.; Brassart, L.; Gohy, J.-F.; Pardoën, T.; Melinte, S.; Vlad, A. Surface Coating Mediated Swelling and Fracture of Silicon Nanowires during Lithiation. *ACS Nano* **2014**, *8*, 9427–9436.

(39) Ramanujapuram, A.; Gordon, D.; Magasinski, A.; Ward, B.; Nitta, N.; Huang, C.; Yushin, G. Degradation and Stabilization of Lithium Cobalt Oxide in Aqueous Electrolytes. *Energy Environ. Sci.* **2016**, *9*, 1841–1848.

(40) Ruffo, R.; La Mantia, F.; Wessells, C.; Huggins, R. A.; Cui, Y. Electrochemical Characterization of LiCoO₂ as Rechargeable Electrode in Aqueous LiNO₃ Electrolyte. *Solid State Ionics* **2011**, *192*, 289–292.

(41) Piper, D. M.; Evans, T.; Leung, K.; Watkins, T.; Olson, J.; Kim, S. C.; Han, S. S.; Bhat, V.; Oh, K. H.; Buttry, D. A.; Lee, S.-H. Stable

Silicon-Ionic Liquid Interface for Next-Generation Lithium-Ion Batteries. *Nat. Commun.* **2015**, *6*, 6230.

(42) Doberdò, I.; Löffler, N.; Laszczynski, N.; Cericola, D.; Penazzi, N.; Bodoardo, S.; Kim, G.-T.; Passerini, S. Enabling Aqueous Binders for Lithium Battery Cathodes – Carbon Coating of Aluminum Current Collector. *J. Power Sources* **2014**, *248*, 1000–1006.