Ion-Conducting Robust Cross-Linked Organic/Inorganic Polymer Composite as Effective Binder for Electrode of Electrochemical Capacitor

Hui Gyeong Park 1, Jin Ju Jeong 2, Jae Hun Kim 2 and Jung-So Lee 1,2,*

1 Department of Chemical Engineering, Graduate School of Chosun University, 309 Pilmun-daero, Dong-gu, Gwangju 61452, Republic of Korea
2 Department of Bio-Chemical Engineering, Chosun University, 309 Pilmun-daero, Dong-gu, Gwangju 61452, Republic of Korea
* Correspondence: jslee15@chosun.ac.kr; Tel.: +82-62-230-7163; Fax: +82-62-230-2474

Abstract: Poly(ionic liquid)s (PILs) are used in many electrochemical energy storage/conversion devices owing to their favorable physical properties. Therefore, PIL binders have been examined as polymeric binders for electrodes in energy storage systems (ESSs) and have shown superior performance. Several innovative technologies have been developed to improve the properties of polymers, with cross-linking being the most effective and easy strategy to achieve this. In this study, we designed a breakthrough complex cross-linking and composite technique that could successfully develop the physical properties of a polymer in a simple one-step process. Additionally, the technique could improve the thermal stability and mechanical properties of the polymer. The proposed polymeric binder showed better adhesion, higher capacitance, and good energy density with improved cyclic stability compared to that shown by conventional polyvinylidene fluoride (PVDF). This study revealed that cross-linked networks in polymeric binders are long-cycle-life features for electrochemical redox capacitors.

Keywords: poly(ionic liquids); polymeric binder; cross-linking; energy storage/conversion devices; pseudocapacitor

1. Introduction

With advancements in technology, modern society demands the development of high-efficiency, high-density, and long-life energy storage devices, ranging from portable electronic devices to electric vehicles [1,2]. Fossil fuels have been used to produce energy for several decades [3]. Formulating and implementing strategies to develop clean and sustainable energy systems to reduce the consumption of fossil fuels and alleviate environmental pollution is of global significance [4,5].

Energy storage systems (ESS) play a prominent role in the proper utilization and storage of green energy [6–12]. Supercapacitors, which store energy by the adsorption of ions or surface redox reactions, are considered the most promising ESSs [13,14].

Supercapacitors offer advantages such as shorter charging/discharging times and higher power densities compared to those offered by lithium-ion batteries (LIBs) [15–17]. Electrochemical double-layer capacitors (EDLCs) store charges electrostatically at the interface between the electrode material and electrolyte [18,19]. In response to fast surface redox reactions, pseudocapacitors (PSEUDOs) store charges in the electrode, providing a capacitive-like electrochemical behavior [20–23]. The active materials of PSEUDO exhibit higher capacitances than those of EDLCs. However, such PSEUDOs often produce compromised rate capability and reversibility because they rely on faradaic redox reactions [24]. Most polymer binders only occupy a small proportion (<5 wt%) of commercial...
electrodes [25–27]. However, they play an important role in physically stabilizing electrodes. When used as binders, polymer materials should not chemically reject organic electrolytes and should instead maintain stable adhesive properties without undergoing side reactions, even in an electrochemical environment [28–31]. Although polyvinylidene fluoride (PVDF) is the most successful and widely used binder for conventional LIBs, it suffers from several limitations, such as having weak intermolecular interactions with active materials and showing an inability to support the fast ion transport required under high rates [32,33].

The homogeneous composite structure of pristine electrodes becomes disrupted due to substantial volume changes, leading to mechanical failure and capacity loss over repeated charge/discharge cycles. Several studies have pointed out that the cyclability-related problems of the most promising advanced electrode materials can be alleviated by using more efficient battery binders [34,35]. An ideal electrode matrix should (1) form strong interactions with active materials to maintain adhesion over cycles; (2) offer strong adhesion toward current collectors to prevent electrode delamination; (3) provide a continuous conductive network within the electrode; and (4) be electrochemically and chemically stable in harsh environments for batteries. A class of polymers that has recently garnered attention is polymeric ionic liquids (PILs), whose high electrochemical stability, conductivity, and good processability support their suitability for electrochemical applications [36–42]. They have been successfully incorporated in supercapacitors, electrochemical sensors, and a variety of energy devices. PILs can wrap powder components while still allowing ion flow, improving cyclability [43].

The cross-linking of polymer binders has been proposed as an effective and simple method for the volume expansion of electrodes [44–46]. Thermal and mechanical analyses that were conducted to examine some cross-linked polymers revealed increased glass transition and rheology in them, similar to those in permanently cross-linked polymer matrices [47].

In this study, we present nickel oxide (NiO) synthesized by the sol–gel method and a cross-linkable organic/inorganic hybrid polymer successfully obtained through the quaternization of poly(N-vinyl imidazole) (PVIm) with a unique functional group containing ethoxysilane [48]. We assumed that the durability would be improved through the formation of Si–O bonds between the polymer chains and the active material from introducing a cross-linkable silane group. We fabricated a pseudocapacitor with PVIm; the corresponding electrode could provide cycle stability through the simultaneous improvement in the ion conductivity and physical properties of the composite through cross-linking. Currently, the main trend is developing devices that can be stored while maintaining the cycle characteristics and also increasing the output energy; continuous research and development on PSEUDOs is expected to create new opportunities because they are located in an industry group.

2. Experimental Section

2.1. Materials

Vinyl imidazole (VIm) (98%, Alfa Aesar, Haverhill, MA, USA), N,N′-azobisisobutyronitrile (AIBN) (98%, JUNSEI, Seoul, Republic of Korea), 3-chloropropyltriethoxysilane (3CPTES) (Sigma Aldrich, St. Louis, MI, USA), dimethylformamide (DMF) (99.5%, JUNSEI), acetone (extra pure grade, DUKSAN), methanol (extra pure grade, DUKSAN), nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) (98%, Alfa Aesar), hexamethylenetetramine (HMTA) (99%, KANTO, Tokyo, Japan), carbon black (99.9%, Alfa Aesar), PVDF 1 wt% solution, and N-methyl-2-pyrrolidone (NMP) (99.5%, SAMCHUN, Seoul, Republic of Korea) were used without any further purification. AIBN was recrystallized from methanol.
2.2. Method
2.2.1. Synthesis of Poly(Vinyl Imidazole) (PVIm)

Vm was polymerized via free-radical polymerization, as shown in Figure 1. Initially, Vm and DMF were briefly added to a round-bottom flask equipped with a magnetic stirrer. AIBN was added to the flask, and the mixture was slowly heated to 70 °C under a nitrogen atmosphere. After radical polymerization for 24 h, the resulting yellow viscous solution was cooled to room temperature and precipitated with acetone; this was followed by filtration, which yielded a white powder. The vacuum was dried overnight at 40 °C. The white powder was dissolved in DMF, and the precipitation process was repeated twice. Finally, the resulting wet powder was dried overnight under vacuum at 60 °C to obtain a white powder of PVIm.

![Figure 1](image-url)

Figure 1. (a) Synthesis of C-PVIm_Si; (b) metal oxide surface reactions.

2.2.2. Quaternization of PVIm with 3CPTES

PVIm_Si was synthesized via the nucleophilic substitution reaction (SN2) of PVIm and 3CPTES. This synthesis was conducted at molar ratios of 100:50, 100:70, and 100:100. PVIm and 3CPTES (50, 10.7 mmol), (70, 14.9 mmol), (100, 21.2 mmol) and DMF (40 mL) were added to a 250 mL round-bottom flask equipped with a magnetic stirrer. The mixture was then stirred at 40 °C for 48 h. The resulting solution was precipitated with acetone, followed by filtration to a white powder. The white powder was dried overnight under vacuum at 40 °C, as shown in Figure 1.
2.2.3. Thermal Cross-Linked Poly(1-Vinyl-Propyltriethoxysilane Imidazolium)·Cl\(^-\) (C-PVIm_Si)·Cl\(^-\)

Finally, the prepared PVIm_Si films were placed in vacuum at 150, 150, and 160 °C for 1, 2, and 1 h, respectively, to conduct thermal cross-linking. We refer to the obtained sample as C-PVIm_Si.

2.2.4. Synthesis of Ni(OH)\(_2\) Nanostructure

Using magnetic stirring, Ni(NO\(_3\))\(_2\)-6H\(_2\)O and HMTA were dissolved in deionized (DI) water. The mixed solution was then transferred into a 100 mL vial, maintained at 100 °C for 4 h, and then cooled naturally. The synthesized nickel hydroxide products were cleaned by washing with DI water. The prepared samples were then freeze-dried for 48 h [47].

2.2.5. Synthesis of Porous NiO Nanostructure

Porous NiO nanostructure powders were obtained by annealing the as-prepared Ni(OH)\(_2\) samples at 300 °C for 2 h. NiO is generally known to exhibit excellent electrochemical properties, including pseudocapacitance [48,49].

2.3. Characterization

The chemical structures of the films were analyzed using Fourier-transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific, Waltham, MA, USA) and proton nuclear magnetic resonance (\(^1\)H-NMR spectra, JEOL-JNM-AL300, Tokyo, Japan) in dimethyl sulfoxide-d\(_6\) (DMSO-d\(_6\)) at 300 MHz. The thermal properties of C-PVIm were investigated using differential scanning calorimetry (DSC, TA Instruments, DSC 29, New Castle, DE, USA) under a N\(_2\) atmosphere (in a temperature range of 25–180 °C and at a heating rate of 5 °C min\(^{-1}\)) and thermogravimetric analysis (TGA, TA Instruments, SDT 650, New Castle, DE, USA) under a N\(_2\) atmosphere (in a temperature range of 25–1000 °C and at a heating rate of 10 °C min\(^{-1}\)). To confirm the degree of chemical cross-linking, the gel content was determined using the solvent extraction method and was calculated using the following equation:

\[
\frac{M_2}{M_1} \times 100\% = \text{gel content, (1)}
\]

where M\(_1\) is the weight of C-PVIm_Si, and M\(_2\) is the weight of the extracted solvent [50].

Based on the American Society for Testing and Materials (ASTM) standards, several 180° peel tests were performed using a universal testing machine (UTM, Shimadzu, AGS-10Knx, Tokyo, Japan). The samples were measured at room temperature (20 mm min\(^{-1}\)).

The electrodes were morphologically and electrochemically characterized using scanning electron microscopy (SEM, Hitachi Regulus 8100, Tokyo, Japan).

2.4. Electrochemical Characterization

The working electrode was prepared by mixing an electroactive material (NiO, 85 wt%), carbon black (10 wt%), PVDF, and PVIm_Si (5 wt%) as a binder. The prepared slurry was measured in a nickel plate electrode, and the PVDF electrode binder was dried at 120 °C for 1 h to remove the NMP. The PVIm_Si binder was manufactured by drying at 120 °C for 1 h to remove the NMP, followed by drying for 1 h at 160 °C; this was the optimal cross-linking condition.

The electrochemical performance of NiO was evaluated using Pt foil as the counter electrode and a KOH solution (2 M) as the electrolyte. A voltage window of −0.05 to 0.4 V was observed at room temperature.

3. Results and Discussion

The experimental method is schematically illustrated in Figure 1. Some PVIm and 3CPTES were sequentially dispersed in NMP and heated to 40 °C for 48 h. To obtain the cross-linking rate, depending on the ratio of silane, polymerization was carried out by controlling the ratio of PVIm to silane (100:50, 100:70, and 100:100). The samples obtained
from these processes were made into films and cross-linked at different temperatures and times (150, 150, and 160 °C for 1, 2, and 1 h, respectively). In addition, the structural formula after the cross-linking of NiO and PVIm_Si, shown in Figure 1b, confirmed the FT-IR peak shown in Figure S1.

Free radical polymerization was used to prepare PVIm, using AIBN as the initiator. PVIm_Si was prepared by the partial functionalization of PVIm with 3CPTES. This reaction proceeded smoothly owing to the weak steric hindrance and strong nucleophilicity of the 3-position nitrogen atom in the imidazole ring, as well as the high reactivity of 3CPTES. Figure 2 shows the 1H-NMR spectra of PVIm_Si 50, 70, and 100 in the range of 0–10 ppm, with DMSO-d6 (yellow dot) as the deuterated reagent. The peaks between 6.7 ppm (H$_{5,4}$) and 7.6 ppm (H$_{5}$) were ascribed to the proton of the imidazole ring. Meanwhile, the peaks at 1.6–2.3 ppm (H$_{1}$) and 2.88–3.2 ppm (H$_{2}$) corresponded to protons from the polymer backbone (CH$_{2}$ and CH$\cdots$). The peaks at 1.2 (H$_{6}$) and 3.4 ppm (H$_{7}$) were ascribed to the ethyl group (CH$_{3}$, CH$_{2}$) [51–54]. The 1H-NMR peaks of PVIm and 3CPTES used for quaternary substitution are shown in Figure S2.

![Chemical structure of PVIm_Si](image)

**Figure 2.** 1H-NMR spectra of PVIm_Si.

The chemical structure of the imidazolium-based binder was confirmed using FT-IR spectroscopy. Figure 3 shows the FT-IR of C-PVIm_Si; the broad absorption band at approximately 3018 and 2983 cm$^{-1}$ can be attributed to the stretching vibrations of C-H (sp$^2$) and C-H (sp$^3$) groups, respectively [55]. The peaks at 2916 and 2846 cm$^{-1}$ were attributed to the PVIm moieties [56,57]. The peak at 1750 cm$^{-1}$ confirmed the presence of an aromatic C=N. The peaks at 1510 to 1276 cm$^{-1}$ confirmed the presence of the imidazole ring [58]. The absorption bands at 1250 to 1084 cm$^{-1}$ were attributed to Si-O-Si and Si-O-C stretching [59–63]. Finally, PVIm_Si was successfully synthesized [64]. Moreover, Figure S3 displays the FT-IR spectrum of C-PVIm_Si with peaks of interest marked.

C-PVIm_Si was prepared via thermally induced cross-linking. It is well known that the thermal treatment of ethoxy silane groups leads to the formation of insoluble cross-linked networks (Si-O-Si) in the polymer matrix. The gel content as a function of the temperature
is shown in Figure 4a. The results confirmed that the gel content significantly increased with the increasing ratio of quaternized silane in the PVIm matrix and thermal treatment temperature up to 160 °C.

Figure 3. FT-IR spectra of PVIm_Si.

Figure 4. (a) Gel content of C-PVIm_Si; (b) TGA curves of C-PVIm_Si; (c) final weight based on TGA.
Excellent thermal stability is a fundamental requirement for PSEUDOs in practical applications. The thermal degradation behavior of the polymer binder was examined using TGA in a nitrogen atmosphere, as shown in Figure 4b. Two degradation steps were clearly observed for the cross-linked binders. The first degradation step from approximately 180 to 350 °C was related to the decomposition of the imidazolium groups. The degradation step above 380 °C was attributed to the degradation of the main polymer chain.

Figure 4c shows the residual weight when the temperature was increased to 1000 °C under TGA. The results confirmed that the remaining weight significantly increased with the increasing ratio of quaternized silane and thermal treatment up to 160 °C. The TGA analysis of the NiO@C-PVIm_Si is displayed in Figure S4.

The force–displacement curves of the Ni electrode, shown in Figure 5, indicate the adhesion between the binder and Ni electrode. The average peel forces of the C-PVIm_Si 50 (2.02 N), C-PVIm_Si 70 (3.01 N), and C-PVIm_Si 100 (3.75 N) binders were also higher than that of the PVDF (2.54 N) binder (Figure 5a).

![Figure 5](image-url)

**Figure 5.** (a) The 180° peel tests for the Ni electrode with different binders; (b) optical images of the tape and electrode surface after the peel test.

Regarding the PVDF binder, uneven exfoliation was observed, and the strength was low. The PVIm_Si binder, on the other hand, showed uniform exfoliation. The results of the mechanical strength analysis confirmed that PVIm_Si produced a higher load value. This was assumed to result in improved adhesion to the electrode through the cross-linking of the PVIm_Si binder.

Moreover, the optical images showed that when the PVDF or C-PVIm_Si was used as a binder, a large portion of the electrode slurry peeled off from the Ni electrode and adhered to the tape side after the peel test (Figure 5b) [65].

Additionally, the solution concentration, the solution temperature in the reactor, and the complexing reagent of Ni^{2+} ions were important factors in preparing high-density spherical Ni(OH)_{2} with excellent performance.

Thus, the concentration of the solutions, complexing reagent, feed-in velocity, intensity of agitation, temperature of the reactor, and pH value of the solution in the reactor were important for optimizing the performance of the product under controlled crystallization. The SEM image shows the external morphology of the Ni(OH)_{2} obtained through the synthesis, where the particles are spherical in shape (Figure 6) [66]. Elemental mapping by energy-dispersive X-ray spectrometry (SEM/EDS) was performed for Ni(OH)_{2} and NiO samples. Obtained compositions from the EDS analysis of individual samples were compared to the corresponding targeted chemical phase. The obtained compositions matched well within the typical errors related to EDS analysis. A representative EDS spectrum and elemental mapping is shown in Figure S5a–j. The obtained data suggest the homogeneous dispersion of Ni, O, in both Ni(OH)_{2} and NiO (Figure S5a–e and f–j), respectively.
Porous NiO nanostructure powders were obtained by annealing the as-prepared Ni(OH)\textsubscript{2} samples. After calcination, a color change from light green to gray was observed, confirming the conversion of Ni(OH)\textsubscript{2} to NiO, as shown in Figure 6 [67]. Moreover, the XRD patterns of Ni(OH)\textsubscript{2} and NiO are shown in Figure S6. The XRD peaks in sky blue can be identified as those of a Ni(OH)\textsubscript{2}, on the basis of the standard pattern in JCPDS card 22-044.

In this study, the working electrode was fabricated as shown in Figure 7. Based on this cross-linking study, the cyclic voltammogram (CV) test for NiO, the active material of supercapacitors, is as shown in Figure 8 [68–70]. To observe the change in the CV curve of the C-PVIm\textsubscript{Si} 100 binder, which exhibited the best physical and thermal stability, different scan rates were obtained. In the Nyquist plot (Figure S7), the impedance behaviour of the Ni electrode is portrayed and shown by a vertical line in the low-frequency region, showing ideal capacitive behavior coupled with low charge transfer resistance (R\textsubscript{ct}). Similarly, the PVDF revealed a larger semicircle than C-PVIm\textsubscript{Si} 100.

![SEM images showing porous NiO nanostructure. (a) Ni(OH)\textsubscript{2} and (b) NiO.](image)

The smallest was observed for C-PVIm\textsubscript{Si} 100 in the high-frequency region, which implied that C-PVIm\textsubscript{Si} 100 had the lowest charge transfer resistance in comparison with others.

Our binder exhibited a higher capacity than the PVDF binder (Figure 8b). When comparing the capacities before and after cross-linking, a significant improvement in the capacity after cross-linking was observed (Figure 8c,d), confirming that the cross-linking rate affected the electrochemical capacity [71–73]. It was inferred that the durability was improved because the binding force between the electrode and binder was increased owing to the cross-linking reaction, revealing that the prepared binder showed a high capacity in PSEUDOs and had cycle stability. Therefore, we firmly believe that our proposed C-PVIm\textsubscript{Si} binder has sufficient potential to replace PVDF.
Porous NiO nanostructure powders were obtained by annealing the as-prepared Ni(OH)$_2$ samples. After calcination, a color change from light green to gray was observed, confirming the conversion of Ni(OH)$_2$ to NiO, as shown in Figure 6[67].

Moreover, the XRD patterns of Ni(OH)$_2$ and NiO are shown in Figure S6. The XRD peaks in sky blue can be identified as those of a Ni(OH)$_2$, on the basis of the standard pattern in JCPDS card 22-044.

In this study, the working electrode was fabricated as shown in Figure 7. Based on this cross-linking study, the cyclic voltammogram (CV) test for NiO, the active material of supercapacitors, is shown in Figure 8[68–70]. To observe the change in the CV curve of the C-PVIm_Si 100 binder, which exhibited the best physical and thermal stability, different scan rates were obtained.

In the Nyquist plot (Figure S7), the impedance behavior of the Ni electrode is portrayed and shown by a vertical line in the low-frequency region, showing ideal capacitive behavior coupled with low charge transfer resistance (Rct). Similarly, the PVDF revealed a larger semicircle than C-PVIm_Si 100.

Figure 7. Schematic illustration of working electrode.

Figure 8. Cyclic voltammogram curve of capacitor at different scan rates of NiO. (a) Cycle test; (b) PVDF; (c) PVIm_Si 100; (d) C-PVIm_Si 100.

4. Conclusions

A PVIm_Si binder was successfully synthesized to improve the cycle characteristics of PSEUDOs. This polymeric binder exhibited a strong binding ability with the electrode slurry and Ni electrode. $^1$H-NMR and FT-IR analyses confirmed the synthesis of PVIm_Si, and the thermal stability and cross-linking degree increased as the ratio of silane increased through TGA and gel content. Additionally, a peel test was performed to confirm the physical stability. Examining the electrochemical properties by manufacturing an electrode to which the C-PVIm_Si binder was applied revealed that the binding force between the electrode and binder was increased owing to the cross-linking effect. The resulting C-PVIm_Si 100 binder exhibited better adhesion and cycle stability than the PVDF binder. Thus, it was confirmed that the produced binder showed a high capacity in PSEUDOs and cycle stability. The C-PVIm_Si binder, which has advantages such as easy synthesis and excellent cross-linking, can be competitively used for its high adhesion and can also be applied to high-capacity electrode materials other than PSEUDOs. This study revealed that cross-linked networks in functional polymers are long-cycle-life features for electrochemical redox capacitors.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/polym14235174/s1, Figure S1: FT-IR spectra of NiO@C-PVIm_Si; Figure S2: $^1$H-NMR spectra. (a) PVIm; (b) 3CPTES; Figure S3: FT-IR spectra of C-PVIm_Si. (a) C-PVIm_Si 50 (150 °C 1 h); (b) C-PVIm_Si 70 (150 °C 1 h); (c) C-PVIm_Si 100 (150 °C 1 h); (d) C-PVIm_Si 50 (150 °C 2h); (e) C-PVIm_Si 70 (150 °C 2h); (f) C-PVIm_Si 100 (150 °C 2h); (g) C-PVIm_Si 50 (160 °C 1 h); (h) C-PVIm_Si 70 (160 °C 1 h) and (i) C-PVIm_Si 100 (160 °C 1 h); Figure S4: a) TGA Curves of NiO@C-PVIm_Si; b) final weight based on TGA.; Figure S5: SEM-EDS elemental map analysis of Ni(OH)$_2$ and NiO. (a), (f) electron image; (b), (g) survey; (c), (h) O atoms; (d), (i) Ni atoms; (e), (j) EDS spectrum.; Figure S6: XRD patterns of Ni(OH)$_2$ and NiO.; Figure S7: EIS spectra of the device showing the internal resistances PVDF and NiO@C-PVIm_100.
Author Contributions: Data curation, H.G.P.; J.J.J. and J.H.K.; Investigation, H.G.P.; Project administration, J.J.J.; Resources, J.-S.L.; Supervision, J.-S.L.; Writing—Original draft, J.-S.L. and H.G.P.; Writing—review and editing, J.-S.L. and H.G.P. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT; Ministry of Science and ICT) (No. 2020R1I1A3071687).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liang, Y.; Zhao, C.-Z.; Yuan, H.; Chen, Y.; Zhang, W.; Huang, J.-Q.; Yu, D.; Liu, Y.; Titirici, M.-M.; Chueh, Y.-L.; et al. A review of rechargeable batteries for portable electronic devices. InfoMat 2019, 1, 6–32. [CrossRef]

2. Sanguesa, J.A.; Torres-Sanz, V.; Garrido, P.; Martinez, F.J.; Marquez-Barja, J.M. A Review on Electric Vehicles: Technologies and Challenges. Smart Cities 2021, 4, 372–404. [CrossRef]

3. Abas, N.; Kalair, A.; Khan, N. Review of fossil fuels and future energy technologies. Futures 2015, 69, 31–49. [CrossRef]

4. Bazmi, A.A.; Zahedi, G. Sustainable energy systems: Role of optimization modeling techniques in power generation and supply—A review. Renew. Sustain. Energy Rev. 2011, 15, 3480–3500. [CrossRef]

5. Shivarama Krishna, K.; Sathish Kumar, K. A review on hybrid renewable energy systems. Renew. Sustain. Energy Rev. 2015, 52, 907–916. [CrossRef]

6. Rahman, A.; Farrok, O.; Haque, M.M. Environmental impact of renewable energy source based electrical power plants: Solar, wind, hydroelectric, biomass, geothermal, tidal, ocean, and osmotic. Renew. Sustain. Energy Rev. 2022, 161, 112279. [CrossRef]

7. Yang, Y.; Bremner, S.; Menictas, C.; Kay, M. Battery energy storage system size determination in renewable energy systems: A review. Renew. Sustain. Energy Rev. 2018, 91, 109–125. [CrossRef]

8. Mohtasham, J. Review Article-Renewable Energies. Energy Procedia 2015, 74, 1289–1297. [CrossRef]

9. Babrowski, S.; Jochem, P.; Fichtner, W. Electricity storage systems in the future German energy sector: An optimization of the German electricity generation system until 2040 considering grid restrictions. Comput. Oper. Res. 2016, 66, 228–240. [CrossRef]

10. Christiansen, C.; Murray, B.; Conway, G.; Chambers, C. Energy Storage Study: Funding and Knowledge Sharing Priorities; AECOM: Sydney, Australia, 2015.

11. Armand, M.; Tarascon, J.M. Building better batteries. Nature 2008, 451, 652–657. [CrossRef] [PubMed]

12. Dunn, B.; Kamath, H.; Tarascon, J.-M. Electrical Energy Storage for the Grid: A Battery of Choices. Science 2011, 334, 928–935. [CrossRef]

13. Tahir, M.B.; Abrar, M.; Tehseen, A.; Awun, T.I.; Bashir, A.; Nabi, G. Chapter 11—Nanotechnology: The road ahead. In Chemistry of Nanomaterials, Awun, T.I., Bashir, A., Tehseen, A., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; pp. 289–308.

14. Castro-Gutiérrez, J.; Celzard, A.; Fierro, V. Energy Storage in Supercapacitors: Focus on Tannin-Derived Carbon Electrodes. Front. Mater. 2020, 7, 217. [CrossRef]

15. Shafiei, N.; Nasrollahzadeh, M.; Hegde, G. Chapter 10—Biopolymer-based (nano)materials for supercapacitor applications. In Biopolymer-Based Metal Nanoparticle Chemistry for Sustainable Applications; Nasrollahzadeh, M., Ed.; Elsevier: Amsterdam, The Netherlands, 2021; pp. 609–671.

16. Pottathara, Y.B.; Tiyyagura, H.R.; Ahmad, Z.; Thomas, S. Chapter 3—Chitin and chitosan composites for wearable electronics and energy storage devices. In Handbook of Chitin and Chitosan; Basile, A., Centi, G., Falco, M.D., Iaquaniello, G., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; Volume 179, pp. 431–458.
50. Lee, J.-S.; Jung, C.-H.; Jo, S.-Y.; Choi, J.-H.; Hwang, I.-T.; Nho, Y.-C.; Lee, Y.-M.; Lee, J.-S. Preparation of sulfonated crosslinked poly(2,6-dimethyl-1,4-phenylene oxide) membranes for direct methanol fuel cells by using electron beam irradiation. *J. Polym. Sci. Part A Polym. Chem.* 2010, 48, 2725–2731. [CrossRef]

51. Yuan, J.; Antonietti, M. Poly(ionic liquid) Latexes Prepared by Dispersion Polymerization of Ionic Liquid Monomers. *Macromolecules* 2011, 44, 744–750. [CrossRef]

52. Marcilla, R.; Alberto Blazquez, J.; Rodriguez, J.; Pomposo, J.A.; Mecerreyes, D. Tuning the solubility of polymerized ionic liquids by simple anion-exchange reactions. *J. Polym. Sci. Part A Polym. Chem.* 2004, 42, 208–212. [CrossRef]

53. Melo, M.A., Jr.; Pires, C.T.G.V.M.T.; Airolci, C. The influence of the leaving iodine atom on phyllisilicate syntheses and useful application in toxic metal removal with favorable energetic effects. *RSC Adv.* 2014, 4, 41028–41038. [CrossRef]

54. Niu, M.; Wang, H.; Chen, J.; Su, L.; Wu, D.; Navrotsky, A. Structure and energetics of SiOC and SiOC-modified carbon-bonded carbon fiber composites. *J. Mater. Chem.* 2010, 20, 150–157. [CrossRef]

55. Niu, M.; Wang, H.; Chen, J.; Su, L.; Wu, D.; Navrotsky, A. Structure and energetics of SiOC and SiOC-modified carbon-bonded carbon fiber composites. *J. Mater. Chem.* 2010, 20, 150–157. [CrossRef]

56. Mecozzi, M.; Pietroletti, M.; Scarpinati, M.; Acquistucci, R.; Conti, M.E. Monitoring of marine mucilage formation in Italian seas investigated by infrared spectroscopy and independent component analysis. *Environ. Monit. Assess.* 2012, 174, 6025–6036. [CrossRef]

57. Wei, L.; Chen, C.; Hou, Z.; Wei, H. Poly(acrylic acid sodium) grafted carboxymethyl cellulose as a high performance polymer binder for silicon anode in lithium ion batteries. *Sci. Rep.* 2016, 6, 19583. [CrossRef] [PubMed]

58. Lee, D.U.; Fu, J.; Park, M.G.; Liu, H.; Ghorbani Kashkooli, A.; Chen, Z. Self-Assembled NiO/Ni(OH)2 Nanoflakes as Active Material for High-Power and High-Energy Hybrid Rechargeable Battery. *Nanotechnology* 2016, 179, 1086–1095. [CrossRef]

59. Liu, J.; Chen, P.; Deng, L.; He, J.; Wang, L.; Rong, L.; Lei, J. A Non-sulfided flower-like Ni-PTA Catalyst that Enhances the Hydrotreatment Efficiency of Plant Oil to Produce Green Diesel. *Sci. Rep.* 2015, 5, 15576. [CrossRef] [PubMed]

60. Sankar, A.; Chitra, S.V.; Jayashree, M.; Parthibavarman, M.; Amirthavarshini, T.; Nair, R. Coarse-grained and coarse-grained models for high-performance pseudocapacitor electrodes: Design and implementation. *Diam. Relat. Mater.* 2022, 122, 108804. [CrossRef]

61. Liu, M.; Chang, J.; Sun, J.; Gao, L. A facile preparation of NiO/Ni composites as high-performance pseudocapacitor materials. *RSC Adv.* 2013, 3, 8003–8008. [CrossRef]

62. Goel, S.; Tomar, A.K.; Sharma, R.K.; Singh, G. Highly Pseudocapacitive NiO Nanoflakes through Surfactant-Free Facile Microwave-Assisted Route. *ACS Appl. Energy Mater.* 2018, 1, 1540–1548. [CrossRef]

63. Chu, J.Y.; Lee, K.H.; Kim, A.R.; Yoo, D.J. Improved electrochemical performance of composite anion exchange membranes for fuel cells through cross linking of the polymer chain with functionalized graphene oxide. *J. Membr. Sci.* 2020, 611, 118385. [CrossRef]

64. Xu, L.; Xin, H.; Su, C. Effect of cross-linking on electrochemical performances of polyaniline as the cathode material of lithium-ion batteries. *Polym. Bull.* 2022, 79, 5261–5278. [CrossRef]

65. Moussa, M.; El-Kady, M.F.; Dubal, D.; Tung, T.T.; Nine, M.J.; Mohamed, N.; Kaner, R.B.; Losic, D. Self-Assembly and Cross-Linking of Conducting Polymers into 3D Hydrogel Electrodes for Supercapacitor Applications. *ACS Appl. Energy Mater.* 2020, 3, 923–932. [CrossRef]