

Applications of Microalgae and Macroalgae Biomass as an Anode Active Material and Binder in Lithium-ion Batteries

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Abstract

Limited resources in energy storage systems and the increasing need for batteries have spurred researchers to explore innovative, low-cost, and environmentally friendly sources. This study, which pioneers macro and microalgae as anode-active material in lithium-ion batteries and employs alginate extracted from brown algae as a binder in silicon anodes, represents a significant leap toward a more sustainable future. The need for sustainable energy storage solutions is not just a possibility but a promising reality that offers more environmentally friendly energy storage solutions. In the first study performed in this context, *Ulva lactuca* and *Spirulina* biomass were prepared as anodes and showed 131.9 and 36.6 mAh/g initial specific capacity values, respectively. Studies conducted to elucidate the reaction mechanism determined that the carbohydrate/protein ratio significantly affects the theoretical capacity of the algal species. In the second study, where alginate extracted from *Cystoseira barbata* was tested as a binder in silicon anodes, the highest initial capacity was 3517 mAh/g, and a capacity retention rate of 28.7% was obtained after 100 cycles. For future studies, higher capacity retention rates might be achieved by making the alginate more flexible with the higher Mannuronate/Guluronate ratio in alginate, which varies depending on the type of brown algae.

Introduction

Environmental pollution, raw material shortage, and energy predicament are some of the crucial global concerns we will have to confront more directly in the future. The persistent population growth intensifies these issues and underscores the necessity for precise management of renewable resources. Within this framework, the storage and conversion of green sources will play a pivotal and strategic role in the energy policies of both nations and enterprises. The advancement of new rechargeable batteries has exhibited a consistently increasing momentum in recent years, aiming to (a) enhance the cyclic performance of energy storage

systems and (b) provide an environmentally benign and competent alternative to fossil fuels in the transportation sector (Hannan et al., 2021). While lithium-based batteries have been touted as a crucial technological and commercial breakthrough, the unequal allocation of lithium reserves and their gradual diminution over time pose significant concerns for the future progress of technologies and materials for recycling (Alessia et al., 2021).

The increasing environmental issues linked to traditional battery materials have led to a heightened interest in sustainable alternatives within the lithium-ion battery sector. As the demand for batteries continues to rise, particularly in electric vehicles and

renewable energy storage, the drawbacks of conventional materials, such as their environmental impact and resource scarcity, have become more pronounced. In response to these challenges, a significant number of researchers and innovators are exploring the untapped potential of both terrestrial and marine biological sources. These alternative materials, derived from plants, algae, and other organic matter, offer promising avenues for the development of eco-friendly battery components. By leveraging the unique properties of these bio-sourced materials, the goal is to create batteries that not only enhance performance and energy efficiency but also align with sustainability goals, reducing the overall carbon footprint of battery production. This innovative approach has the potential to revolutionize the industry and pave the way toward greener energy solutions. (Jin et al., 2021; Liu et al., 2020). This shift towards marine resources not only addresses environmental concerns but also opens up a world of possibilities for the future of energy storage, instilling a sense of optimism in the industry.

Intensive studies are carried out on planktonic (phytoplankton and zooplankton) organisms, microbial and single-celled organisms, and products obtained from marine resources have started to constitute an essential part of the world economy due to their various chemical characteristics. The most critical indicators are using these resources in biofuel (Kumar et al., 2021), fertilizer (Emadodin et al., 2020), animal feed additives (Eryalcin et al., 2013), live prey production (Eryalcin, 2019; Morshedi & Eryalcin, 2023), food supplements (Senadheera et al., 2023), and especially recently in energy production (Duca & Toscano, 2022; Kiehadrouinezhad et al., 2023). Marine organisms are exposed to different environmental conditions due to the different physicochemical parameters such as salinity, temperature, pressure, light intensity, water current, nutrients, pH, dissolved oxygen and carbon dioxide, and the presence of inorganic and organic compounds in marine ambient and therefore those various parameters can cause them to have different compounds unique to them. For this reason, they can be used in multiple industries. Due to their characteristics, intensive studies are carried out on planktonic organisms, microbial and single-celled organisms, and products obtained from marine resources have become an essential part of the world economy (Choudhary et al., 2021; Verissimo et al., 2021).

This study effectively utilizes both microalgae and macroalgae from marine sources to thoroughly investigate their impacts on energy storage performance. Microalgae serve as the essential foundation of food webs in both marine and freshwater ecosystems. They are used for several purposes, such as aquaculture, biofuel, feed ingredients, live prey production, crop fertilizer, bioremediation, and wastewater treatments. Depending on the species, they contain essential nutrients like fatty acids, polysaccharides, and pigments. Among them, *Spirulina*

sp. has high biomass potential under open-system cultivation. They have a substantial content of polysaccharides, fatty acids, vitamins, and proteins, making their application by the food industry in many ways (Andrade et al., 2018).

In addition, macroalgae are also very important in several areas, such as chemistry, cosmetics, and protein source production. For instance, *Ulva lactuca* (green algae) is an edible green macroalgae in the division of Chlorophyta. They are found in coastal areas of the marine environment where nutrients are abundant. Therefore, their organic structure content varies depending on environmental factors (Dominguez & Loret, 2019). *Cystoseira barbata* is another macroalgal brown algae species living in shallow waters or on shoreline rocks. Due to their living environment, they exhibit adaptations that protect them from the constant crashing of waves. The bodies of *Cystoseira barbata* are very flexible, allowing them to bend or navigate with wave action. One of the most important reasons they have this flexibility is that they contain high amounts of alginate in their cell walls, giving them flexibility (Remya et al., 2022; Sokolan et al., 2020).

Alginates obtained from brown seaweed varieties are broadly used for their rheological properties and attract significant attention in commercial applications. They are used extensively as thickeners in the food industry and for different formulations in the pharmaceutical industry (Puscaselu et al., 2020). Different applications have been tried in lithium-ion batteries by taking advantage of the distinct features of the three species mentioned above. The first study used *Spirulina* and *Ulva lactuca* as anode active material. As it is known, researches are being carried out to remove heavy metals from wastewater by taking advantage of the biosorption properties of algae (Kratochvil & Volesky, 1998; Pena-Castro et al., 2004). Using the same approach here, the aim is to leverage the biosorption properties of these species to store lithium within their organic structures, representing a novel approach that has not been previously documented in the literature.

In the second study, sodium alginates were produced from alginic acids extracted from *Cystoseira barbata*, and they were tested as a binding polymer in silicon anodes. Since silicon has a much higher theoretical capacity against graphite, it is one of the most important alternatives for new-generation anodes. Despite its high capacity (4200 mAh/g), the most significant drawbacks are the change in the crystal structure and the volume increase in the unit cell as the amount of lithium entering the Si structure increases during the cycle (charge and discharge process) (Taskin et al., 2023). This problem causes the existing crystal structure to deteriorate, leading to rapid capacity fading due to increased lithium ratio in the lithium-silicon composition with subsequent cycles. Many studies have tested different polymeric binders to eliminate the problems related to this volumetric expansion in anode materials with high theoretical capacity (Eshetu &

Figgemeier, 2019). Bio-based alginate has been tested at different ratios to overcome these problems and enhance the cycling performance of silicon anodes. Alginates have a high number of carboxyl groups in their structure. These groups can form hydrogen bonds with the hydroxy groups on the surface of silicon that help suppress the high volumetric expansion (Jang et al., 2023).

Another issue emphasized in this study is the potential environmental impact of using invasive/non-native species (*Ulva lactuca*, *Cystoseira barbata*) as biosources. There are various crucial ecological problems in the European seas owing to extreme pollution loads (i.e., nutrients), climate change, and transport of ballast waters, resulting in dreadful changes in the marine ecosystems (Cinar et al., 2014; Gallardo et al., 2016, Yucel et al., 2024). These factors intensify the competition for marine ecosystems amongst native and invasive/non-native species, introducing further stress on natural biodiversity. Therefore, it is crucial to consider the potential environmental impact when exploiting the potential of undesired marine species to produce high-value-added materials from the Black Sea.

Material and Methods

Microalgae *Spirulina* sp.

Spirulina powders produced using organic farming principles in the Hainan Island region of the South China Sea were obtained by Naturiga company.

Macroalgae (*Ulva lactuca*)

Ulva lactuca seaweeds were collected from the Golden Horn beach and washed with distilled water to remove unwanted substances (stones, sands, insects, etc.). After cleaning, the seaweeds were kept at room temperature for a day and dried in the vacuum oven at 50 °C for 16 hours. Dried seaweeds were ground into powder form in a blade grinder. Carbon black coating was applied to *Ulva lactuca* powders with two different carbon black ratios (10%, 20%) via ball miller at 1000 rpm for 5 hours.

Sodium Alginate Production

To obtain sodium alginate, harvested *Cystoseira barbata* was washed with 1 liter of distilled water and dried at 65°C for 30 hours before extraction. Twenty-five grams of dried algae were kept in 800 mL of 2% formaldehyde at room temperature for 24 hours and then washed with distilled water. Then, 0.2 M HCl (800 mL) was added and left for 24 hours. At the end of this period, the samples were rewashed with distilled water before extraction with 2% sodium carbonate for 3 hours at 100°C. The soluble fraction was collected by centrifugation, and the polysaccharides were precipitated with 95% ethanol. Collected sodium

alginate was washed twice with 100 mL of acetone and dried at 65°C. Then, sodium alginate powder dissolved in 100 mL of distilled water and precipitated again with ethanol (v/3v). The obtained sodium alginate powders were tested with silicon nanopowders (TOB Machine).

Electrode Preparation

In the preparation of electrodes in which algae were used as active material, carbon black (TOB Machine) was added to enhance the electrical conductivity, and PVDF (TOB Machine) was used to ensure the mechanical integrity of the electrode. The ratios of the powders were set as active material/carbon black/PVDF: 80/10/10. The exact ratios were also used for carbon-coated *Ulva lactuca* powders. The weight of the active material in the prepared powder mixture was 1.5 g, and the powder mixture was turned into slurry by dropping 8 ml of NMP (Alfa Aesar).

In silicon anodes where *Cystoseira barbata* was used as a binder, two different powder mixture ratios were tested and adjusted as silicon powder/carbon black/sodium alginate 60/10/30 and 70/10/20, respectively. The silicon (TOB Machine) powder weight in the mixture was 0.5 g, and 10 ml of distilled water was used for slurry preparation. All slurries were mixed in the ball miller at 600 rpm for 1 hour to reach a homogeneous state and were cast on copper foils. After the coating process, the electrodes were kept at 70°C for 12 hours under vacuum. Li metal foil (TOB Machine), a polypropylene membrane (Celgard), and a solution of 1 mol/l LiPF₆ in propylene carbonate (PC) (Sigma-Aldrich) were used as the counter electrode, separator, and electrolyte, respectively.

Electrochemical Tests

Electrochemical analyses of the electrodes were performed by using CR2032 coin cells. Galvanostatic charge-discharge tests were procured at room temperature on an 8 Channel Battery Analyzer (TOB Machine - BST8-WA) at a constant temperature (25°C). The tests were carried out in the 0.05-1.2 V range, and the current density was applied as 14 mA/g and 300 mA/g for algae-based and silicon anodes, respectively. Cyclic voltammetry and impedance analysis were performed on a potentiostat (Gamry Instruments - Interface 1000). For the CV analysis, the scanning speed was set to 0.1 mV/s with a 0.02-1.2 V range. The electrochemical impedance spectroscopy (EIS) analyses were operated at 0.1 V in the range of 1 MHz to 10 mHz.

Characterizations

The study utilized a Hitachi UV-vis instrument (U-2001, Tokyo, Japan). A UV-vis sample of diluted *Spirulina* powder in a PC electrolyte was prepared and placed in a clean crystal cuvette free of spots and fingerprints. In this case, the PC electrolyte served as the reference. The

FTIR spectra of samples are procured via the KBr method (Perkin Elmer) at room temperature, and the spectra are analyzed at 400-4000 cm⁻¹.

Results and Discussion

Spirulina, *Ulva lactuca*, and carbon coated *Ulva lactuca* powders were used as anode-active materials, and their sample codes and process parameters were given in Table 1. Cycling performance analyses of the samples against metallic lithium were shown in Figure 1. The initial discharge capacity of *Ulva lactuca* powders at 0.1 C was observed as 131.9 mAh/g. After the first cycle, there is a rapid decrease in capacity, and in the second cycle, it drops to 41.5 mAh/g with a capacity retention of 31.5%. At the end of the 100th cycle, the discharge capacity decreased to 5.7 mAh/g. However, the initial discharge capacity of *Spirulina* powder starts at 36.6 mAh/g at 0.1C, much lower than the *Ulva lactuca*. After the first cycle, the same rapid fade in capacity occurred, and in the second cycle, it decreased to 8.7 mAh/g with a capacity retention of 23.8%. Two details stand out in

these electrochemical tests. The first was the rapid capacity decline after the first cycle, and the second was the difference between the initial discharge capacities of two different algae species.

Two possible reasons exist for the rapid capacity decrease after the first cycle. One is the possibility that the reactions are irreversible, and the other is the deterioration of the algae's structure due to the organic solvents inside the electrolyte. Based on the results obtained, it was determined that both micro and macro algae could retain lithium ions in their structures. However, it is crucial to clarify the chemical compositions of *Ulva lactuca* and *Spirulina* individuals to elucidate how lithium was retained within the cell.

Most macro and microalgae cell structures consist of organic compounds, and the chemical compositions of the cell structures are shown in Table 2. While *Ulva lactuca* individuals contain high amounts of polysaccharides, *Spirulina* contains high amounts of protein. In addition to polysaccharides and protein, they contain low amounts of lipids and relatively high amounts of inorganic compounds.

Table 1. Sample codes and parameters of anode active materials

Sample Code	Active Material	Decoration Ratio (wt.%)	Decoration Material	Decoration Process	Process Parameters
Spi-Bare	<i>Spirulina</i> sp.	-	-		
Ulva-Bare	<i>Ulva Lactuca</i>	-	-		
Ulva-10%	<i>Ulva Lactuca</i>	10	Carbon Black	Ball Milling	1000 rpm / 5 hr
Ulva-20%	<i>Ulva Lactuca</i>	20	Carbon Black	Ball Milling	1000 rpm / 5 hr

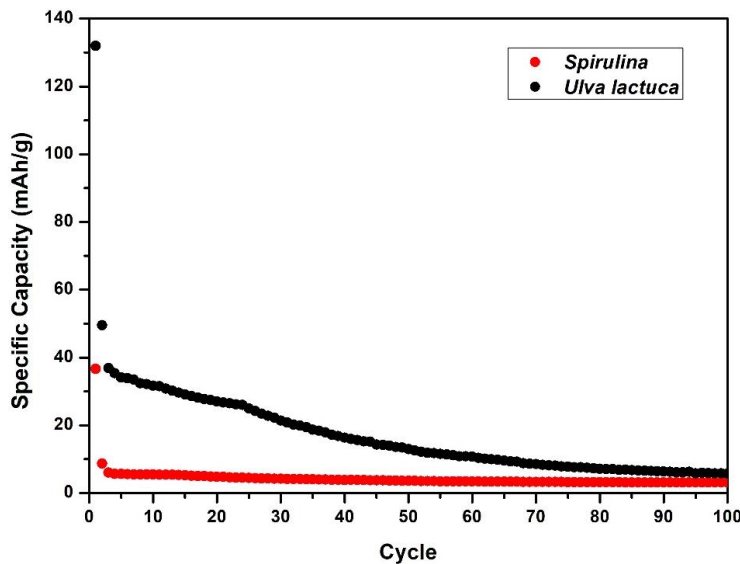


Figure 1. Capacity-cycle graphics of *Ulva lactuca* and *Spirulina* sp. as an anode active material.

Table 2. Proximate compositions of *Ulva lactuca* and *Spirulina* individuals (Breure, 2014)

Component	<i>Ulva lactuca</i> (% DW)	<i>Spirulina</i> sp. Powder (% DW)
Crude Lipid	3,5	1,5
Polysaccharides	46,4	12
Crude Protein	17,8	66
Inorganic compounds	20	7

The inorganic compounds of these algae consist of minerals such as iron, magnesium, calcium, and chlorine. The literature shows that metals such as iron (Zhao et al., 2012), magnesium (Zhang et al., 2019), and calcium (Fang & Chowdari, 2001) can be used as anode active materials in lithium-ion batteries. Therefore, these inorganic structures within the algae are the first factor that effectively retains lithium. The protein structure is another content in which lithium ions can be stored within the algae structure. The amino acid contents of the *Ulva lactuca* and *Spirulina* are shown in Table 3.

The amino acid content of *Spirulina* individuals has a very high amount of protein in their structure; the most important ones are glutamic acid, aspartic acid, alanine, arginine, leucine, and valine. The chemical structures of some significant amino acids for *Spirulina* sp. and *Ulva lactuca* are shown in Figures 2a and 2b, respectively. Compared to *Ulva lactuca* individuals, *Spirulina* contains much more amino acids. Looking at the chemical structures of these amino acids, it is

predicted that lithium ions that enter the algae structure can interact with end groups such as carboxyl (-COOH), hydroxyl (-OH), and amide (-N₂) and hold on in there with secondary bonds.

Another vital content in which lithium ions can be stored is the polysaccharides found in algae. Research on *Ulva lactuca* shows that approximately 40% of the polysaccharides they contain are soluble, and 60% are insoluble. Over 95% of insoluble polysaccharides are cellulose and hemicellulose (Breure, 2014). Most soluble polysaccharide content consists of glucose, rhamnose, and xylose and they contain high amounts of hydroxyl end groups (Figure 3). In addition, considering that natural sugars also contain carboxyl end groups, polysaccharides are predicted to have a significant lithium storage potential, and studies have shown that the polysaccharides in *Ulva lactuca* individuals are similar to those in *Spirulina* individuals but vary only in percentage (Saxena et al., 2022; Shekharam et al., 1987).

Table 3. Some crucial amino acid contents of *Ulva lactuca* and *Spirulina* individuals (Noaman et al., 2016; Liestianty et al., 2019)

Amino acids	<i>Ulva lactuca</i> (mg/g)	<i>Spirulina</i> sp. (mg/g)
Non-essential		
Glutamic acid	14.7	92
Aspartic acid	13.9	60
Alanine	13.8	47
Arginine	6.5	44
Serine	16.2	33
Glycine	12.9	32
Proline	9.6	31
Total	87.6	339
Essential		
Leucine	10	55
Valine	9.1	45
Isoleucine	6.5	36
Threonine	6.6	33
Lysine	1.2	30
Phenylalanine	6.5	28
Total	39.9	227

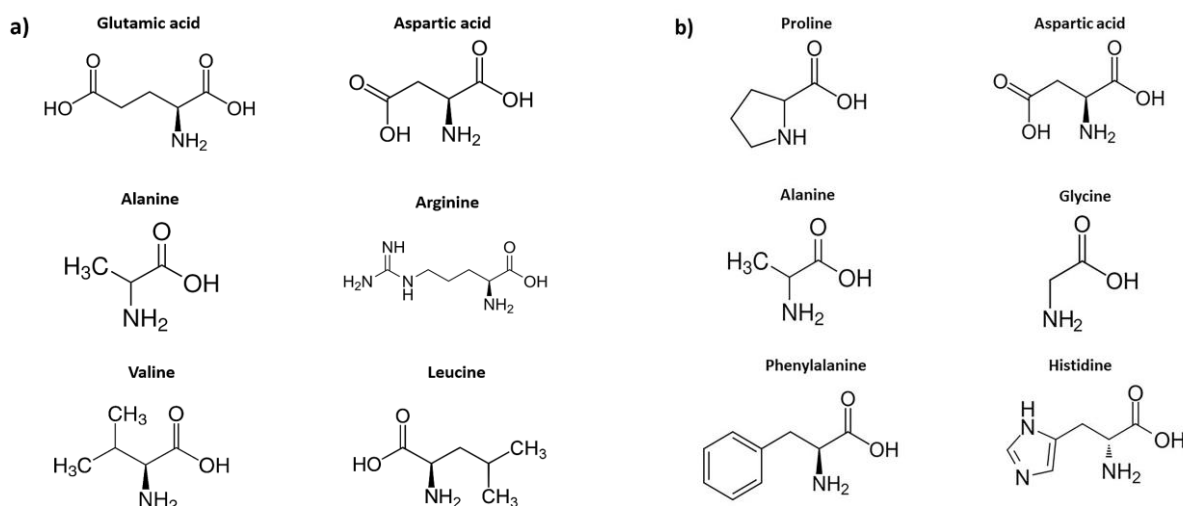


Figure 2. Chemical structure of some important amino acids in a) *Spirulina* and b) *Ulva lactuca* (Khairy et al., 2013; Liestianty et al., 2019).

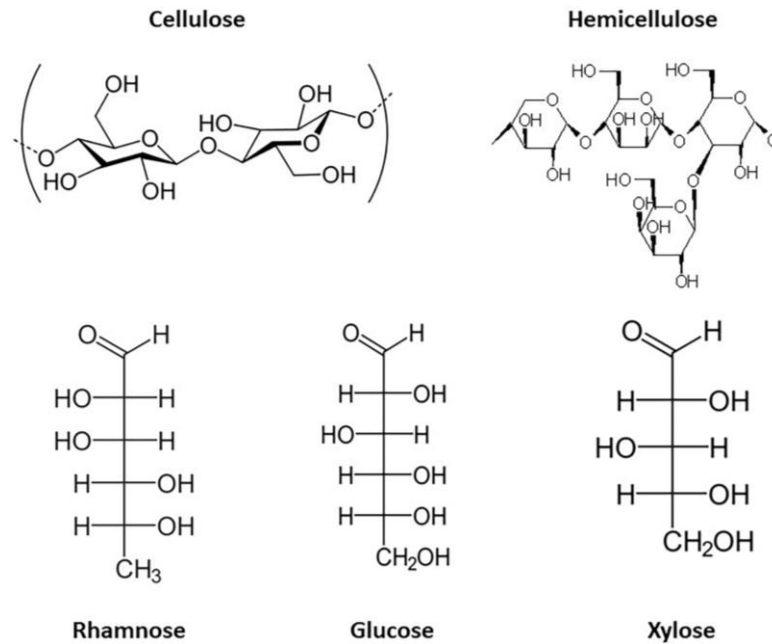
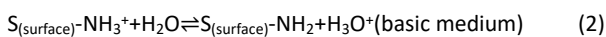
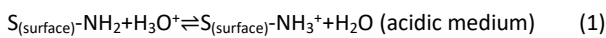


Figure 3. Chemical structure of some essential polysaccharides in *Ulva lactuca* (Breure, 2014).

When all these results are evaluated, it is seen that *Ulva lactuca* individuals contain high amounts of hydroxyl and low amounts of carboxyl and amide end groups in their structures since they are rich in polysaccharides. However, since *Spirulina* individuals are rich in protein, they contain high amounts of carboxyl and amide and low amounts of hydroxyl end groups in their structures.

Many studies have been published on different organic compounds containing carboxyl and hydroxyl groups, such as those in the structure of algae. These end groups can form secondary bonds with lithium and be used as an active material for lithium-ion batteries. Conductive polymers such as polyaniline, polyacetylene, polythiophene, nitroxide radicals, organic salts, and carbonyl compounds can be given as examples (Bhosale et al., 2018; Lyu et al., 2017). It can also be seen in various structures such as lithium sulfonyl bis(fluorosulfonyl)imide, lithium carbonyl bis(fluorosulfonyl)imide, and lithium trichloromethane sulfonate, where lithium can form salt by interacting with organic structures through secondary bonds (Ahmed et al., 2019).

In addition to carboxyl and hydroxyl end groups, amide end groups also have the possibility of secondary bond interaction with lithium. However, in the research conducted for the amide end group, although it can interact with lithium ions, this depends on the pH of the environment (Balkis, 2021).



The chemical proton exchange of reactive amine groups (R-NH₂) is directly related to the pKa of amine compounds, and it is known that the pKa of amines is

approximately 10. If the pH of the environment is below 10, amines will act as Lewis bases, and if it is above 10, they will behave as Lewis acids according to equations 1 and 2. Since the pH values of the electrolytes used in lithium-ion batteries are approximately 7, the amide end groups in the amino acids will behave like a Lewis base and be positively charged, thus eliminating the possibility of secondary interaction with lithium ions. For this reason, only hydroxyl and carboxyl end groups remain that can interact with lithium ions in polysaccharide and protein structures.

The reasons for the approximately 3.5-fold specific capacity difference between *Ulva lactuca* and *Spirulina* in their first discharge capacities are thought to be due to the different chemical compositions of these organisms. After the deductions mentioned earlier, it is understood that the most crucial factor in the capacity differences is the amount of hydroxyl and carboxyl end groups in the algal structures. A comprehensive analysis of amino acids indicates that the number of carboxyl and hydroxyl end groups per unit is notably lower in comparison to the end groups present in polysaccharides. The most important reason for this specific capacity difference is that *Ulva lactuca* individuals consist of polysaccharides and contain more inorganic substances than *Spirulina* individuals.

UV tests were applied to examine the assertion that algae dissolved in the electrolyte may be the primary factor contributing to the significant capacity loss observed following the initial charging process. For this purpose, *Spirulina* and *Ulva lactuca* powders were kept in the electrolyte for ten days, and then the suspended particles were filtered, and UV Spectroscopy analyses were performed (Figure 4). Adsorption peaks observed at wavelengths 659, 610, and 410 are due to chlorophylls coming from *Spirulina*. When peaks in the wavelength range of 400 to 280 are examined, it is

stated in the literature that they are due to proteins dissolved in the electrolyte, and the broad intensity peak at 250 is cellulose.

To reduce capacity fade and prevent side reactions occurring on the surface of *Ulva lactuca* powders, they were decorated with carbon black via ball miller to facilitate algae interaction with organic solvents in the electrolyte. The initial discharge capacity of Ulva-10% and Ulva-20% at 0.1 C was measured as 136.8 and 141.2 mAh/g, respectively. Although there is a slight increase in the initial capacity with the increasing carbon black ratio in the electrode, after the first cycle a similar rapid capacity decay also occurred in those samples. In the second cycle, specific discharge capacity values decreased to 47.5 and 50.9 mAh/g with capacity retention of 34.7% and 36% for Ulva-10% and Ulva-20%, respectively (Figure 5). These results show that surface

decoration treatments couldn't prevent the dissolution of algae.

The FT-IR spectrum of sodium alginate obtained from *Cystoseira Barbata* biomass was illustrated in Figure 6. A broad band at $3,269\text{ cm}^{-1}$ was ascribed to hydrogen-bonded O–H stretching vibrations, while the bands at $2,891$ and $1,602\text{ cm}^{-1}$ were assigned to C–H stretching and carboxylate O–C–O asymmetric stretching vibrations, respectively. The absorption at $1,413\text{ cm}^{-1}$ was appointed to C–OH deformation vibration with the involvement of the carboxylate group's O–C–O symmetric stretching vibration. The bands observed at $1,305$, $1,087$, and $1,034\text{ cm}^{-1}$ were associated with C–C–H (and O–C–H) deformation, C–O stretching vibrations, and C–O (and C–C) stretching vibrations of pyranose rings, respectively. Furthermore, additional signals at 890 and 813 cm^{-1} were designated

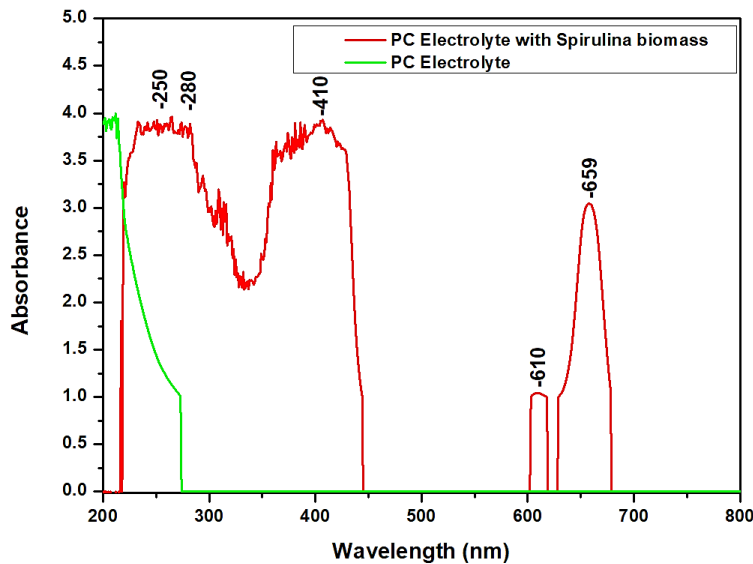


Figure 4. UV spectra of untreated PC electrolyte and PC electrolyte incubated with Spirulina biomass for 10 days..

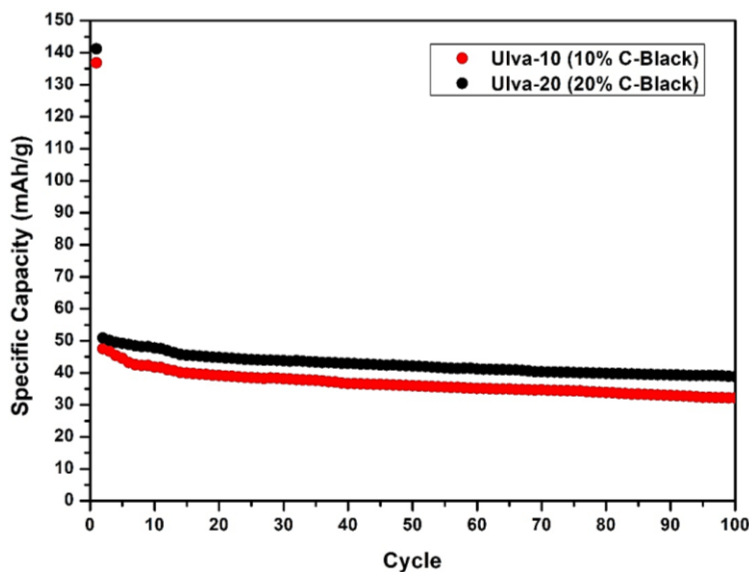


Figure 5. Capacity-cycle graphics of a) Ulva-10% and b) Ulva-20% as anode active material.

to the α -L-gulopyranuronic asymmetric ring vibration and to the mannuronic acid residues, respectively.

Sodium alginates (SA) were tested in silicon anodes with two ratios. Half cells were prepared by setting the binder ratios as 20% and 30% of the total electrode mass. The capacity-voltage and capacity-cycle graphs of these half-cells are shown in Figure 7. Considering the discharge specific capacity-cycle curves obtained from sodium alginate as a binder, the first discharge capacity

at 0.1 C for the 20% SA and 30% SA were measured as 3517.1 and 3221.5 mAh/g, respectively. After the first cycle, there was a slight decrease in the capacities of the two samples due to the formation of the SEI layer and a certain amount of pulverization. In the second cycle, specific discharge capacity values of 2693 and 2867 mAh/g were obtained for 20% and 30% SA, respectively. Due to the high volumetric expansion of silicon, there was a faster decrease in capacity values with the

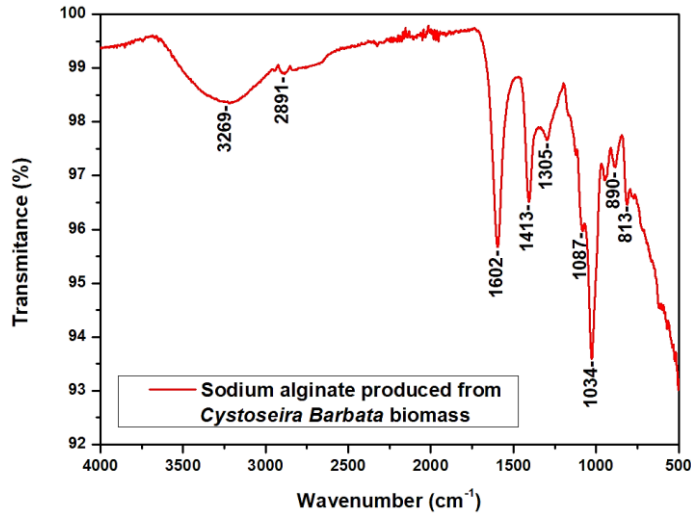


Figure 6. FT-IR spectrum of sodium alginate produced from *Cystoseira barbata* biomass.

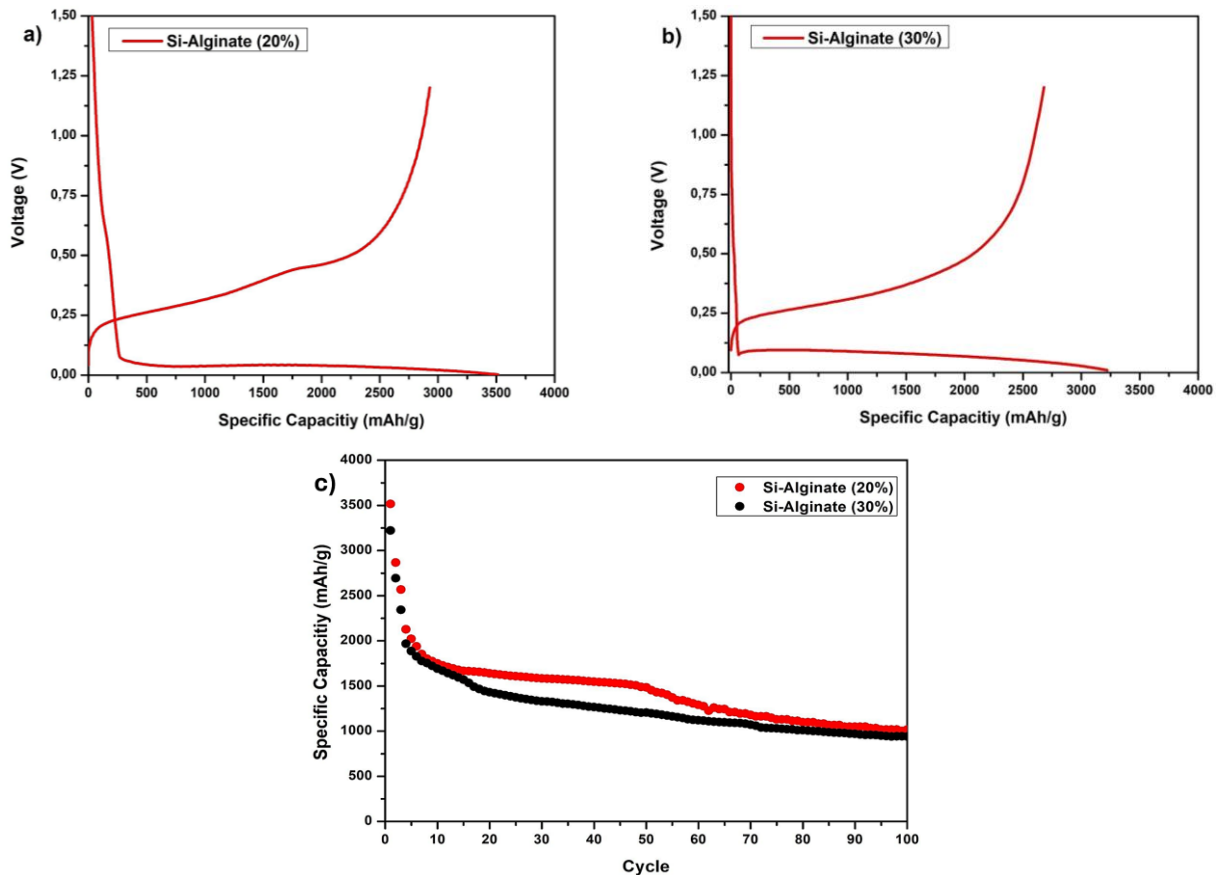


Figure 7. Capacity-voltage graphics of silicon anodes containing a) 20% sodium alginate and b) 30% sodium alginate c) Capacity-cycle graphics of silicon anodes with %20 and %30 sodium alginate as a binder.

following cycles. At the end of the 100th cycle, the discharge capacities decreased to 1010.2 and 940.1 mAh/g, where capacity retention values were calculated as 28.7% and 29.1% for 20% and 30% SA, respectively.

Despite the high theoretical capacity of silicon, it can be seen that as the amount of lithium entering the Si structure increases during the cycle, the lattice structure changes, and the unit cell volume increases. This situation causes the existing crystal structure to deteriorate and the capacity to decrease due to the increase in the lithium ratio in the lithium-silicon composition with subsequent cycles. Many studies have tested different polymeric binders to eliminate the problems related to this volumetric expansion in anode materials with high theoretical capacity (Eshetu & Figgemeier, 2019, Yuca et al., 2018). Studies have shown that synthetic and bio-derived polymers containing carboxyl groups, such as polyacrylic acid (PAA) and carboxymethyl cellulose (CMC), show promising properties as binders for Si-based anodes (Karkar et al., 2017).

Unlike many polysaccharides commonly found in land plants, alginates, the main components of algae and many aquatic microorganisms, contain sodium carboxylate groups in their monomeric units. High carboxylate content in the binders leads to more possible binder-Si interactions and, thus, better electrode stability (Bridel et al., 2010). Chemically, sodium alginate is a copolymer of 1→4 linked b-D-mannuronic acid (M) and a-L-guluronic acid (G) residues. The different compositions and sequences of M and G monoblocks in alginates provide algae with various physical and biological properties. For instance, algae growing in coastal areas have higher G content than algae growing in streams, making alginate gels more rigid (Andriamanantoanina & Rinaudo, 2010; Smidsrod & Draget, 1997).

The ratio of M-G monoblocks in alginates can vary from 0.3 to 9, with a typical value of ~1 in commercial samples (Draget et al., 1997). The literature states that the M/G ratios of alginates obtained from *Cystoseira barbata* are around ~0.65 (Trica et al., 2019). As indicated in Table 4, this value is relatively low

compared to other seaweed types, which causes sodium alginate to have a more rigid structure.

Cyclic voltammetry analyses in the half-cell of the silicon anode, where sodium alginate was used at a rate of 20%, are examined in Figure 8. In the potential range of 0.02~1.2 V, the corresponding reduction peak for the first cycle was at 0.067 V. The only significant oxidation peak was recorded at 0.38 V. Both peaks show lithium intercalation/deintercalation within the structure, and the broad peak of the initial cycle in the cathodic region also includes SEI formation due to electrolyte degradation.

The electrochemical impedance results achieved for the first and fifth cycle of Si-Alginate (20%) anode at 0.1 V is shown in Figure 9. The Nyquist plot contains a semicircle at medium and high-frequency regions, followed by a sloping line in the low-frequency domain. The equivalent circuit for the electrode is embedded in the related Nyquist plot. Solvent resistance (R_s) denotes electrolyte resistance, and the semicircle at the medium-to-high frequency region is signified by a surface (R_{sf}) and charge transfer resistance (R_{ct}) due to the Li^+ migration. Finally, the sloping line in the low-frequency region is attributed to the Warburg impedance (W), indicating lithium ions' solid-state diffusion into the bulk material (Cetintasoglu & Keles, 2021).

Resistance values depending on the designed circuit model are shown in Table 5. Upon reviewing the values of R_{sf} and R_{ct} presented in the table, it is evident that both parameters demonstrate an increasing trend with each subsequent cycle. Deterioration of electrode integrity due to pulverization of particles as a result of the intercalation of lithium ions into the silicon structure and the formation of new SEI layers with low electrical conductivity are also stated in the literature as the main reasons for the increase of impedance.

Conclusion

This pioneering article shows that marine resources can be used as binders and active materials in lithium-ion batteries. It also provides a deeper insight

Table 4. M/G ratio of alginates extracted from different seaweeds (Saji et al., 2022).

Species	Mannuronic acid (%)	Guluronic acid (%)	M/G ratio
<i>Ascophyllum nodosum</i>	46	54	0.65
<i>Bifurcaria bifurcata</i>	65	35	1.88
<i>Fucus guiryi</i>	82	18	4.41
<i>Fucus vesiculosus</i>	59	41	1.44
<i>Laminaria digitata</i>	59	41	1.44
<i>Laminaria hyperborea</i> , leaf	56	44	1.28
<i>Laminaria hyperborea</i> , root	30	70	0.43
<i>Laminaria japonica</i>	65	35	1.86
<i>Laminaria ochroleuca</i>	72	28	2.52
<i>Macrocystis pyrifera</i>	61	39	1.56
<i>Saccharina longicruris</i>	41	59	0.69
<i>Saccorhiza polyschides</i>	63	37	1.73
<i>Sargassum vulgare</i>	56	44	1.27

into the relationship between the algae's reaction mechanism and electrochemical performance. *Ulva lactuca* biomass demonstrated a specific capacity of 131.9 mAh/g in the electrochemical analysis of algae as a negative electrode, and this value is almost three times higher than *Spirulina*. When the reaction mechanisms were examined, it was seen that the most important reason for this difference was due to the protein/ polysaccharide ratio. It has been observed that hydroxyl bonds are of great importance in retaining lithium, and it has been determined that amide groups do not form secondary bonds with lithium due to the pH

value of the electrolyte. Upon using alginate extracted from *Cystoseira Barbata* biomass, the silicon anode demonstrated an initial capacity of 3517 mAh/g. The sample with 20% alginate delivered the best performance, retaining 28.7% of its capacity after 100 cycles. Since the M/G ratio of the extracted alginate varies in different brown algae species and affects the flexibility of alginate, it is predicted that alginates obtained from brown algae species with a higher M/G ratio will give much better cycling performance in anode active materials with high volumetric expansion.

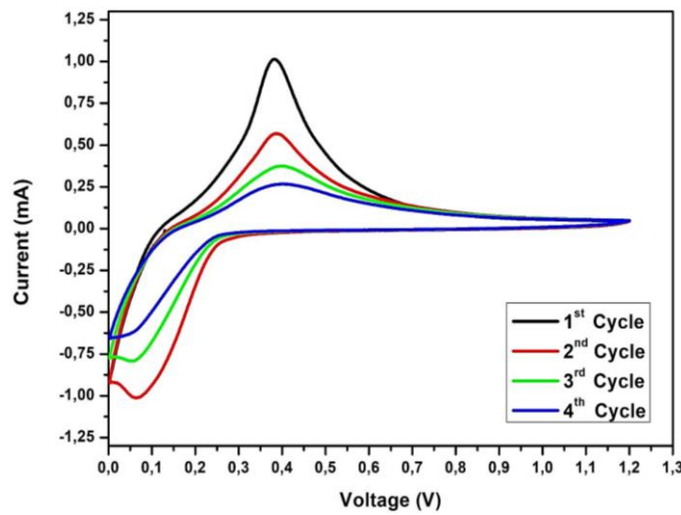


Figure 8. Cyclic voltammety analysis of Si-Alginate (20%) anode.

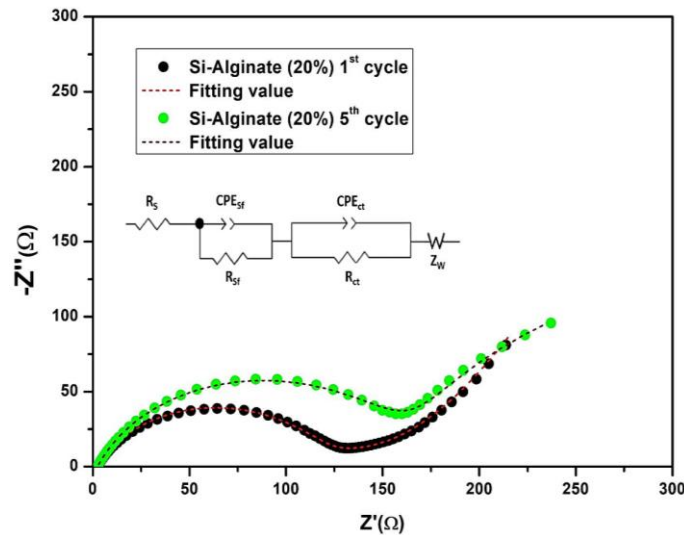


Figure 9. Electrochemical impedance spectroscopy and its equivalent circuit model of Si-Alginate (20%) anode.

Table 5. Rs, Rsf and Rct values calculated according to the relevant equivalent circuit model.

Cycle number	Impedance Value		
	Rs (Ω)	Rsf (Ω)	Rct (Ω)
1st Cycle	2.52	114.8	20.66
5th Cycle	2.34	151.1	149.9

Ethical Statement

Since no live animals were involved in the study, Ethical Approval is not required.

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Author Contribution

All authors participated in the data analysis, contributed to writing the manuscript, and approved the final version.

Conflict of Interest

The authors declare that they have no known competing financial or non-financial, professional, or personal conflicts that could have appeared to influence the work reported in this paper.

References

- Ahmed, F., Rahman, M. M., Sutradhar, S. C., Lopa, N. S., Ryu, T., Yoon, S., Kim, W. (2019). Novel divalent organo-lithium salts with high electrochemical and thermal stability for aqueous rechargeable Li-ion batteries. *Electrochimica Acta*, 298, 709-716. <https://doi.org/10.1016/j.electacta.2018.12.161>
- Alessia, A., Alessandro, B., Maria, V. G., Carlos, V. A., & Francesca, B. (2021). Challenges for sustainable lithium supply: A critical review. *Journal of Cleaner Production*, 300, 126954. <https://doi.org/10.1016/j.jclepro.2021.126954>
- Andrade, L. M., Andrade, C. J., Dias, M., Nascimento, C., & Mendes, M. A. (2018). Chlorella and spirulina microalgae as sources of functional foods. *Nutraceuticals, and Food Supplements*, 6(1), 45-58. <https://doi.org/10.15406/mojfpt.2018.06.00144>
- Andriamanantoanina, H., & Rinaudo, M. (2010). Characterization of the alginates from five madagascan brown algae. *Carbohydrate Polymers*, 82(3), 555-560. <https://doi.org/10.1016/j.carbpol.2010.05.002>
- Balkis, B. (2021). Development and application of silica aerogel-chitosan based nanocomposite material for the removal of pharmaceuticals from the marine environment. (MSc Thesis. 734084, Istanbul University, Turkey)
- Bhosale, M. E., Chae, S., Kim, J. M., Choi, J. Y. (2018). Organic small molecules and polymers as an electrode material for rechargeable lithium ion batteries. *Journal of Materials Chemistry A*, 6(41), 19885-19911. <https://doi.org/10.1039/C8TA04906H>
- Breure, M. S. (2014). Exploring the potential for using seaweed (Ulva lactuca) as organic fertilizer (Doctoral dissertation, MSc Thesis Plant Production Systems. PPS-80436, Wageningen University, Netherlands).
- Bridel, J. S., Azais, T., Morcrette, M., Tarascon, J. M., & Larcher, D. (2010). Key parameters governing the reversibility of Si/carbon/CMC electrodes for Li-ion batteries. *Chemistry of materials*, 22(3), 1229-1241. <https://doi.org/10.1021/cm902688w>
- Cetintasoglu, M. E., & Keles, O. (2021). Effects of sonication power on electrochemical performance of ZrO₂-decorated LiMn₂O₄ cathode material for LIBs. *Bulletin of Materials Science*, 44, 1-11. <https://doi.org/10.1007/s12034-021-02368-8>
- Choudhary, P., Khade, M., Savant, S., Musale, A., Chelliah, M. S., & Dasgupta, S. (2021). Empowering blue economy: From underrated ecosystem to sustainable industry. *Journal of Environmental Management*, 291, 112697. <https://doi.org/10.1016/j.jenvman.2021.112697>
- Cinar, M. E., Arianoutsou, M., Zenetos, A., & Golani, D. (2014). Impacts of invasive alien marine species on ecosystem services and biodiversity: a pan-European review. *Aquatic Invasions*, 9(4), 391-423. <http://dx.doi.org/10.3391/ai.2014.9.4.01>
- Dominguez, H., & Loret, E. P. (2019). Ulva lactuca, a source of troubles and potential riches. *Marine drugs*, 17(6), 357. <https://doi.org/10.3390/md17060357>
- Draget, K. I., Skjåk-Bræk, G., & Smidsrod, O. (1997). Alginate based new materials. *International journal of biological macromolecules*, 21(1-2), 47-55. [https://doi.org/10.1016/S0141-8130\(97\)00040-8](https://doi.org/10.1016/S0141-8130(97)00040-8)
- Duca, D., & Toscano, G. (2022). Biomass energy resources: feedstock quality and bioenergy sustainability. *Resources*, 11(6), 57. <https://doi.org/10.3390/resources11060057>
- Emadodin, I., Reinsch, T., Rotter, A., Orlando-Bonaca, M., Taube, F., & Javidpour, J. (2020). A perspective on the potential of using marine organic fertilizers for the sustainable management of coastal ecosystem services. *Environmental Sustainability*, 3, 105-115. <https://doi.org/10.1007/s42398-020-00097-y>
- Eryalçın, K. M. (2019). Nutritional value and production performance of the rotifer Brachionus plicatilis Müller, 1786 cultured with different feeds at commercial scale. *Aquaculture International*, 27(3), 875-890. <https://doi.org/10.1007/s10499-019-00375-5>
- Eryalçın, K. M., Roo, J., Saleh, R., Atalah, E., Benítez, T., Betancor, M., Hernandez-Cruz, M. C., & Izquierdo, M. (2013). Fish oil replacement by different microalgal products in microdiets for early weaning of gilthead sea bream (Sparus aurata, L.). *Aquaculture Research*, 44(5), 819-828. <https://doi.org/10.1111/j.1365-2109.2012.03237.x>
- Eshetu, G. G., Figgemeier, E. (2019). Confronting the challenges of next-generation silicon anode-based lithium-ion batteries: role of designer electrolyte additives and polymeric binders. *ChemSusChem*, 12(12), 2515-2539. <https://doi.org/10.1002/cssc.201900209>
- Eshetu, G. G., Figgemeier, E. (2019). Confronting the challenges of next-generation silicon anode-based lithium-ion batteries: role of designer electrolyte additives and polymeric binders. *ChemSusChem*, 12(12), 2515-2539. <https://doi.org/10.1002/cssc.201900209>
- Fang, L., Chowdari, B. V. R. (2001). Sn-Ca amorphous alloy as anode for lithium ion battery. *Journal of Power Sources*, 97, 181-184. [https://doi.org/10.1016/S0378-7753\(01\)00615-2](https://doi.org/10.1016/S0378-7753(01)00615-2)
- Gallardo, B., Clavero, M., Sánchez, M. I., & Vilà, M. (2016). Global ecological impacts of invasive species in aquatic ecosystems. *Global change biology*, 22(1), 151-163. <https://doi.org/10.1111/gcb.13004>

- Gheorghita Puscaselu, R., Lobiuc, A., Dimian, M., & Covasa, M. (2020). Alginate: From food industry to biomedical applications and management of metabolic disorders. *Polymers*, 12(10), 2417. <https://doi.org/10.3390/polym12102417>
- Hannan, M. A., Wali, S. B., Ker, P. J., Abd Rahman, M. S., Mansor, M., Ramachandaramurthy, V. K., Ramachandaramurthy, K. M. Muttaqi, Mahlia, T. M. I., & Dong, Z. Y. (2021). Battery energy-storage system: A review of technologies, optimization objectives, constraints, approaches, and outstanding issues. *Journal of Energy Storage*, 42, 103023. <https://doi.org/10.1016/j.est.2021.103023>
- Jang, W., Kim, S., Kang, Y., Yim, T., & Kim, T. H. (2023). A high-performance self-healing polymer binder for Si anodes based on dynamic carbon radicals in cross-linked poly (acrylic acid). *Chemical Engineering Journal*, 469, 143949. <https://doi.org/10.1016/j.cej.2023.143949>
- Jin, C., Nai, J., Sheng, O., Yuan, H., Zhang, W., Tao, X., & Lou, X. W. D. (2021). Biomass-based materials for green lithium secondary batteries. *Energy & Environmental Science*, 14(3), 1326-1379. <https://doi.org/10.1039/DOEE02848G>
- Karkar, Z., Guyomard, D., Roué, L., Lestriez, B. J. E. A. (2017). A comparative study of polyacrylic acid (PAA) and carboxymethyl cellulose (CMC) binders for Si-based electrodes. *Electrochimica Acta*, 258, 453-466. <https://doi.org/10.1016/j.electacta.2017.11.082>
- Khairy, H. M., & El-Shafay, S. M. (2013). Seasonal variations in the biochemical composition of some common seaweed species from the coast of Abu Qir Bay, Alexandria, Egypt. *Oceanologia*, 55(2), 435-452. <https://doi.org/10.5697/oc.55-2.435>
- Kiehbardroudinezhad, M., Hosseinzadeh-Bandbafha, H., Pan, J., Peng, W., Wang, Y., Aghbashlo, M., & Tabatabaei, M. (2023). The potential of aquatic weed as a resource for sustainable bioenergy sources and bioproducts production. *Energy*, 278, 127871. <https://doi.org/10.1016/j.energy.2023.127871>
- Kratochvil, D., & Volesky, B. (1998). Advances in the biosorption of heavy metals. *Trends in biotechnology*, 16(7), 291-300. [https://doi.org/10.1016/S0167-7799\(98\)01218-9](https://doi.org/10.1016/S0167-7799(98)01218-9)
- Kumar, D., Pugazhendhi, A., Bajhaiya, A. K., & Gugulothu, P. (2021). Biofuel production from Macroalgae: present scenario and future scope. *Bioengineered*, 12(2), 9216. <https://doi.org/10.1080/21655979.2021.1996019>
- Liestianty, D., Rodianawati, I., Arfah, R. A., Assa, A., Patimah, Sundari, Muliadi. (2019). Nutritional analysis of spirulina sp to promote as superfood candidate. In IOP Conference Series: Materials Science and Engineering, 509, 012031. <https://doi.org/10.1088/1757-899X/509/1/012031>
- Liu, J., Yuan, H., Tao, X., Liang, Y., Yang, S. J., Huang, J. Q., Yuan, T. Q., Titirici, M. M., & Zhang, Q. (2020). Recent progress on biomass-derived ecomaterials toward advanced rechargeable lithium batteries. *EcoMat*, 2(1), e12019. <https://doi.org/10.1002/eom2.12019>
- Lyu, H., Liu, J., Mahurin, S., Dai, S., Guo, Z., Sun, X. G. (2017). Polythiophene coated aromatic polyimide enabled ultrafast and sustainable lithium ion batteries. *Journal of Materials Chemistry A*, 5(46), 24083-24090. <https://doi.org/10.1039/C7TA07893E>
- Morais, T., Inácio, A., Coutinho, T., Ministro, M., Cotas, J., Pereira, L., & Bahcevandziev, K. (2020). Seaweed potential in the animal feed: A review. *Journal of Marine Science and Engineering*, 8(8), 559. <https://doi.org/10.3390/jmse8080559>
- Morshedi, V., Eryalcin, K. M., Esmaeili, N., Niromand, M., Gamoori, R., Urku, C., & Safari, O. (2023). Rotifer enrichment with DHA did not improve growth and survival rate of yellowtail clownfish (*Amphiprion clarkii*) larvae. *Aquaculture International*, 1-22. <https://doi.org/10.1007/s10499-023-01279-1>
- Noaman, N. H., Akl, F. M., Shafik, M. A., Abdel-Kareem, M. S., & Menesi, W. M. (2016). Effect of ultraviolet-B irradiation on fatty acids, amino acids, protein contents, enzyme activities and ultrastructure of some algae. *Advances in Biology & Earth Sciences*, 1(1), 126-152. <https://doi.org/10.21608/egyjs.2013.115212>
- Pena-Castro, J. M., Martinez-Jerónimo, F., Esparza-Garcia, F., & Canizares-Villanueva, R. O. (2004). Heavy metals removal by the microalga *Scenedesmus incrasatulus* in continuous cultures. *Bioresource technology*, 94(2), 219-222. <https://doi.org/10.1016/j.biortech.2003.12.005>
- Remya, R. R., Samrot, A. V., Kumar, S. S., Mohanavel, V., Karthick, A., Chinnaiyan, V. K., Umapathy, D., & Muhibbullah, M. (2022). Bioactive potential of brown algae. *Adsorption Science & Technology*, 2022, 9104835. <https://doi.org/10.1155/2022/9104835>
- Saji, S., Hebden, A., Goswami, P., Du, C. (2022). A brief review on the development of alginate extraction process and its sustainability. *Sustainability*, 14(9), 5181. <https://doi.org/10.3390/su14095181>
- Saxena, R., Rodríguez-Jasso, R. M., Chávez-Gonzalez, M. L., Aguilar, C. N., Quijano, G., Ruiz, H. A. (2022). Strategy Development for Microalgae *Spirulina platensis* Biomass Cultivation in a Bubble Photobioreactor to Promote High Carbohydrate Content. *Fermentation*, 8(8), 374. <https://doi.org/10.3390/fermentation8080374>
- Senadheera, T. R., Hossain, A., & Shahidi, F. (2023). Marine bioactives and their application in the food industry: A review. *Applied Sciences*, 13(21), 12088. <https://doi.org/10.3390/app132112088>
- Shekharam, K. M., Venkataraman, L. V., Salimath, P. V. (1987). Carbohydrate composition and characterization of two unusual sugars from the blue green alga *Spirulina platensis*. *Phytochemistry*, 26(8), 2267-2269. [https://doi.org/10.1016/S0031-9422\(00\)84698-1](https://doi.org/10.1016/S0031-9422(00)84698-1)
- Smidsrod, O., & Draget, K. I. (1997). Alginate gelation technologies. *Food colloids: Proteins, lipids and polysaccharides*, 279.
- Sokolan, N., Kuranova, L., Voron'ko, N., & Grokhovskiy, V. (2020). Development of Basic Technology for Obtaining Sodium Alginate from Brown Algae. *KnE Life Sciences*, 1-11. <https://doi.org/10.18502/kl.v5i1.6011>
- Sun, L., Liu, Y., Shao, R., Wu, J., Jiang, R., & Jin, Z. (2022). Recent progress and future perspective on practical silicon anode-based lithium ion batteries. *Energy Storage Materials*, 46, 482-502. <https://doi.org/10.1016/j.ensm.2022.01.042>
- Taskin, O. S., Yuca, N., Papavasiliou, J., Avgouropoulos, G., Karabayir, E., Cetintasoglu, M. E., Guney, E., Kalafat, I., Cetin, B., Guzel, E., Urper, O., & Wang, K. (2023). Ambidextrous polyanthracene/poly (ethylene glycol) copolymer for high capacity silicon anode in Li-ion batteries. *Journal of Polymer Research*, 30(11), 434. <https://doi.org/10.1007/s10965-023-03804-5>
- Trica, B., Delattre, C., Gros, F., Ursu, A. V., Dobre, T., Djelveh, G., & Oancea, F. (2019). Extraction and characterization

- of alginate from an edible brown seaweed (*Cystoseira barbata*) harvested in the Romanian Black Sea. *Marine Drugs*, 17(7), 405. <https://doi.org/10.3390/md17070405>
- Veríssimo, N. V., Mussagy, C. U., Oshiro, A. A., Mendonça, C. M. N., de Carvalho Santos-Ebinuma, V., Pessoa, A., Oliveira, R. P. S., & Pereira, J. F. B. (2021). From green to blue economy: Marine biorefineries for a sustainable ocean-based economy. *Green Chemistry*, 23(23), 9377-9400. <https://doi.org/10.1039/D1GC03191K>
- Yuca, N., Cetintasoglu, M. E., Dogdu, M. F., Akbulut, H., Tabanlı, S., Colak, U., & Taskin, O. S. (2018). Highly efficient poly (fluorene phenylene) copolymer as a new class of binder for high-capacity silicon anode in lithium-ion batteries. *International Journal of Energy Research*, 42(3), 1148-1157. <https://doi.org/10.1002/er.3913>
- Yucel, S., Ersoy Korkmaz, N., Aksu, A., & Caglar, N. (2024). Evaluation of carbon dioxide partial pressure and air-sea fluxes in the Sea of Marmara. *International Journal of Environment and Geoinformatics*, 11(3), 147-155. <https://doi.org/10.30897/ijegeo.1523105>
- Zhang, Z., Zhao, M., Xia, M., Qi, R., Liu, M., Nie, J., Lu, X. (2019). Magnesium anodes with extended cycling stability for lithium-ion batteries. *Advanced Functional Materials*, 29(41), 1806400. <https://doi.org/10.1002/adfm.201806400>
- Zhao, X., Xia, D., Zheng, K. (2012). Fe₃O₄/Fe/carbon composite and its application as anode material for lithium-ion batteries. *ACS Applied Materials and Interfaces*, 4(3), 1350-1356. <https://doi.org/10.1021/am201617j>