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ORIGINAL ARTICLE

Rechargeable-hybrid-seawater fuel cell

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A novel energy conversion and storage system using seawater as a cathode is proposed herein. This system is an intermediate between a battery and a fuel cell, and is accordingly referred to as a hybrid fuel cell. The circulating seawater in this open-cathode system results in a continuous supply of sodium ions, which gives this system superior cycling stability that allows the application of various alternative anodes to sodium metal by compensating for irreversible charge losses. Indeed, hard carbon and Sn-C nanocomposite electrodes were successfully applied as anode materials in this hybrid-seawater fuel cell, yielding highly stable cycling performance and reversible capacities exceeding 110 mAh g^{-1} and 300 mAh g^{-1} , respectively.

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INTRODUCTION

The shift toward sustainable energy is one of the key challenges faced by the modern society and an important part of science and technology development. The performance of sustainable energy technologies must be improved to enable the more efficient utilization of intermittent-renewable electricity sources. In addition, because of the climate change, that is, global warming, because of carbon dioxide emissions,^{1–3} investment is needed in renewable energy sources for electricity generation and transport. Both aims rely on the development of energy storage devices that can balance intermittent supply with consumer demands. Among the various energy conversion and storage systems, rechargeable batteries are attracting substantial attention. In particular, rechargeable lithium-ion batteries are considered a promising power source for hybrid electric vehicles and electric vehicles because of their high power and energy density.⁴ However, the continuous growth of the lithium-battery market might induce a lack of resources such as lithium and cobalt. Thus, scientists from several countries have started to explore battery technologies that use alternatives to lithium, such as sodium or magnesium.^{5,6} Among these alternatives, sodium possesses several advantages, such as low cost and natural abundance. In principle, the reversible storage mechanisms for sodium ions are very similar to those for lithium ions. In addition, the voltage and cycling stability of sodium-ion batteries are competitive with those of lithium-ion batteries.

The same trend is indeed observed for new battery chemistries that utilize oxygen as the active cathode species; sodium has recently attracted attention as a replacement for lithium in these alkali-metal-air batteries.^{7–11} Such batteries are promising energy storage systems that provide very high theoretical energy densities; however, the use of pure alkali metals (both Li and Na) as anodes create safety and cost

issues associated with their reactivity and the expense of the required dry-assembly process.

Thus, we have designed a novel energy conversion and storage system using seawater, or more precisely, the NaCl dissolved in seawater, as a sodium source. The use of naturally-abundant seawater as a sodium source renders unnecessary any additional processing and allows for a substantial reduction of the manufacturing cost for energy storage and conversion devices. The herein-reported device is an intermediate system between batteries and fuel cells and is thus referred to as a hybrid fuel cell. Differing from conventional batteries, which comprise alkali-metal-containing intercalation or insertion materials as electrodes in a closed system, this novel concept gains its active material from seawater, which is circulated in the open cathode. Such an abundant supply of active material (sodium dissolved in seawater) enables the use of various alloying-anode materials, such as Si, Sn or Ge, overcoming the limitation introduced by the irreversibility of the first and, to a lesser extent, subsequent alloying processes.¹² Si, Sn and Ge anode materials, in fact, provide high theoretical and practical capacities but are affected by high Coulombic irreversibility (also caused by continuous solid-electrolyte interface-layer growth owing to particle fracturing), which makes their use in conventional Li-ion batteries unfeasible. In fact, when lithium transition-metal oxides, such as LiCoO_2 , are used as the cathode and source of lithium ions in combination with these alloying anodes, the low Coulombic efficiency of the latter results in the reduced lifetime of the lithium-ion full cell owing to the limited supply of alkali ions.¹³ However, circulating seawater in an open-system electrode corresponds to a continuous supply of sodium ions, which gives this system superior cycling stability and allows the application of various anodes by compensating for irreversible charge losses. The negative electrode

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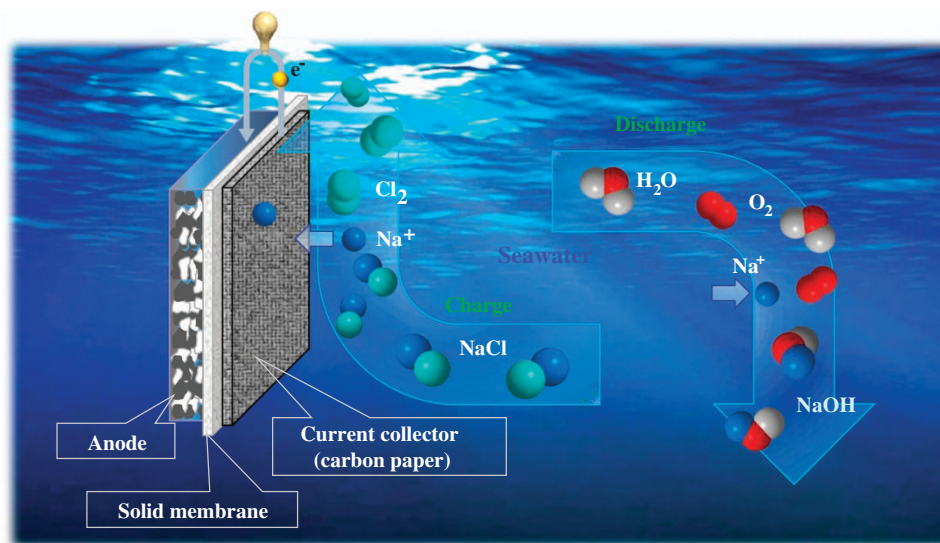


Figure 1 Schematic illustration of the designed hybrid-seawater fuel cell and a schematic diagram at the charged–discharged state.

of this novel hybrid battery/fuel cell system is, instead, closed and separated from the open-seawater positive electrode by a NASICON solid electrolyte (Figure 1). The negative electrode might be composed of sodium metal, in metal-seawater configuration, or a sodium-ion host (e.g., an alloying material), in full sodium-ion configuration.

MATERIALS AND METHODS

Characterization techniques

X-ray diffraction (XRD) was performed using a D8 Advance Bruker AXS (Karlsruhe, Germany) apparatus equipped with a Cu-K α X-ray source ($\lambda = 1.5406 \text{ \AA}$). Fourier transform infrared absorption spectra were recorded with a Fourier transform interferometer (VERTEX 80/80v, Bruker UK Limited, Coventry, UK). The ion concentration of seawater was determined using inductively-coupled plasma spectrometry (Atomscan 25, Optima 4300DV, Waltham, MA, USA). Ionic conductivity measurements were performed by dielectric spectroscopy in the frequency range 100 μHz to 10 MHz using a Novocontrol broadband dielectric spectrometer (Montabaur, Germany) with a cryofurnace. Electrochemical impedance spectroscopy was performed utilizing a Solartron 1470E (Shildon, UK). For the electrochemical impedance spectroscopy study, a Pt/NASICON/Pt cell was prepared by Pt sputtering. Charge–discharge and cycling performance tests were carried out using an automatic galvanostatic charge-discharge unit (WBCS3000 battery cyler, Seoul, Korea) at room temperature. The experiments were carried out applying a current density of 0.05 mA cm^{-2} .

Preparation of materials and hybrid-seawater fuel cell

NASICON was prepared by a solid-state reaction. $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, SiO_2 and ZrO_2 (from Aldrich, St Louis, MO, USA) were mixed and then calcined at 400°C and 1100°C . After repeated mixing and calcination, the powder was pressed into a pellet, which was subsequently sintered at 1230°C .

Hard carbon, used as a negative electrode, was purchased from MeadWestvaco (St Normal, IL, USA). A tin-carbon nanocomposite (Sn-C) was synthesized according to a previously reported method.¹⁴ In brief, tin (II) acetate (Sigma-Aldrich) and sucrose (Acros Organics, Seoul, Korea) were dissolved in deionized water (Millipore, Frankfurt, Germany) in a 1:5 weight ratio. Acetic acid was added to the solution to improve the solubility of tin (II) acetate. The solution was then heated to $\sim 300^\circ\text{C}$ until a dry solid material remained, which was briefly ground using an agate mortar, prior to annealing at 1000°C under argon for 3 h.

For electrochemical studies, the negative electrode was fabricated from an 80:10:10 (wt.%) mixture of hard carbon or Sn-C, SuperP carbon black

(TIMCAL, Bodio, Switzerland) as a conductive additive, and poly(vinylidene fluoride) (Aldrich) as a binder. Seawater containing NaCl was used as the positive electrode.

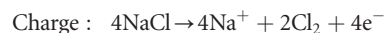
For the non-aqueous liquid electrolyte on the negative-electrode side, a 1 M solution of NaClO_4 (Sigma-Aldrich) in ethylene carbonate /diethyl carbonate (DEC; 1/1 vol.%, Sigma-Aldrich) was utilized. As the solid electrolyte, a NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) ceramic electrolyte with a diameter of 20 mm and a thickness of 2 mm was used. The conductivity was determined to be $\sigma_{\text{Na}} = 9 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature by dielectric spectrometry. A carbon paper with a thickness of $280 \mu\text{m}$ (Fuel Cell Store, College Station, TX, USA) was used as the current collector in the positive-electrode compartment containing seawater. The Sn-C anode was kept in liquid electrolyte (1 M NaClO_4 in ethylene carbonate/DEC) for 1 day and washed by DEC for the stored Sn-C anode.

RESULTS

Redox reaction of seawater in hybrid-seawater fuel cell

The design of the hybrid-seawater fuel cell and the reactions occurring at the positive-current collector (carbon paper) are schematically illustrated in Figure 1.

The redox processes at the seawater-positive electrode can be described as follows:



The negative electrode is wet with a non-aqueous electrolyte and separated from the cathodic compartment by a highly ionically conductive, ceramic, solid electrolyte ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) film (Supplementary Figure 1).

During charge of the hybrid-seawater fuel cell (Figure 2a), the Na^+ ions present at the cathode diffuse through the NASICON electrolyte and transfer to the negative electrode whereas gaseous Cl_2 is released. Although O_2 evolution ($E = 3.94 \text{ V}$) is thermodynamically preferred to Cl_2 evolution ($E = 4.07 \text{ V}$), the observed charge voltage of salt water can be related to the reaction involved with both Cl_2 and O_2 gas evolution. In addition, the ratio of Cl_2 evolution is practically higher than O_2 when the salt water NaCl (aqueous) is under the electrolytic process owing to the higher overpotential of O_2 evolution.^{15,16} Upon discharge, the oxygen dissolved in seawater is reduced, resulting

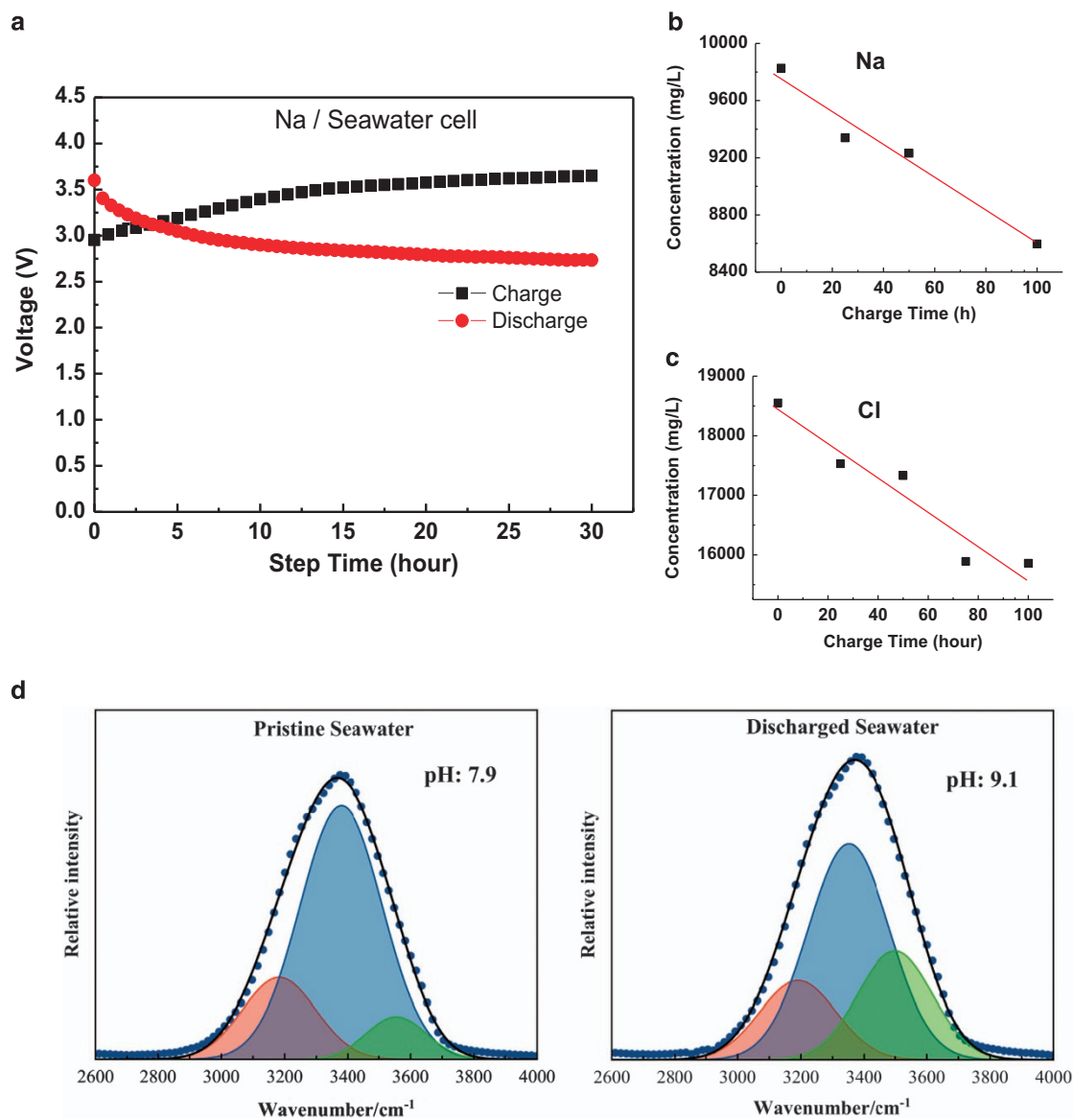


Figure 2 (a) Charge–discharge profile of Na/seawater cells; (b and c) changes of Na^+ and Cl^- concentration with charging time; (d) FT-IR (Fourier transform infrared) spectrum of the OH-stretching region (H_2O bridging mode at 3180 cm^{-1} , H-bonded interlayer H_2O surrounding the interlayer anion at 3380 cm^{-1} and metal-OH stretching mode at 3580 cm^{-1}) including the corresponding pH values.

in the formation of NaOH in the presence of water and sodium ions. The participation of oxygen in the reduction reaction boosts the theoretical discharge potential to 3.11 V from 1.88 V in de-aerated water.

To confirm the proposed charge and discharge processes, various complementary analytical methods were used. Upon charge, the consumption of Na^+ and Cl^- ions from the cathode compartment was investigated by inductively-coupled plasma spectrometry and ion chromatography (Figures 2b and c). The concentration of both ions (Na^+ and Cl^-) in seawater decreased with increasing charging time, resulting from Na^+ transport in the anodic compartment and Cl_2 gas evolution, respectively. During discharge, the formation of NaOH is revealed by the increase of the pH value. Further evidence for NaOH formation is provided by Fourier transform infrared spectroscopy (Figure 2d). The metal-OH stretching mode at 3580 cm^{-1} significantly increases after discharge, indicating the generation of NaOH upon discharge.¹⁷

Electrochemical performance of hybrid-seawater fuel cell with alternative anodes

The charge–discharge profiles of the hybrid-seawater fuel cell tested with different negative-electrode materials are presented in Figure 3. To investigate the deposition of sodium metal, a bare Ni current collector was initially used on the anode side (Supplementary Figure 2). During charge, Na^+ ions diffuse from the cathode (seawater) through the electrolyte to be deposited as cluster-like, metallic sodium on the surface of blank Ni foil (Supplementary Figure 3). The long charge curve indicates the electrochemical reaction of seawater.

Using hard carbon as the sodium-ion negative-electrode resulted in very reversible charge–discharge profiles (Figure 3a). In the first cycle, the discharge capacity (sodium uptake) was 114.4 mAh g^{-1} , whereas the irreversible capacity amounted to 60 mAh g^{-1} (applied current density: 0.05 mA cm^{-2}). However, this latter value decreased with increasing cycle number, although the reversible capacity slightly decreased. Such an electrochemical performance is typical of hard carbons, indicating

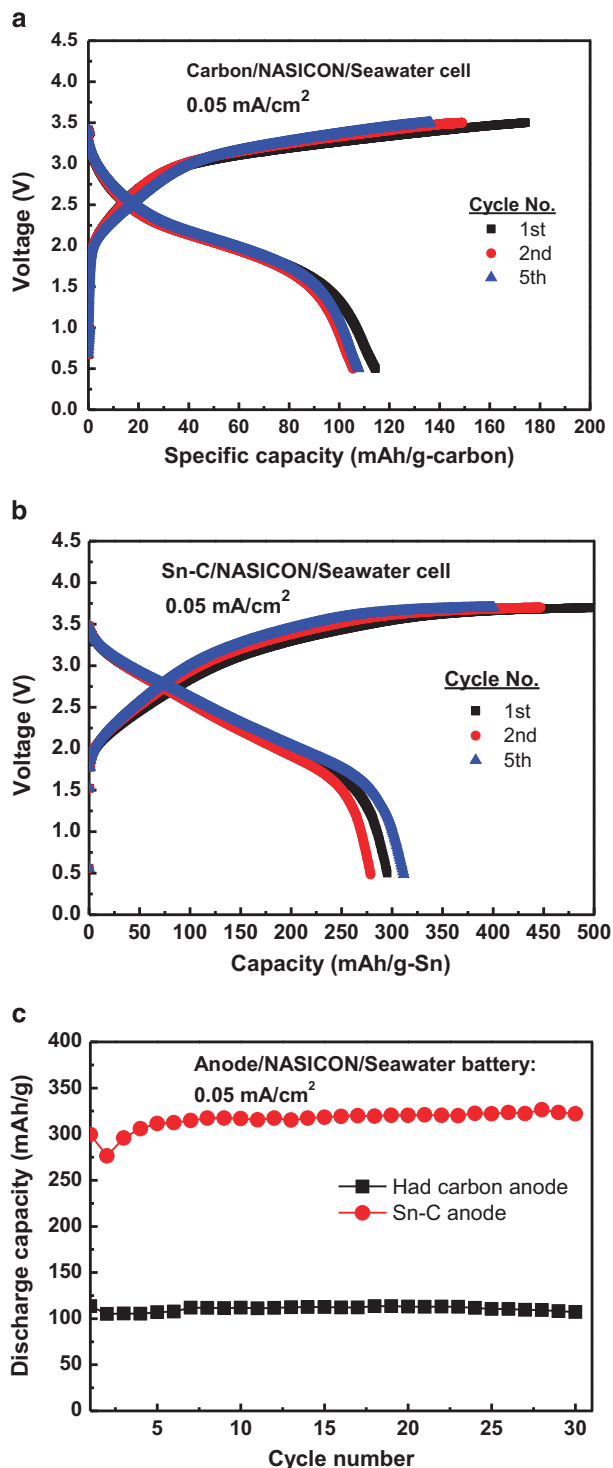


Figure 3 (a) Charge–discharge curves of seawater-hybrid fuel cells with (a) hard carbon and (b) Sn/C anodes; (c) cycling performance recorded with negative electrodes in a hybrid-seawater fuel cell system (room temperature, 0.05 mA cm^{−2}).

that seawater can serve as the source of sodium ions as well as conventional cathode materials in sodium-ion batteries. The great advantage of seawater in an open-cell configuration compared with such cathode materials is the practically unlimited supply of sodium.

To confirm the suitability of this cell configuration with alloying materials, a Sn-C anode (Figure 3b) was also employed. The interest in

using a Sn-based anode material originates from the high theoretical capacity of tin ($\sim 847 \text{ mAh g}^{-1}$), leading to the formation of inter-metallic $\text{Na}_{15}\text{Sn}_4$. The sodium-storage capacity, usually undermined by the poor cyclability resulting from the large specific volume changes in charging and discharging, is made available by the encapsulation of Sn nanoparticles in an amorphous but conductive carbon matrix, hereafter referred to as Sn-C nanocomposite.¹⁴ XRD analysis of this nanocomposite shows only the presence of metallic tin, whereas no tin oxide species are detected (Supplementary Figure 4). A combined SEM-EDX (scanning electron microscopy with energy dispersive X-ray) analysis further reveals the micron-size of the composite particles and the homogenous distribution of the encapsulated tin nanoparticles within the micron-sized carbon particles (Supplementary Figure 5). Electrodes based on this Sn-C nanocomposite as the anode in a full-cell configuration showed a first-cycle irreversible capacity of $\sim 200 \text{ mAh g}^{-1}$, and the reversible capacity was $\sim 300 \text{ mAh g}^{-1}$ (all capacity values given here for Sn-C electrodes refer to the weight of the nanocomposite). The rather high irreversible capacity is generally related to electrolyte decomposition at the particle surface, resulting in the formation of a solid-electrolyte interphase, as well as, structural rearrangement occurring upon the first sodiation within the micron-sized composite particles.¹⁴ For subsequent cycles, the reversible capacity increased to $> 300 \text{ mAh g}^{-1}$ at the 5th cycle, accompanied by a continuously decreasing irreversible capacity ($\sim 90 \text{ mAh g}^{-1}$ at the 5th cycle).

Generally, the performance of both the anode materials (hard carbon and Sn-C nanocomposite) in combination with the seawater cathode is very stable upon continuous cycling, showing a remarkably low capacity fading of only 0.02% and 0% after 30 cycles for the hard carbon and Sn-C anode, respectively (Figure 3c). These results again highlight the great advantage of an almost infinite supply of sodium ions by employing the open-system seawater cathode.

Analysis of sodiated anode materials

The two alternative anode materials were investigated by *ex situ* analytical methods in the charged and discharged states. The hard carbon electrode showed a very homogenous distribution of sodium within the carbon particles (Supplementary Figure 6), confirming the suitability of alternative anodes for the herein-presented hybrid-seawater fuel cell.

The *ex situ* investigation of the Sn-C-based electrode (Figure 4) clearly revealed the presence of the $\text{Na}_{15}\text{Sn}_4$ phase (JCPDS #31-1327), the end-member of the electrochemical alloying reaction of tin and sodium (Figure 4b). This result is in good agreement with the characteristic potential profile observed for Sn-C/Na half-cells, exhibiting different potential plateaus that indicate the formation of various intermediate-intermetallic Sn-Na alloy phases (Supplementary Figure 7).^{18,19} Moreover, the preserved XRD pattern for the Sn-C electrode stored in electrolyte for 1 day indicates the absence of parasitic side reactions and confirms the successful protection of the anode from contact with seawater by the NASICON electrolyte. The Sn-C electrodes were carefully disassembled, washed by DEC, and then investigated by X-ray photoelectron spectroscopy and SEM-EDX. Figure 4c shows high-resolution X-ray photoelectron spectroscopy core-level spectra of Na 1s. After the first charge, the intensity of Na 1s significantly increases, indicating Na^+ uptake upon charge. In addition, the *ex situ* SEM-EDX analysis of Sn-C-based electrodes before and after electrochemical sodiation is consistent with the findings for the hard carbon-based electrode, revealing a very homogenous sodium distribution in the nanocomposite (Figure 4d). These results demonstrate the possibility of replacing highly-reactive metallic sodium by

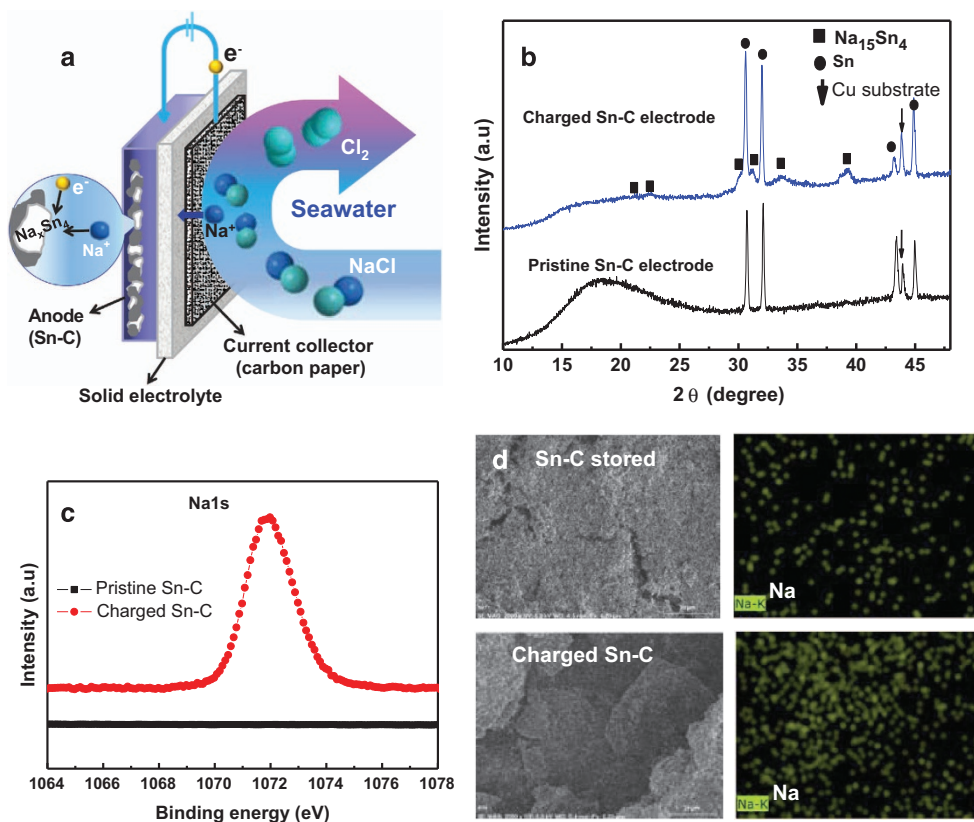


Figure 4 (a) Schematic illustration of a Sn-C-based hybrid-seawater fuel cell in the charged state; (b) *ex situ* X-ray diffraction (XRD) patterns; (c) *ex situ* X-ray photoelectron spectroscopy (XPS); and (d) Scanning electron microscopy with energy dispersive X-ray (SEM-EDX) analysis of Sn-C anode stored in electrolyte and charged Sn-C anode.

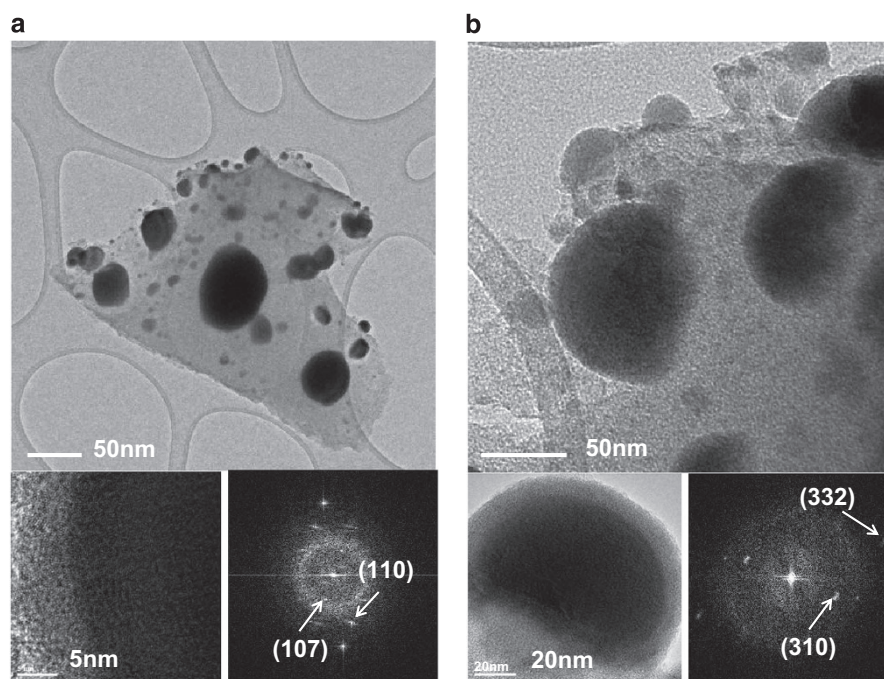


Figure 5 *Ex situ* high resolution transmission electron microscopy (HR-TEM) bright-field images of the Sn-C nanocomposite anode in the pristine (a) and charged (b) states (for each inserted in the bottom: enlarged HR-TEM images of a selected area (left) and the corresponding fast Fourier transform (FFT) patterns (right)).

suitably designed high-capacity alloying materials for such hybrid-seawater fuel cells.

Figure 5 shows high-resolution transmission electron microscopy images including FFT (fast Fourier transform) analysis (bottom right in Figures 5a and b) of a selected area (bottom left in Figures 5a and b), revealing the presence of Sn nanoparticles dispersed in a carbon matrix with an average size of ~ 50 nm for the pristine sample (Figure 5a). The FFT analysis of a selected area clearly shows that the observed d-spacing corresponds to the (110) and (107) lattice planes of metallic Sn, confirming the results obtained by XRD (Supplementary Figure 4). For the sodiated sample, slightly larger nanocrystallites are observed (dark regions in Figure 5b), with an average size of ~ 70 nm, again dispersed in an amorphous carbon matrix. The larger size is owing to the volume expansion of Sn nanoparticles upon sodiation, resulting from the formation of Sn-Na alloy. In fact, FFT analysis of the fully sodiated sample reveals that the observed d-spacing is in very good agreement with the (332) and (310) lattice planes of $\text{Na}_{15}\text{Sn}_4$, confirming that, upon sodiation (i.e., discharge to 0.01 V), $\text{Na}_{15}\text{Sn}_4$, the end member of the electrochemical alloying process of Sn and Na, was formed.

DISCUSSION

In summary, we presented the novel concept of a hybrid-seawater fuel cell consisting of a closed-negative electrode, a NASICON solid electrolyte, and an open seawater-positive electrode. Hard carbon and a Sn-C nanocomposite were successfully applied as alternative-anode materials for this hybrid-seawater fuel cell, presenting a highly stable cycling performance and reversible capacities exceeding 110 mAh g^{-1} and 300 mAh g^{-1} for hard carbon and Sn-C, respectively. In particular, in the case of the Sn-C anode, the performance was substantially enhanced by the almost infinite supply of sodium ions using the open-system seawater-based positive electrode. Thus, in addition to the simplicity of the overall concept, the utilization of redox processes in seawater represents a new and very promising approach for cost efficient and environmentally friendly large-scale energy storage devices.

The reliable electrochemical performance of the newly developed hybrid-seawater fuel cell is clearly demonstrated in this work. The exceptional capacity retention upon cycling is attributed to the stable working potential of seawater for the occurring electrochemical reaction. The theoretical redox potential is slightly decreased by only ~ 0.3 V owing to the presence of other chemical species dissolved in the seawater. However, the redox process at the seawater-positive electrode containing dissolved NaCl as the sodium-ion source is highly reversible, indicating that the NASICON solid film provides a very suitable electrolyte system for such devices under these operating conditions. In fact, no significant structural changes were observed on either side of the solid electrolyte, neither the one in contact with the non-aqueous electrolyte (anode side) nor that in contact with seawater (cathode side), as confirmed by *ex situ* XRD analysis (Supplementary Figure 8).

To study the underlying electrochemical reaction, we analyzed the negative electrodes before and after charging using blank Ni foil, as well as, both hard carbon- and Sn-C-based alternative anodes. Clusters of several micrometers in size were observed on the Ni tap, indicating the plating of sodium upon charge. For the alternative anode materials, a homogenous sodium distribution was observed after charging. From these experimental results, it is concluded that sodium ions in seawater are reversibly stored within these active materials. Furthermore, the hybrid-seawater fuel cell provides highly stable cyclability; remarkably, the Sn-C nanocomposite

performed better in the hybrid-seawater fuel cell than in sodium-ion half-cells.

By using seawater as the positive electrode, the hybrid-seawater fuel cell provides several benefits, enabling the achievement of a reliable, cost efficient, and green energy conversion and storage system. Owing to the simplicity of this device, the hybrid fuel cell should be rather easily scaled up. Moreover, the hybrid-seawater fuel cell proposed herein is an alkali-metal-free system, so it is safer than alkali-metal-based batteries. The redox potential is suitable to obtain high-energy-density devices. The circulated seawater within the open system acts as an infinite source of Na^+ , allowing the extension of the Sn-C cycle life and suggesting that other alternative sodium-ion anodes would be compatible with this system. Therefore, hybrid fuel cells using seawater as the positive electrode show great promise as next-generation energy conversion and storage systems that allow both high energy density and low environmental impact at a low cost. In addition, this system can be easily scaled up. It appears noteworthy that the gaseous Cl_2 released upon charge might be trapped somehow and later utilized for other applications. Indeed, the production of gaseous Cl_2 might provide another great advantage of this technology, adding some value to this new device.²⁰

CONFLICT OF INTEREST

The authors declare no conflict interest.

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Supplementary Information accompanies the paper on the NPG Asia Materials website (<http://www.nature.com/am>)