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Long cycle life of a metal-free hybrid seawater fuel cell with an ether-based electrolyte

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In this work, the design of a new metal-free hybrid seawater fuel cells consisting of a flowing seawater cathode and hard carbon anode was proposed. The electrochemical performance of the cell was investigated with two different electrolytes, i.e., 1M $NaClO_4$ in ethylene carbonate (EC)/propylene carbonate (PC), and 1M $NaCF_3SO_3$ in tetraethylene glycol dimethyl ether (TEGDME). The TEGDME-based electrolyte showed a good cycle performance for 100 cycles, whereas EC/PC showed poor cycle stability already after 30 cycles. Our results showed that a low conducting solid-electrolyte interphase (SEI) was formed with a thick layer, and the PVdF binder was degraded during the redox reaction when the EC/PC-based electrolyte was used. In contrast, the TEGDME-based electrolyte induced the formation of a more efficient SEI layer without degradation of the binder.

Lithium-air batteries have received much attention owing to their high-energy density, which is 10 times higher than that of lithium-ion batteries.[1] However, the costs of lithium raw materials have roughly doubled since the first applications of the lithium-ion batteries. The costs may continue to increase through large-scale commercialization of lithium-battery storage systems because of their increasing demand and limited supply. In contrast, sodium resources are virtually inexhaustible and easily accessible. Moreover, sodium is placed below lithium in the periodic table, i.e., the two metals have a similar electrochemical equivalent and standard potential. In this respect, sodium-air batteries have the potential to meet large-scale energy storage needs. In sodium-air batteries, sodium is typically used in its metal state as the anode; for this purpose, sodium is generally extracted from seawater.[2,3] Although the use of sodium-metal anodes ensures high-energy densities, it may causes safety issues; in addition, costs may rise as additional processing steps may be required for sodium extraction.

To address these issues, we have designed a novel hybrid seawater fuel cell, which makes direct use of seawater as cathode material.[4,5] The cell proposed in this work is unique in that the cathode-active material, e.g., seawater, is not stored in the battery. During the battery-charge process, the Na^+ ions generated from NaCl dissolved in flowing seawater transfer to the negative electrode, while gaseous Cl_2 is released. During discharge, The Na^+ ions are transferred back to seawater and the oxygen dissolved in seawater is reduced, resulting in the formation of NaOH in the presence of water and sodium ions. The charge-discharge reactions for the hybrid seawater fuel cell can be written as

Charge: $4NaCl \rightarrow 4Na^+ + 2Cl_2 + 4e^-$ E=4.07 V *vs*. Na

Discharge: $4Na^+ + 2H_2O + O_2 + 4e^- \rightarrow 4NaOH$ E=3.11 V *vs*. Na

Notably, the use of hard carbon as anode makes our hybrid seawater fuel cell a metal-free system; moreover, the electrochemical properties mainly depend on the characteristics of the components (e.g., electrolyte and solid membrane).

Several studies have shown the important role played by the nature of the electrolyte in enhancing the electrochemical properties of sodium batteries;[6-10] in particular, ethylene carbonate (EC)/propylene carbonate (PC) solvent formulation showed good results in alloy compound-based sodium batteries with both $NaClO_4$ and $NaPF_6$ salts.[9,11] Similarly, tetraethylene glycol dimethyl ether (TEGDME) showed good electrochemical properties with the $NaCF_3SO_3$ salt in sodium-metal batteries.[12,13] This suggests that these systems may be used as electrolytes for sodium ion-based batteries.

In this study, 1M $NaClO_4$ in EC/PC and 1M $NaCF_3SO_3$ in TEGDME were chosen as electrolytes, and their cycle performance evaluated in our metal-free hybrid seawater fuel cell with an optimised cell construction based on NASICON ($Na_3Zr_2Si_2PO_{12}$) solid electrolyte to ensure compatibility. Notably, this is the first study that explores the influence of the electrolyte on the performance of a metal-free hybrid seawater fuel cell, showing an improvement of the cycle life with the use of TEGDME.

The configuration of the metal-free hybrid seawater fuel cell, based on a hard carbon/liquid electrolyte/solid electrolyte/flowing seawater system, is shown in Fig. 1 (Fig. S1†).

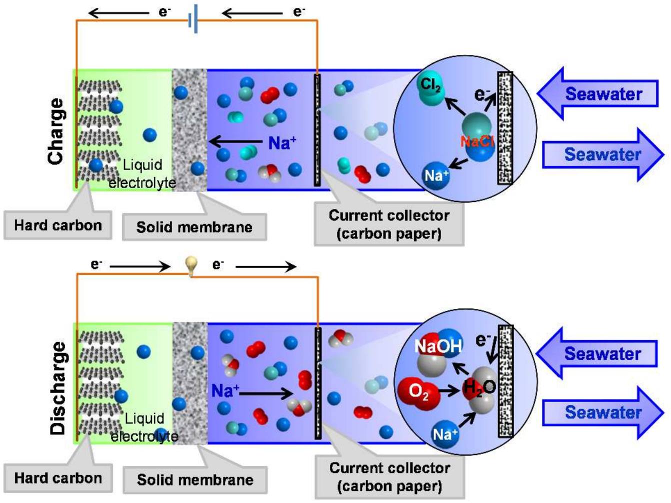

Fig. 1 Schematic illustration of the designed metal-free seawater battery with a diagram of the charge-discharged states.

The NASICON solid electrolyte at the interface between liquid electrolyte and flowing seawater showed a monoclinic structure (C2/c space group) and ionic conductivity of 7.0×10^{-4} S cm^{-1} at room temperature (Fig. S2†). The practical potential of the oxidation reaction in Na/seawater cell was 3.6 V; the reduction potential was 2.8 V (Fig. S3†). In addition, we investigated the charge-discharge performance of the hard carbon anode in the two electrolytes (Fig. S4†). The potentiogram sloped from 1.18 to 0.1 V during the initial reduction, followed by a long flat region between 0.1 and 0 V, reaching 290 mAh g^{-1} and 340 mAh g^{-1} for EC/PC and TEGDME, respectively. During the following oxidation, a capacity of 120–170 mAh g^{-1} was observed close to 0 V vs. Na/Na$^+$; then, the potential gradually increased to 1.2 V, suggesting that the hard carbon anode underwent a reversible sodiation; it's irreversible capacity in EC/PC and TEGDME were determined to be 47 mAh g^{-1} and 37 mAh g^{-1}, respectively (Fig. S4†).

In addition, the EC/PC and TEGDME-based electrolytes were evaluated in the metal-free hybrid seawater fuel cell in terms of charge/discharge performances at room temperature; typical flat curves at 3.46 and 2.26 V, and at 3.55 and 2.47 V, for EC/PC- and TEGDME-based electrolytes, respectively, were obtained for the charge and discharge reactions with a voltage separation (ΔV) of 1.2 V and 1.08 V, respectively (Fig. 2a). This indicates that the cell resistance of the latter is lower, and it performs better than the former, considering the higher-charge delivery and discharge capacities tested under the same current densities. The initial charge and discharge capacities at 0.2 C (0.05 mA cm^{-2}) were determined to be 174 and 115 mAh g^{-1}, respectively, for 1M $NaClO_4$ in EC/PC; 176 and 126 mAh g^{-1}, respectively, for 1M $NaCF_3SO_3$ in TEGDME. TEGDME showed a higher active-material utilization rate during discharge, and its irreversible capacity was lower than that of EC/PC. Both electrolytes showed a stable cycle performance up to 30 cycles (Fig. 2b). However, after 30 cycles, the EC/PC cycle performance decreased rapidly to 80 cycles, whereas TEGDME was still stable after 100 cycles. A comparison of the cycle properties also showed a better retention of the initial property by TEGDME compared with that of EC/PC. After 100 cycles, TEGDME retained 90% of the first cycle discharge capacity at 0.1 C-rate (to compare with 39% for EC/PC). TEGDME showed instability during 3 cycles. The gradual increase of discharge capacity may be due to a slow penetration of the electrolyte, which leads to a higher viscosity in the hard carbon anode. Thus, the evaluation of the electrochemical properties showed a higher performance of the cell when the TEGDME-based electrolyte was used. These results are extremely encouraging, considering that the seawater cathode combined with $NaCF_3SO_3$ of the TEGDME-based electrolyte well performed even at 25 °C.

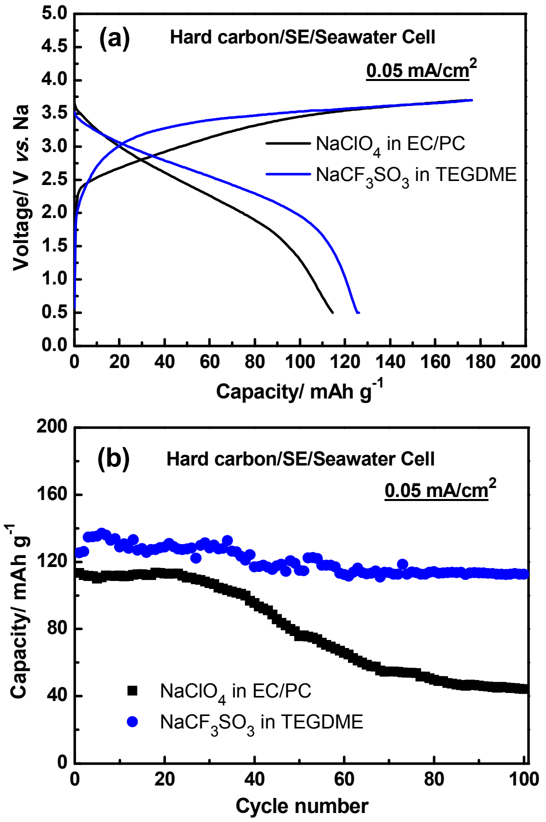

Fig. 2 (a) Charge-discharge curves and (b) cycling performance of the metal-free seawater batteries with the two different electrolytes (1M $NaClO_4$ in EC/PC and 1M $NaCF_3SO_3$ in TEGDME, room temperature, 0.05 mA cm^{-2}).

Na_2CO_3, sodium alkyl carbonate ($NaOCO_2R$), and polymers, such as polycarbonate and polyethylenoxide, are some of the discharge compounds to form a solid electrolyte interphase (SEI) that have been reported for sodium-ion batteries containing alkyl carbonate-based electrolytes.[8,14] TEGDME also forms a SEI layer with the decomposition products of $AOCH_2R$ and A_2CO_3 (A=Li or Na).[15] X-ray photoelectron spectroscopy (XPS) measurements were carried out to investigate the surface layers formed by the electrochemical reactions of the two electrolytes (Fig. 3). The strong peak at 284.5 eV in the pristine hard carbon anode spectra was assigned to the sp^2 carbon in the C–C bond of graphene of the hard carbon anode. The intensity of the sp^2 carbon peak was significantly reduced upon sodiation due to the formation of the SEI on the hard carbon anode surface; as a result, its position was shifted towards a lower binding energy because of the low electronegativity of sodium. Other peaks originated from the poly(vinylidene fluoride) (PVdF) binder (CF_2 at 290.5 eV) and the functional groups on the hard carbon electrodes.[16] After 50 cycles, the sp^2 carbon peak at 284.5 eV almost disappeared, indicating that the hard carbon anode in both cells is covered by the decomposition products of the electrolyte; this result is confirmed by SEM (Fig. S5†). The peaks at 290.0 eV were

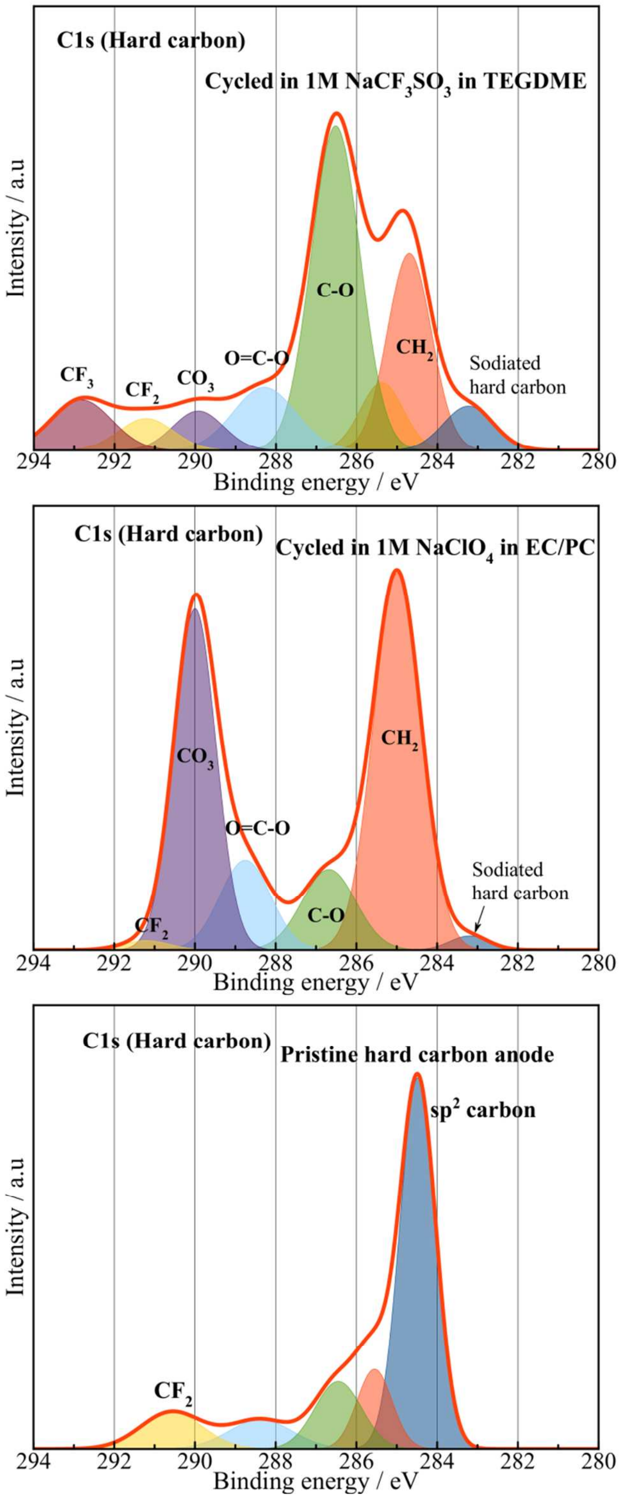

Fig. 3 XPS C 1s spectra of the surface of the hard carbon anode cycled in 1M NaClO$_4$ in EC/PC and 1M NaCF$_3$SO$_3$ in TEGDME (after 50 cycles).

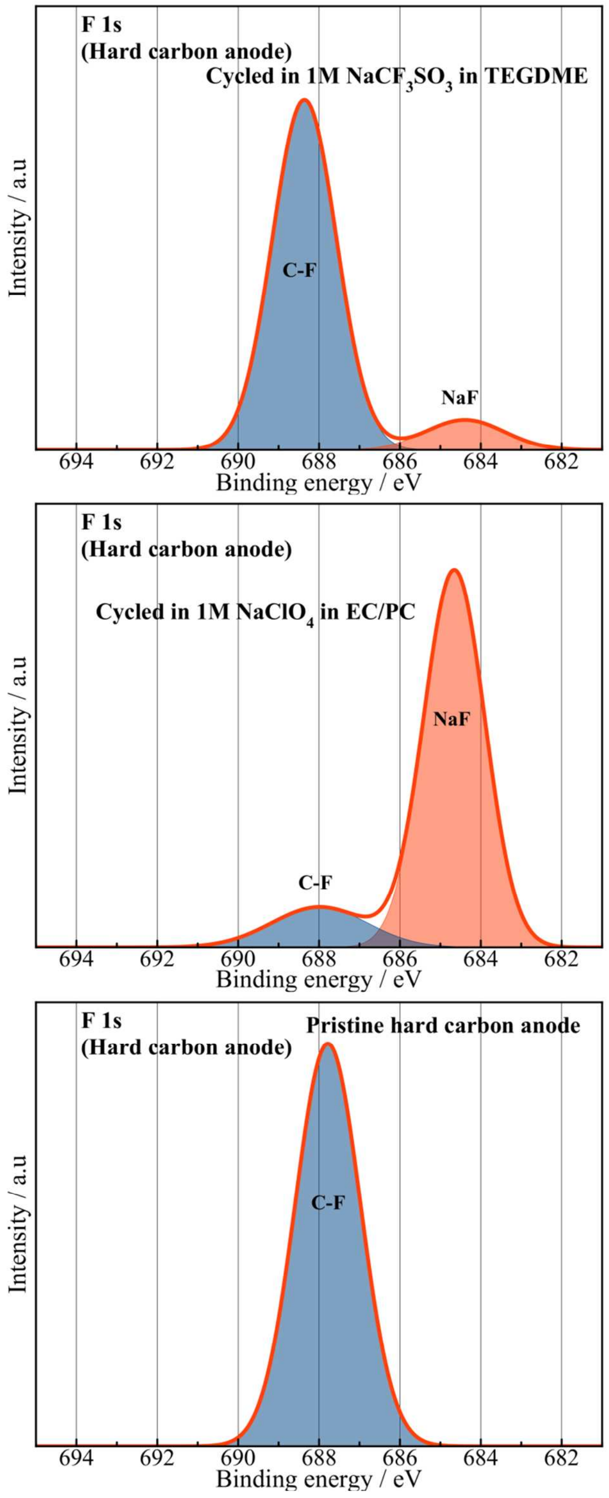

Fig. 4 XPS F 1s spectra of the surface of the hard carbon anode cycled in 1M NaClO$_4$ in EC/PC and 1M NaCF$_3$SO$_3$ in TEGDME (after 50 cycles).

assigned to compounds such as Na$_2$CO$_3$ and sodium alkyl carbonates; peaks at 288.5, 286.6, and 284.9 eV were assigned to O=C-O, the ester linkage CO, and CH$_2$, respectively. The difference between the two electrolytes becomes evident at 284.9 eV and 290.0 eV. In particular, the peak intensities associated with CH$_2$ and CO$_3$ in EC/PC are stronger than those in TEGDME electrolyte. Since CH$_2$ originated from the alkyl/alkylene groups and polymer species, a larger amount of hydrocarbon compounds was found in the surface film formed by the EC/PC-based electrolyte. In addition, the CO$_3$ intensity originated from alkali and alkyl carbonates of SEI was higher in EC/PC than in TEGDME, suggesting a thicker SEI layer.

The thick SEI layer in the EC/PC electrolyte showed a higher interface resistance than that in TEGDME (Fig. S6†). In addition, because some electrolytes may induce the decomposition of the PVdF binder,[17] the intensity of the CF_2 peak was monitored. Our results showed that the intensity of the CF_2 peak in EC/PC decreased, in contrast to that in TEGDME. The decomposition of the binder was confirmed by F 1s spectra (Fig. 4). The pristine hard carbon anode showed a single peak, which was assigned to the C-F bond of the PVdF binder. The $NaCF_3SO_3$ salt led to a small shift of the C-F peak to a higher binding energy in TEGDME. The cycled hard carbon showed two peaks, e.g., one with a higher binding energy (~688.0 eV, which originated from C-F of the binder) and one with a lower binding energy (~684.1 eV, which originated from NaF formed during the redox reaction in the SEI).[15] Since there is no fluorine source in the EC/PC-based electrolyte, the lower-binding energy peak indicates the decomposition of the binder during the electrochemical reaction, suggesting that fluorine partially reacted with sodium when using the EC/PC electrolyte. In addition, the binder decomposition might cause an electrochemical reaction of the hard carbon anode with insulating electron transfer.

In contrast, the degradation of the binder was not observed in the TEGDME-based electrolyte; $NaCF_3SO_3$ partially decomposed to form NaF, which caused the C-F peak to shift towards a lower binding energy.[12] The F 1s spectra of the hard carbon anode cycled in 1M $NaClO_4$/TEGDME clearly suggests that NaF originated from the $NaCF_3SO_3$ salt (Fig. S7†). Also, some NaF SEI compound improved the cycle stability in metal-free seawater fuel cell, comparing with the non-NaF formation in 1M $NaClO_4$/TEGDME. Therefore, we concluded that the high cycle performance of the metal-free hybrid seawater fuel cell with 1M $NaCF_3SO_3$ in TEGDME is due to an efficient SEI layer and stability of the binder.

Conclusions

In summary, in this work we designed a metal-free hybrid seawater fuel cell based on a hard carbon/liquid electrolyte/solid electrolyte/flowing seawater system. In order to maximise the cycle stability of the cell, two different electrolytes were employed, namely 1M $NaClO_4$ in EC/PC and 1M $NaCF_3SO_3$ in TEGDME; these have recently been shown to improve sodium batteries. In contrast to the EC/PC-based system, the metal-free hybrid seawater fuel cell cycled using the TEGDME-based electrolyte showed a stable cycle performance (even after 100 cycles). XPS and EIS clearly showed that the formation of the SEI layer is more efficient with the TEGDME-based electrolyte; in addition, the binder decomposition was observed only in the metal-free hybrid seawater fuel cell with the EC/PC-based electrolyte. Thus, the results presented in this work prove that the electrolyte containing 1M $NaCF_3SO_3$ in TEGDME ensures a stable electrochemical performance of the proposed metal-free hybrid seawater fuel cell.

Experimental Section

Seawater was used as positive electrode material. The hard carbon negative electrode was fabricated from a 80:10:10 (wt%) mixture of hard carbon (MeadWestvaco Co. U.S.A.), Super-P carbon black (TIMCAL) as the current conductor, and PVdF (Sigma Aldrich) as the binder. For the hybrid multi-layer electrolyte, liquid electrolyte and NASICON ceramic plate as the solid electrolyte were used. The NASICON solid electrolyte was prepared by a solid-state reaction method: $Na_3PO_4{\cdot}12H_2O$, SiO_2, and ZrO_2 (obtained from Sigma Aldrich) were mixed and then calcined at 400 and 1100 °C; after several mixing and calcination steps, the powder was pressed into a pellet, which was subsequently sintered at 1230 °C.

The carbon paper (Fuel Cell Store, Inc.,) employed as current collector was placed in the flowing-seawater positive electrode. The assembled cell was exposed to seawater and connected to a testing station. A battery cell tester (WBCS3000) was employed to perform the charge and discharge tests at different current densities. XPS spectra of the hard carbon anode were obtained with a PHI 5500 spectrometer, and Al Ká (1485.6 eV) was used as the X-ray source at an anode voltage of 13.8 kV. The electrolytes on the surface of the hard carbon anode were removed by soft tissue for XPS measurements.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Schematic illustration of seawater fuel cell, ionic conductivity and XRD of solid electrolyte, charge-discharge curves and cycle performance, EIS and Video of working meal-free seawater cell]. See DOI: 10.1039/c000000x/

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