A molten Mg corrosion method for preparing porous Ti foam as self-supported Li–O₂ battery cathodes

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Abstract

All-metal self-supported cathodes, especially porous noble metals, are attractive alternatives for settling the issue of carbon- and binder-decomposition in Li–O₂ batteries. However, the high cost of noble metals hinders their practical application. In the present study, nanoporous Ti foam is prepared using a molten Mg corrosion method for the first time. Electron microscope images demonstrate that, nanoporous Ti foam is obtained by treating Ti–Mo alloy plates in molten Mg at 650 °C for 3 hours. Then, the foam is coated with a layer of Au nanoparticles by cool-sputtering and used as self-supported Li–O₂ battery cathodes. The nanoporous foam can decrease the consumption of gold markedly compared with traditional porous Au foam. Benefiting from the high stability, conductivity, and porosity of Ti foam, the Li–O₂ batteries exhibit good durability (cycling 118 rounds at 1 C rate within a 1000 mAh g⁻¹ capacity limitation).

Keywords: Li oxygen battery; Cathode; Porous Ti; Molten Mg corrosion

1. Introduction

Porous metal foam is widely used in various areas, such as catalysts and catalyst supports, water purification, and current collectors of energy storage and conversion devices [1]. Generally, the most widely used materials of metal foam are Au, Ag, Ni, Al, and Cu, etc. Common methods to prepare porous metals include sintering metal powders, replication of polymeric sponge, freeze casting, and de-alloy [1]. However, few porous metals have a tough and self-supported nanoporous structure because of the intrinsic properties of the metals or the limitation of manufacturing methods [1-8]. The nanoporous metals have large surface area and abundant inner space to accommodate active materials as catalyst supports and current collectors [2,3]. Unfortunately, nanoporous metals usually have not tough structures for using as self-supported electrodes, which is unfavorable for the stability and durability as using them in energy storage and conversion devices [9-13].

Ti and its alloys have been widely used for dental and orthopedic implants, owing to their good chemical stability, mechanical properties and biocompatibility [14,15]. Recently, Ti and its alloys in the form of porous structure have attracted increasing interest as current collectors or catalyst supports (e.g. in Li-O₂ batteries (LOBs) and fuel cells), because they can provide not only a favorable channel net for mass transport but also stable surface to prevent side reactions [16,17]. Chemical/electrochemical corrosion of some species with high oxidizing ability in operation environment of these devices limits the materials of current collectors in several alternatives [18-19], in which, Ti is the most attractive owing to its low cost

1 compared with precious metals and high stability compared with Ni, Al, and Cu etc
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3 [16,17]. Although several methods were proposed to prepare porous Ti foam, the
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5 nanoporous structures were reported sparsely. Herein, we use a molten Mg corrosion
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7 method to prepare porous Ti foam, and the electrochemical properties of LOBs when
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9 using the porous Ti foams as current collectors are measured. It is worth noting that
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11 using molten Mg corrosion to prepare porous Ti is reported firstly to the best of our
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13 knowledge.
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20 2. Experimental

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23 *Sample Preparation:* Porous Ti foam were prepared on circular Ti alloy plates (Ti-Mo
24 alloy, Mo=0.3 wt%, 15 mm diameter, 0.5 mm thickness) purchased from Baiji Jinkai
25 Corporation of China. The raw Ti plate was buried with Mg powder (Alladin Com.
26 China) in a crucible and heat-treated in Ar atmosphere for several hours. Then the Ti
27 plate was immersed in 1 mol dm⁻³ HCl solution 24 h to remove metal Mg and
28 magnesium oxide. The obtained porous Ti foam was rinsed with deionized water fully
29 and dried overnight. Au nanoparticles were deposited on the Ti foam by a Leica EM
30 SC050 cool-sputtering device at a current of 20 mA for 80 s. Weights of the deposits
31 were measured by means of a micro-balance (Mettler Toledo, USA) with an accuracy
32 of 0.01 mg. The mass of Au nanoparticles was around 1.0 mg cm⁻². The Au coating
33 amount corresponds to the geometric surface of Ti supports (15mm diameter plates),
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56 *Instruments for Characterization:* Scanning electron microscope (SEM) images were
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58 obtained on a Hitachi Su-8100. The X-ray diffraction (XRD) patterns were obtained
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on a PANalytical X'pert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were obtained on a JEOL-2100. X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (ThermoFisher Scientific Company) using Al K α (1486.6 eV) radiation. The base pressure was about 1×10^{-8} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The surface area of the materials was analyzed by the Brunauer-Emmett-Teller (BET) method with a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020. The gas used was N₂ with a liquefaction temperature of -195.87 °C, and the gas desorption time was 6 h. The total pore volume and pore size distribution were evaluated by the Density functional theory (DFT) model. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests of the batteries were carried out on a CHI 660 electrochemical workstation.

Li–O₂ battery tests: The Swagelok type Li–O₂ batteries were assembled inside an MBraun glove box. The cells were constructed by placing a 15 mm diameter Li disk on the bottom, covering it with a piece of glass fiber separator (20 mm diameter, Whatman), adding excess electrolyte (1.0 mol dm⁻³ LiTFSI in tetraethylene glycol dimethyl ether (TEGDME)), placing a Au nanoparticle modified porous Ti foam disk (15 mm diameter) on the separator, and sealing the Swagelok cell. All the electrochemical measurements to the batteries were carried out in pure O₂ at 1 atm

(99.99%). A BTS-2000 Neware Battery Testing System was employed for charge/discharge tests.

3. Results and discussion

In industrial process, the raw Ti foam plates are manufactured by pressing sintered Ti particles, and they are usually used as catalyst supports or water filters [16]. SEM images of a raw Ti-Mo alloy plate are shown in Fig. S1a. The higher amplification image in inset of Fig. S1a demonstrates smooth surface of the raw Ti alloy plate. For the application in water filtration or catalyst supports, the addition of Mo in Ti alloy plates is a common strategy to improve heat resistance and mechanical strength. However, Mo peaks are undetected in the XRD pattern of raw plates due to the low content, as shown in Fig. 1. The pattern of raw Ti plates can be assigned to Ti metal (JCPDS: 65-9622 $a=2.951$, $b=2.951$, $c=4.686$). Fig. S1b shows SEM image of the plate heat-treated in Mg for 3 h. The surface becomes rough compared with the raw sample visibly resulted from the covering of Mg. XRD pattern of the plate treated with molten Mg verified that, the rough cover is Mg metal (JCPDS: 65-3365 $a=3.209$, $b=3.209$, $c=5.210$ and 65-7219 $a=2.953$, $b=2.953$, $c=2.953$). After dissolving the cover with hydrochloric acid fully, the surface morphology is notably different compared with raw samples, as shown in the SEM images in Fig. 2. Moreover, the samples treated with Mg at different temperatures exhibit visibly different morphology. Pores with size of hundreds nanometers generate when the temperature over 650 °C (Fig. 2b), and the pores collapse at 750 °C (Fig. 2c), even vanish at 800 °C (Fig. 2d). There is no pore on the sample obtained at 550 °C (Fig. 2a) because of

the lower temperature than Mg's fusion point. Accordingly, we consider the pores generating from molten Mg corrosion [21]. Specially, widespread and deep pores can be found in the samples obtained from 650 °C, as shown in Fig. 2e and f. The XRD pattern of the sample after dissolving off Mg ("Porous Ti foam" in Fig. 1) reveals the porous framework comprising Ti (JCPDS: 65-9622) and Mo (JCPDS: 65-7442 $a=3.147$, $b=3.147$, $c=3.147$) metals. The clearer Mo peaks indicate the remaining framework contains more Mo metal than raw samples.

Fig. 1.

Fig. 2.

Scheme 1.

We suggest the formation process of pores in Ti foam can be described by the schematic diagram in Scheme 1. Mo element can penetrate into Ti powder along with grain boundaries, and forms alloy with Ti on the boundaries in manufacturing process of Ti alloy plates as we know. Mo is a high fusion point metal making it hard to be corroded by molten Mg [21]. The Ti-Mo alloy on the boundaries remains, while the Ti in grains is corroded by molten Mg, resulting in a porous structure after removing Mg. This hypothesis can be verified by investigating the pore walls of as-prepared samples. HRTEM images and SAED patterns of the pore walls scraped from the as-prepared samples at 650 °C (Fig. 2b, e and f) demonstrate a Ti-Mo alloy comprising Ti and Mo nanocrystals, as shown in Fig. 3. HRTEM images of selected areas from Fig. 3a are shown in Fig. 3b and c, which can be assigned to Ti (002) and Mo (110) planes, respectively. Furthermore, SAED patterns of the walls in inset of

Fig. 3a reflect the coexistence of Ti and Mo nanocrystals in the walls. To reveal the role of Mo in pores forming, comparative experiments were carried out on pure Ti foils (99%, Alfa Aesar). SEM image of pure Ti foil after molten Mg corrosion in Fig. S2 shows no pores generating on the foil. Accordingly, we suggest the molten Mg corrosion leads pores forming in Ti-Mo alloy plates, and the pore structures depend on heat-treating temperature seriously because of higher corrosion ability of Mg at higher temperatures [21], as shown in the SEM images (Fig. 2c and d). Another factor deciding the structures of Ti foam is the heat-treating time, as seen from the plates treated at 650 °C with different times in Fig. 4. Apparently, the pore size increases with the corrosion time. Pores of the sample treated for 6 h are larger than those with shorter times. Meanwhile, the pore walls are corroded to be thinner with the treating time increasing. Nevertheless, the walls collapse as the time rising to 12 h. The variation of the samples' morphology with treating times can also support the proposed mechanism above. The molten Mg can corrode Ti metal at high temperatures, but the grain boundaries remain owing to its alloying with Mo. Similarly with the situation at high temperature, the grain boundaries collapses due to the excessive corrosion as the treating time over 12 h.

Fig. 3.

Fig. 4.

Fig. 5.

The N₂ adsorption/desorption measurements were carried out on raw Ti plates and nanoporous Ti foam obtained from 650 °C with 6 h. As shown in Table S1, the

1 BET surface area and pore volume were enlarged over 5 and 40 times, respectively,
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3 after molten Mg corrosion. The adsorption/desorption isotherms and pore distribution
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5 curves of the two samples are presented in Fig. 5. After corrosion, the Ti foam
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7 possesses plentiful pores in size of 10-100 nm (Fig. 5d) leading the isotherm
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9 appearing a hysteric loop (Fig. 5b) identified as type-IV isotherm. This suggests the
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11 existence of mesopores in the sample besides the primary macropores. Contrarily, raw
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13 Ti plate has not pores in this range, revealed from whether isotherm (Fig. 5a) or pore
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15 distribution curve (Fig. 5c). Therefore, the obtained Ti plate possesses not only
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17 macropores that in size of hundreds nm, but also abundant nanopores in size of
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25 10-100 nm.
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31 The abundant pores in size of a wide range are attractive to electrochemical
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33 energy storage devices. Herein, we have investigated electrochemical properties of the
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35 porous foam as self-supported LOB cathodes, whose performances are sensitive to the
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37 pore structure of cathodes [22]. Au nanoparticles were deposited on the framework as
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39 cathode catalyst, as shown in SEM image in Fig. 6a. XPS of the as-deposited Au
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41 nanoparticles is shown in Fig. 6b, which is characterized by a doublet containing
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47 binding energy of 84.0 eV (Au 4f_{7/2}) and 87.5 eV (Au 4f_{5/2}). The two peaks have a
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49 binding energy difference of 3.5 eV and a peak area ratio of 4:3, which corresponds to
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51 the characteristics of Au (0) [23]. We have studied the electrochemical active areas of
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53 the foam, which can reflect the amount of active sites in electrochemical processes
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58 more veritably compared with the BET surface areas. In comparison with other
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1 detection protocols, CV of electroactive species in a conducting aqueous solution is a
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3 valuable means of probing the electrochemical characterization of the nonstandard
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5 electrode [24]. The Au modified porous foam was electrochemically characterized by
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7 CV in 0.5 mol dm⁻³ H₂SO₄. The Au nanoparticles coated raw Ti plate with the same
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9 geometric surface area was also characterized under the same conditions for
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11 comparison (Fig. S3). The CV curves show that the porous foam has a significant
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13 larger CV area compared with raw Ti plates, indicating the porous foam has a much
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15 larger effective surface area due to the porous morphology. Assuming that a specific
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17 charge of 386 μC cm⁻² is required for gold oxide reduction [25,26], the porous foam
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19 has a total active surface of 5.6 cm², while the value of raw Ti plate is very small. The
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21 significant enhancement represents a much larger electrochemical active area of the
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23 porous foam.
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33 Fig. 7.

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35 The electrochemical properties of LOBs are shown in Fig. 7, in which, capacities
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37 are all calculated based on the mass of Au catalyst. Fig. 7a presents discharge/charge
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39 curves of the batteries (at a current density of 0.2 A g⁻¹ (0.2 mA cm⁻²) in the potential
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41 range of 2.0–4.2 V) based on the foam obtained from four temperatures. It can be
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43 found that the foam from 650 °C has the best discharge/charge properties. The battery
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45 on the sample from 650 °C can release a capacity of more than 15000 mAh g⁻¹, while
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47 the other batteries release no more than 4000 mAh g⁻¹. We consider the widespread
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49 pores in Ti foam are responsible for ultrahigh capacity on the sample of 650 °C, as
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51 shown in Fig. 2e and f. Owing to porous structure of the sample from 750 °C (Fig. 2c),
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the battery exhibits more capacity (3800 mAh g^{-1}) than the other two batteries (around 2000 mAh g^{-1} on the samples from 550 and 800°C).

Fig. 8.

Fig. 9.

Discharge/charge curves of the battery (based on Ti foam from 650°C) at different rate current densities within same capacity limitation can describe the variation of overpotentials with discharge/charge currents, as shown in Fig. 7b. The battery has a discharge potential of 2.5 V (vs. Li^+/Li , similarly hereinafter) and a charge potential of 3.2 V at a current density of 1.0 A g^{-1} (1.0 mA cm^{-2}) within a capacity limitation of 1000 mAh g^{-1} . The overpotentials increase with the rate current rising slightly, that the charge potential maintains around 3.6 V at a current density of 2.0 A g^{-1} (2.0 mA cm^{-2}). The cycle performance of the battery was studied at 2.0 A g^{-1} , as shown in Fig. 7c, d and e. Fig. 7d and e show the momentary potential depending on running time and the end potentials of discharge/charge processes depending on cycle number, respectively. We can see that the battery can maintain near 120 cycles at 2.0 A g^{-1} before sudden death. The electrochemical behavior during the 1-20 and 20-30 cycles are shown in Fig. S4, including discharge/charge curves and time dependent potential variation curves. Obviously, the overpotentials increase sharply in the initial 20 cycles (Fig. S4a and b), especially the charge overpotential. Then, they maintains well after the 20th cycle, as shown in Fig. S4c and d. Discharge/charge curves of the 10th, 50th, and 100th cycles in Fig. 7f exhibit similar patterns, revealing consistent cathode processes in cycling. SEM test of the foam after

cycling was carried out to investigate the stability of porous frameworks. As seen from Fig. 8a, a layer of undecomposed discharge product deposits on the foam. The pore structure remains well in the foam, as shown in Fig. 8b and c. Therefore, tough framework and stable composition of the cathodes are responsible for the good cycle performance. The kinetics of oxygen transport in cathodes at different stage can be measured by EIS, as shown in Fig. 9a. The Nyquist plots of as-assembled battery and after cycling almost have the same patterns, indicating good recovering ability of the cathodes. However, the undecomposed precipitate grows continuously on the catalyst in a long cycle test, causing the resistance of electrochemical reaction (semicircles) increasing. Accordingly, the radius of semi-circle in Nyquist plot is larger than pristine state, as shown in Fig. 9a. Furthermore, the diffusion coefficients of oxygen at the two stages are calculated from Fig. 9b and Equation 1, 2 and 3 [27]:

$$\sigma = \left[\frac{RT}{\sqrt{2}n^2 F^2 AC_{O_2}} \right] \frac{1}{\sqrt{D_{O_2}}}, \quad (\text{Equation 1})$$

converted to

$$D = \frac{R^2 T^2}{2n^4 F^4 A^2 \sigma^2 C_{O_2}^2}, \quad (\text{Equation 2})$$

where the meanings of n is the number of electrons per-molecule during O_2 reaction, A is the surface area of the anode, D is the diffusion coefficient of O_2 , R is the gas constant, T is the absolute temperature, F is the Faraday constant, C is the concentration of lithium ion, and σ is the Warburg factor which has relationship with Z_{re} :

$$Z_{re} = R_D + R_L + \sigma \omega^{-1/2}, \quad (\text{Equation 3})$$

where the meanings of Z_{re} is the real part of the resistance in the low frequency region, ω is corresponding frequency. Fig. 9b shows the relationship between Z_{re} and square root of frequency ($\omega^{-1/2}$) in the low-frequency region. The ratio of diffusion coefficients of O_2 in pristine cathode and after cycling is 1.5:1. The values in same order magnitude means the O_2 transport channels are unhindered in cycling, which is significant for battery durability [16]. Compared with the previous Li- O_2 battery cathodes based on Au nanoparticle modified nanostructured metals, such as the Au nanoparticle coated Ni nanowires prepared by Jaephil Cho and his coworkers [28], our porous Ti foam supported Au cathodes have better durability and rate capability. We suggest the high stability of Ti metal is responsible for the good durability [16], and the high electronic conductivity of all-metal structure results in the good rate capability.

4. Conclusion

We have explored a molten Mg corrosion method to prepare porous framework in Ti foam firstly in the present study. The self-supported porous foam was used as cathode supports of LOBs without any carbon or binder, which are considered to decompose in battery cycling [29, 30]. The most attractive improvement in our work is the cathodes are constructed with porous Ti framework—a non-precious metal, and Au nanoparticles—a highly efficient catalyst. The unique architecture supplies not only a porous catalyst for the electrochemical reactions, but also a stable and low cost framework for LOB cathodes.

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Figure Captions:

Fig. 1. XRD patterns of raw Ti foam, Ti foam heat-treated with Mg and the foam after dissolving Mg in acid.

Fig. 2. SEM images of Ti foam corroded by molten Mg at different temperatures: (a) 550, (b) 650, (c) 750, and (d) 800 °C; (e, f) images with different magnifications of the samples obtained at 650 °C.

Scheme 1. Schematic diagram of preparing porous Ti foam.

Fig. 3. TEM images of pore walls scraped from the samples prepared at 650 °C: (a) image in low magnification, (b, c) HRTEM images of selected areas in (a), inset in (a) is SAED pattern of the walls.

Fig. 4. SEM images of Ti foam corroded by molten Mg at 650 °C for different times: (a) 1, (b) 3, (c) 6, and (d) 12 h.

Fig. 5. Adsorption/desorption isotherms (a, b) and pore distribution curves (c, d) of raw Ti foam and porous Ti foam.

Fig. 6. SEM (a) image and XPS (b) pattern of Au nanoparticles deposited by cool spurting.

Fig. 7. Electrochemical properties of the LOBs with porous Ti foam as cathode support. (a) discharge/charge curves of the batteries on Ti foam corroded at different temperatures. (b-f) battery performances on Ti foam corroded at 650 °C: (b) discharge/charge curves at 1 and 2 A g⁻¹; (c) cycle performance at 2 A g⁻¹ within a capacity limitation of 1000 mAh g⁻¹; (d) momentary potential depending on running time of the cycling test; (e) end potentials of

discharge/charge processes depending on cycle number; (f) discharge/charge curves of the 10th, 50th, and 100th cycles.

Fig. 8. SEM images of the porous Ti foam after cycling test.

Fig. 9. Impedance study of porous Ti cathodes at the stages of pristine battery and after cycle test: (a) Nyquist plots; (b) the relationships between Z_{re} and $\omega^{-1/2}$ at low-frequency region.

Figures:

Fig. 1

Fig. 2

Scheme 1

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Graphical abstract: