

Supplementary materials

Carrageenan-induced Highly Stable Zn Anode by Regulating Interface Chemistry

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Experimental

Materials

Zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 99%), carrageenan (denoted as Carr, cas: 9000-07-1), N-Methyl-2-pyrrolidone (NMP, $\text{C}_5\text{H}_9\text{NO}$, 99%), Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$, 99%) and Vanadium pentoxide (V_2O_5 , 99%) were purchased from Aladdin. Polyvinylidene fluoride (PVDF, Arkema) and conductive carbon black (Timical) were purchased from Saibo Electrochemical Materials Pte Ltd. Glass microfiber filter (Whatman GF/D, Diameter 47mm, 1823-047) was obtained from Huidi Pte Ltd. Zn foils (30 μm , 99.9%), Cu foam (1.2 mm, 99.9%), Titanium mesh and stainless steel were provided by Shengshida Metallic Materials Pte Ltd.

Electrolyte preparation

The 1 M ZnSO_4 aqueous electrolyte was prepared using $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and deionized water based on the molar ratio. Certain amount of Carr was introduced into the ZnSO_4 electrolyte to obtain the electrolyte containing different amounts of additive. The bare ZnSO_4 electrolyte was denoted as “without Carr”. The electrolyte with 1 mg mL^{-1} Carr was signed as “with Carr”. The electrolyte with 0.1 and 0.5 mg mL^{-1} Carr were denoted as “with 0.1 Carr ” and “ with 0.5 Carr”, respectively.

Fabrication of Zn||Zn and Zn||Cu cell

The Zn plating/stripping tests were performed on Zn symmetrical cells. Two pieces of Zn foil were used as electrodes for Zn||Zn cell. The GE-Whatman glass fiber was employed as the separator. Coulombic efficiency (CE) measurements were carried out on asymmetrical Zn||Cu cells. Zn foil and copper foam were used as electrodes. The electrolyte and glass fiber in Zn||Cu cell were the same as that in Zn||Zn cell.

Fabrication of Zn||VO₂ full Cell

VO_2 was synthesized by the hydrothermal method. Typically, 1.2 g of V_2O_5 was dispersed in 40 mL of deionized water under string, followed by adding 1.8 g of $\text{H}_2\text{C}_2\text{O}_4$. Then, the above suspension was heated at 80 °C for 1 h. After that, the solution was transformed into a hydrothermal reactor, and maintained at 180 °C for 4 h. When the reactor cooled down to room temperature, the product was washed with deionized water for several times to obtain the VO_2 . The cathode was prepared by mixing VO_2 with conductive carbon black and PVDF at the weight

ratio of 7:2:1 and dissolving the above mixture in an appropriate amount of NMP to form homogeneous slurry. The obtained slurry was then spread onto the titanium mesh, and dried in a vacuum oven at 60 °C overnight. The mass loading of the above cathode active materials was about 2.0~4.0 mg cm⁻². Zinc foil and glass fiber were used as the anode and separator, respectively.

Electrochemical Test

The performances of Zn||Zn symmetric cells, Zn||Cu asymmetric cells, and Zn||VO₂ full cells were carried out on a Neware CT-3008 battery test system. The Zn||Zn cells were tested at 5 mA cm⁻² / 1 mAh cm⁻², 5 mA cm⁻² / 5 mAh cm⁻², and 10 mA cm⁻² / 5 mAh cm⁻², respectively. The Zn||Cu asymmetric cells were carried out at 1 mA cm⁻² / 0.5 mAh cm⁻². For Zn||VO₂ cell, the rate performance was tested at various current densities (0.1, 0.2, 0.5, 1, 2 and 5 A g⁻¹) and the cycling performance was evaluated with the voltage range of 0.3~1.5 V under 1 A g⁻¹. The specific capacities were evaluated according to the mass of active materials. The corrosion, diffusion, and hydrogen evolution behaviors of Zn foil anode were tested under an electrochemical workstation (CHI 660e) with a three-electrode system (Zn foil as work electrode, Pt as counter electrode, and Ag/AgCl as reference electrode). The Tafel plot was recorded with a potential range of ±0.3 V versus open-circle potential of the system at a scan rate of 1 mV s⁻¹. The hydrogen evolution performance was collected by linear sweep voltammetry (LSV) with a potential range of -1~-1.6 V at a scan rate of 1 mV s⁻¹. The diffusion curves were measured by chronoamperometry method under an overpotential of -150 mV. The cyclic voltammetry (CV) for the nucleation overpotential was tested with a voltage range of -1.4~-0.2 at a scan rate of 1 mV s⁻¹ (Zn foil as counter electrode, Ti as work electrode, and Ag/AgCl as reference electrode). The electrochemical potential window was tested at 1 mV s⁻¹ (steel-mesh as working electrode and counter electrode, and Ag/AgCl electrode as reference electrode). Electrochemical impedance spectroscopy (EIS) was implemented within a range of 10⁵ to 10⁻² Hz.

Characterization

The properties of electrolyte were studied by the Raman (Thermo, DRX-2), Fourier transform infrared (FT-IR, Bruker Alfar), and contact angle meter (Jinhe, JY-PHB). The Zn foil (pristine, soaked and cycled) and VO₂ were characterized by the X-ray diffraction with Cu K α ($\lambda=1.54060$ Å) (XRD, Rigaku, Ultima IV), field-emission scanning electron microscopy (SEM,

Hitachi SU8600) and X-ray photoelectron spectroscopy (XPS, Thermo Fly K-Alpha). The images of Zn deposition process were obtained on an industrial optical microscope (Aoweisi, AW33T-4K).

Results

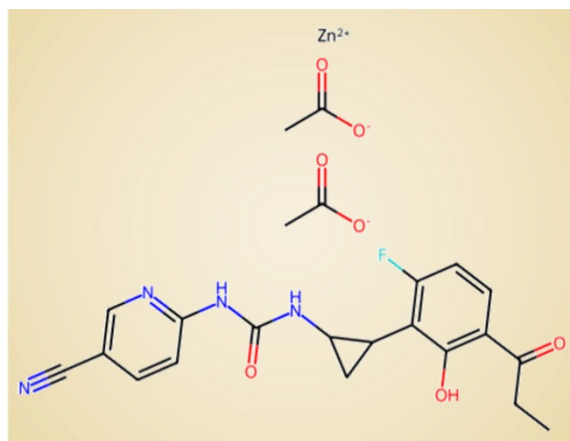


Fig. S1 Molecule structure of carrageenan

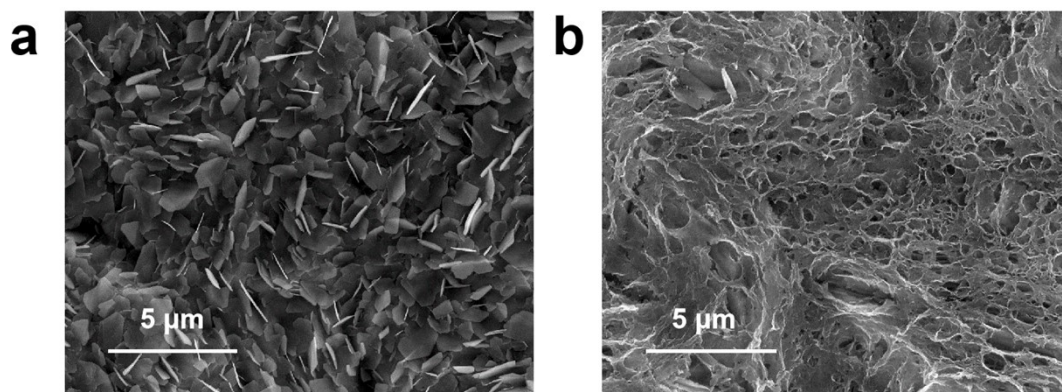


Fig. S2 SEM images of Zn anode after LSV test. (a) without Carr; (b) with Carr

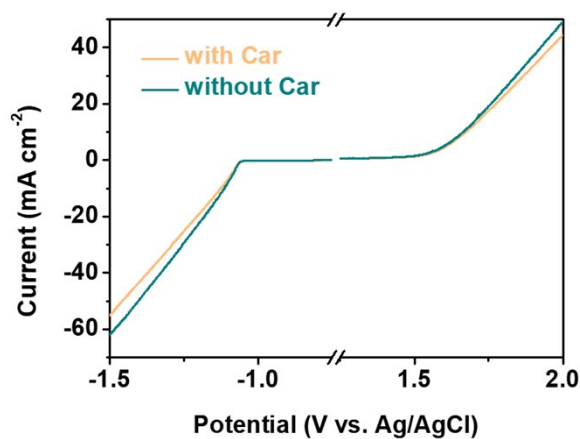


Fig. S3 The overall electrochemical stability window.

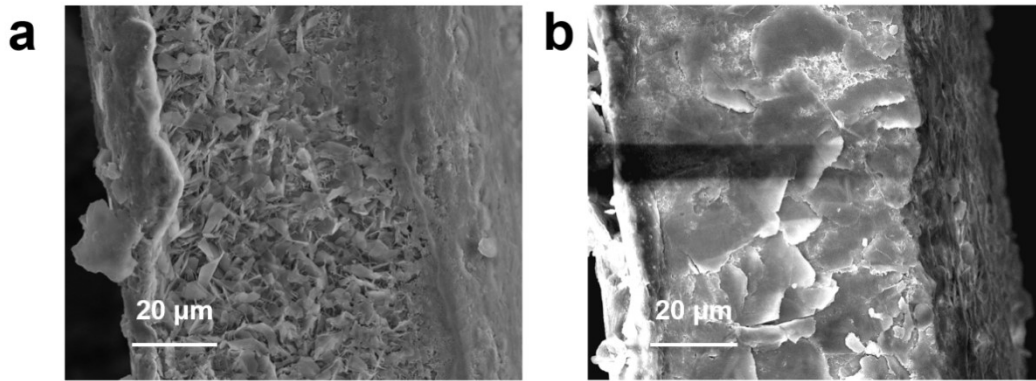


Fig. S4 SEM images of the lateral view of Zn anode after immersion. (a) without Carr; (b) with Carr

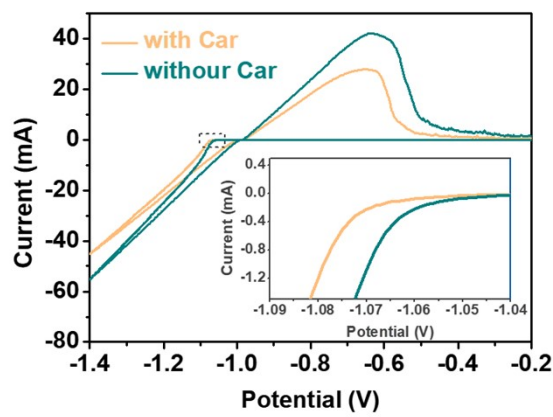


Fig. S5 Cyclic voltammetry curves in different electrolytes at a scan rate of 1 mV s^{-1} using a three-electrode system.

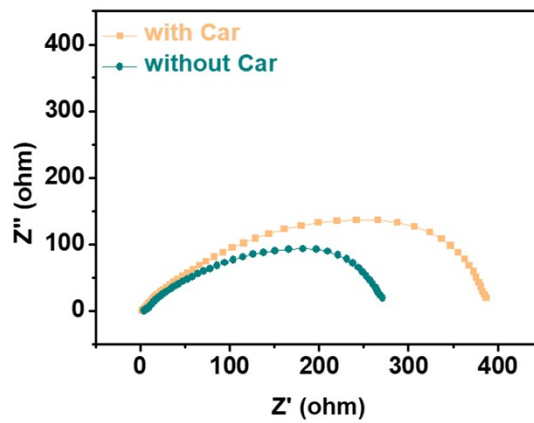


Fig. S6 EIS spectra of Zn||Zn cells after 10 cycles;

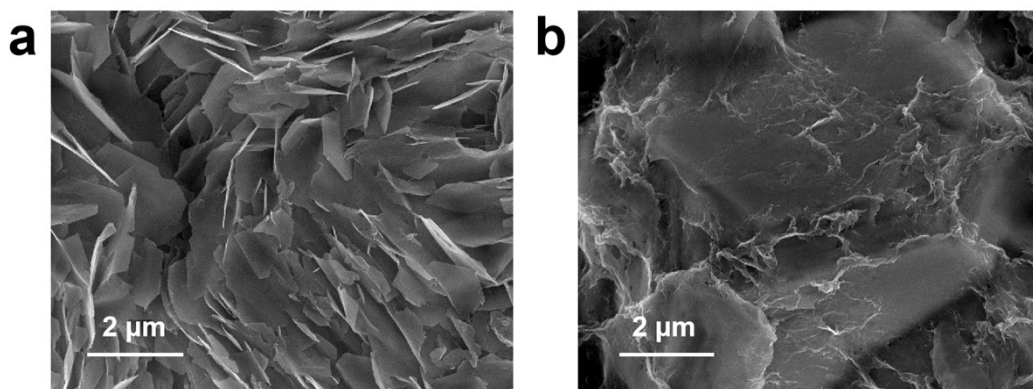


Fig. S7 SEM images of Zn anode after CV test. (a) without Carr; (b) with Carr

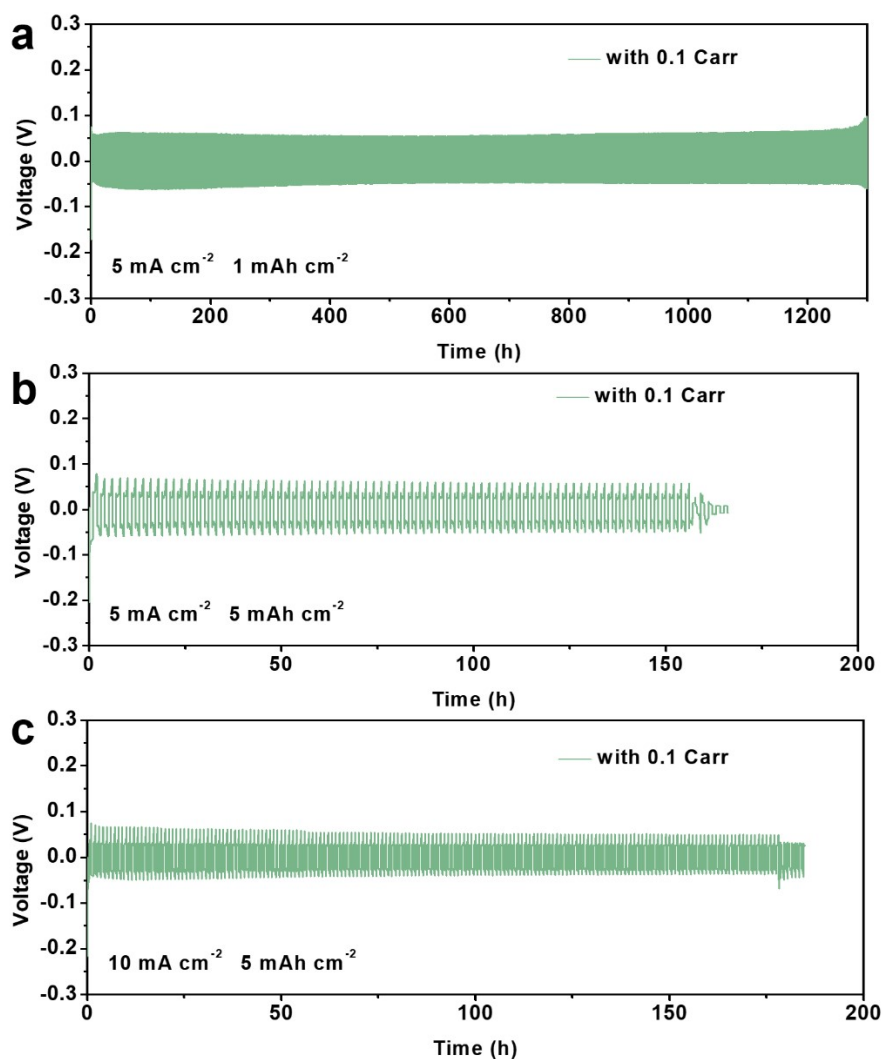


Fig. S8 The cycling performance of the Zn||Zn cells using the electrolyte containing 0.1 mg mL^{-1} Carr at (a) 5 mA cm^{-2} / 1 mAh cm^{-2} ; (b) 5 mA cm^{-2} / 5 mAh cm^{-2} ; (c) 10 mA cm^{-2} / 5 mAh cm^{-2} .

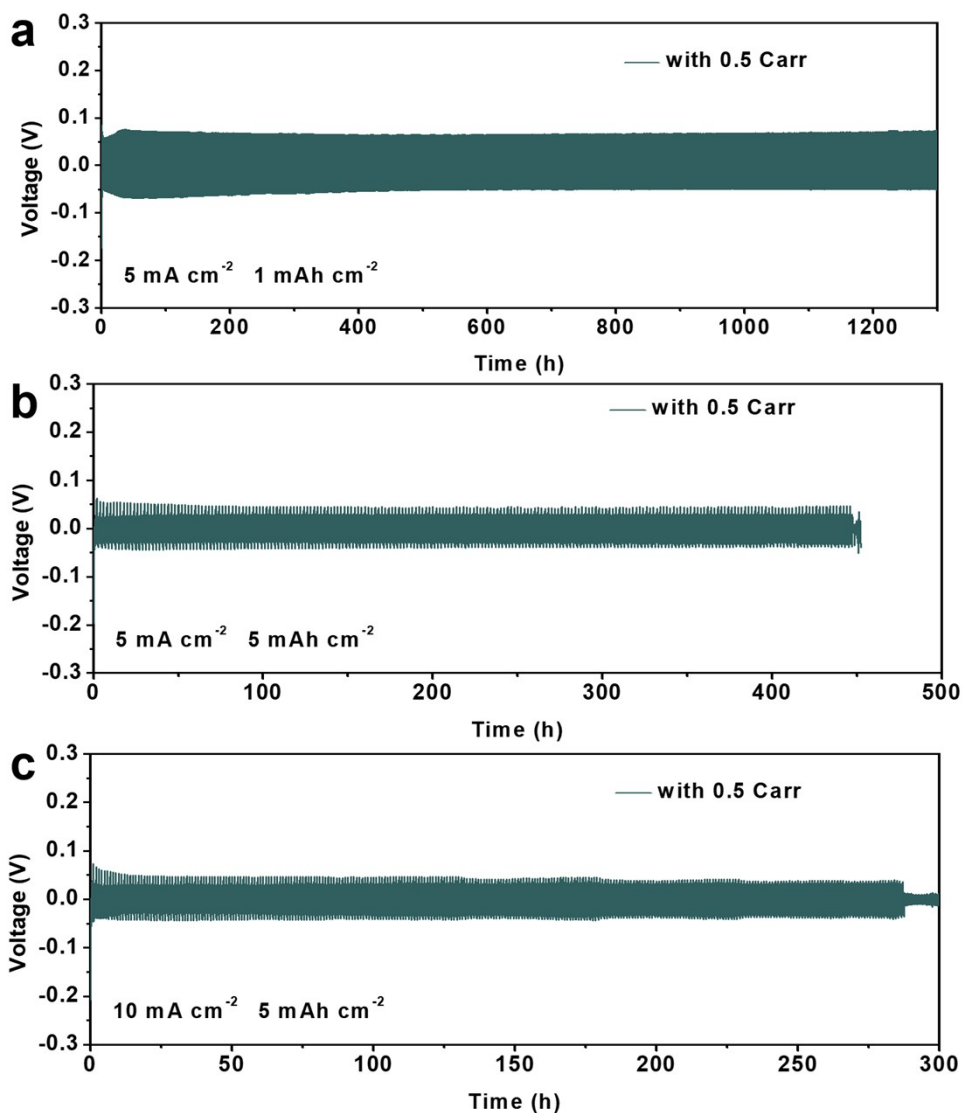


Fig. S9 The cycling performance of the Zn||Zn cells using the electrolyte containing 0.5 mg mL^{-1} Carr at (a) $5 \text{ mA cm}^{-2} / 1 \text{ mAh cm}^{-2}$; (b) $5 \text{ mA cm}^{-2} / 5 \text{ mAh cm}^{-2}$; (c) $10 \text{ mA cm}^{-2} / 5 \text{ mAh cm}^{-2}$.

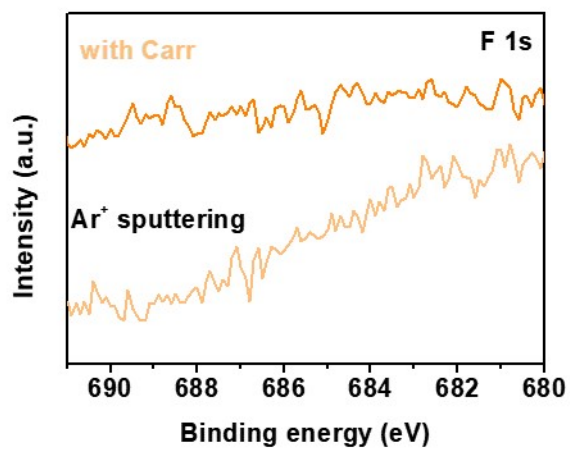


Fig. S10 F 1s XPS spectrum of electrolyte with Carr.

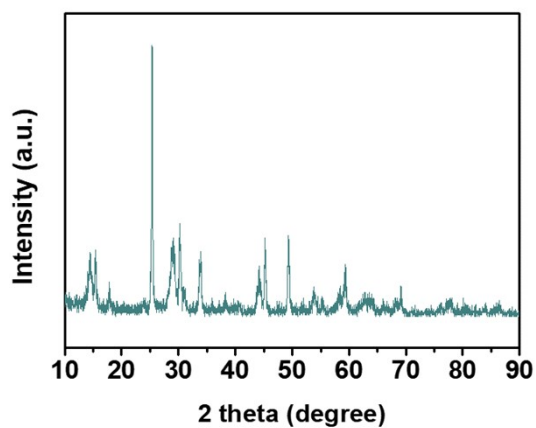


Fig. S11 The XRD pattern of prepared VO₂.

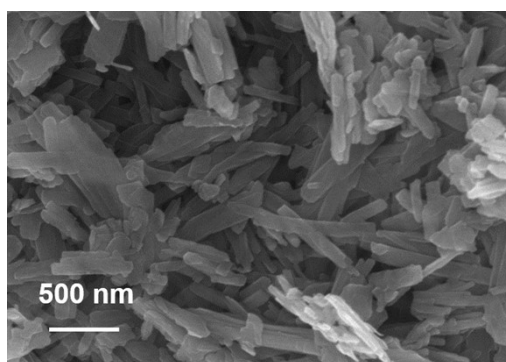


Fig. S12 The SEM image of prepared VO₂.

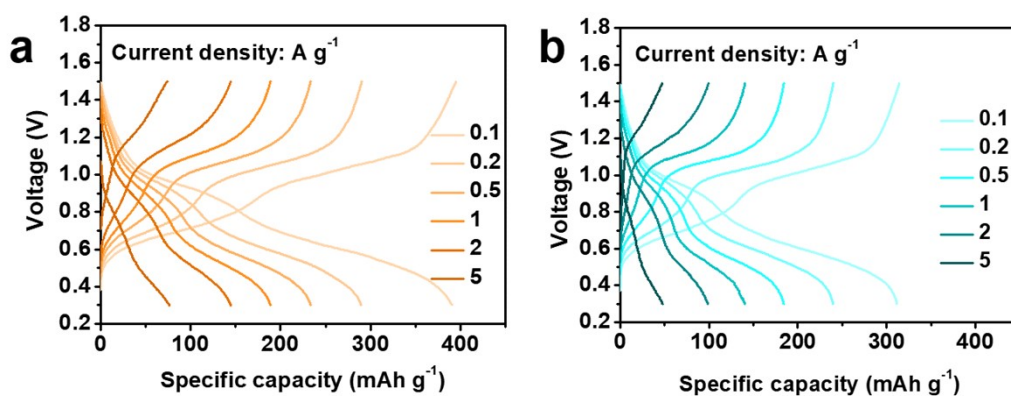


Fig. S13 Galvanostatic charge-discharge curves at different current densities in electrolyte (a) with and (b) without Carr.