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Retaining the specific capacitance under electrochemical stress: A pH-induced self-protection mechanism for manganese dioxide pseudocapacitive electrodes

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ABSTRACT

In this study, we report the enhanced electrochemical performance of a MnO_2 electrode modified with a pH-sensitive co-polymer, activated at acidic pH, and designed to counteract MnO_2 degradation in aqueous aqueous pseudocapacitors. The conformation of this polymer is controlled by the local pH changes that occur at the electrode/electrolyte interface during electrochemical stress associated to oxygen evolution.

As a proof of concept, we demonstrate that the addition of the pH-sensitive polymer contributes to improved electrode integrity and lifetime under over-polarization with oxygen evolution. After undergoing 10 cycles of electrochemical stress, the MnO_2/pH-sensitive polymer composite retains ~ 70 % of its capacitance. This remarkable result stands in stark contrast with the pristine MnO_2 electrode which fails catastrophically under the same stress conditions. We believe that this pH-induced self-protection mechanism represents a significant advancement in the development of novel smarter self-healing electroactive materials for the next generation of energy storage devices.

1. Introduction

Electrochemical stress resulting from overcharge or deep-discharge of the electrodes is common during the operation of energy storage devices. This stress involves sudden current peaks which are responsible for the mechanical and/or chemical deterioration and premature failure of metal compound-based electrode. These events occur frequently when electrodes operate in eco-friendly aqueous electrolytes, in which the potential window is constrained by the evolution of oxygen (OER, Eq. 1) and hydrogen (HER, Eq. 2) occurring at anodic and cathodic potentials, respectively. Both reactions induce local pH changes at the electrode, causing either acidification or alkalinization, along with the release of O_2 and H_2 gases, respectively. These factors, collectively, accelerate damage of the electrode material.

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^- \quad (1)$$

$$H_2O + e^- \rightarrow 1/2H_2 + HO^- \quad (2)$$

Manganese dioxide (MnO_2) has been widely used as electroactive material for pseudocapacitors due to its well-known pseudocapacitive response, resulting in fast and reversible faradaic reactions at the surface, and high theoretical capacitance (1370F g^{-1}) in aqueous electrolytes [1]. However, deviations of the pH of the electrolyte from neutral values negatively affect the electrochemical response of MnO_2 electrodes. These can manifest as dissolution and formation of Mn^{2+} species under acidic pH, or a transformation into poorly conductive structures, e.g., $Mn(OH)_2$ at more alkaline pH conditions. Consequently, the electrochemical stress under operation compromises the electrochemical performance of MnO_2 electrodes, decreasing their reliability and long-term cycling. Hence, it is imperative to extend the lifespan of the MnO_2 electrodes by developing smarter materials capable of autonomously repairing damage while maintaining the electrochemical activity. In literature, self-healing materials have been widely debated concerning their mechanical damage [2–8]. Nevertheless, the design of self-healing materials triggered by (electro)chemical stimuli, like unavoidable pH changes in aqueous electrolytes, has yet to be explored. As

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far as the author's knowledge extends, this remains a significant scientific challenge.

To develop our concept, we hypothesize that MnO_2 particles are enveloped either uniform or non-uniformly by a pH-sensitive polymer that senses local pH variations at the electrode surface. This polymer can then safeguard the particles during electrochemical stress, as shown in Fig. 1. Depending on the pH, the responsive polymer can expand (i.e., opens) or contract (i.e., collapses) as the polymeric chains undergo protonation or deprotonation, respectively. Hence, this strategy ensures the protection of MnO_2 electrodes precisely 'when' and 'where' required, improving their lifetime. Ideally, the combination of both basic and acid pH-sensitive polymers in the same composite would be able to provide complete protection of MnO_2 electrodes during OER and HER events.

In this work, we focus on a composite material comprising MnO_2 particles and a pH-sensitive polymer capable of self-protection under acidic conditions created by OER onset. The results show that is possible to counter detrimental effects caused by local acidification on the electrochemical performance of MnO_2 electrodes, extending their lifetime. The scientific advances reported in this work are, not only vital for extending the reliability of MnO_2 electrodes but also represent a groundbreaking leap in the development of smarter self-healing materials for electrochemical energy storage.

2. Materials and methods

The preparation of the MnO_2 material followed the procedure previously reported [9]. The pH-responsive co-polymer, denoted as pH-P, was prepared by a free radical polymerization and consisted of 90 % of acrylic acid (AA) and 10 % of [2-(acryloyloxy)ethyl]trimethylammonium chloride (AETMA). Firstly, AETMA was mixed in water at pH 3 with the V-50 initiator (Wako, 99 %). The mixture was purged with Argon for 15 min and then heated up to 56 °C. After 1 h, AA was added to the mixture that reacted for 4 h. For the preparation of the pH-sensitive composite (25 w/w % pH-P) MnO_2 and the previously freeze-dried pH-P were dispersed in DMSO, mixed, and stirred for 48 h at room temperature. The final product, denoted MnO_2/pH-P, was centrifuged and washed with ultrapure water (15 MΩ cm at 25 °C) and ethanol at 10000 rpm for 10 min and dried at 50 °C.

The working electrodes were prepared by mixing 80 % of active material, 15 % of conductive carbon, and 5 % of PVDF in DMSO. The ink-like material (~1 mg) was coated onto a 1 cm^2 Toray® carbon paper and dried at 50 °C for 12 h.

Electrochemical experiments were carried out using a Gamry Interface 1010E Potentiostat (Gamry Instruments) in a three-electrodes electrochemical cell with 0.5 M Na_2SO_4 electrolyte. Cyclic voltammograms were recorded at 50 mV s^{-1} and the galvanostatic charge/discharge curves were obtained at 1 A/g. A regular potential window between 0.0 and 0.8 V vs. SCE was used. For the OER electrochemical stress was extended up to 1.80 V.

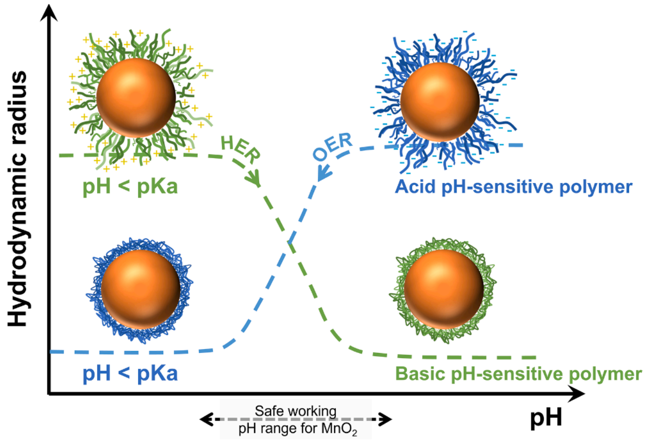

Fig. 1. Opening/collapsing of pH-sensitive polymers under acidic pH (blue) and basic pH (green). Orange spheres correspond to MnO_2 particles.

The specific capacitance (C_S) was determined using Eq. 3, where i is the current (Amperes), m is the mass of the active material (grams), t is the time of the discharge process (seconds), and V is the discharge potential range (Volt):

$$C_s = \frac{i \times \Delta t}{m \times \Delta V} \qquad (3)$$

Scanning Ion-Selective Electrode Technique (SIET) was used to determine the local pH value. Equipment and software are, respectively, from Applicable Electronics™ and Science Wares™. Micro-electrodes were prepared using a H^+ ionophore II cocktail A (Fluka, 95297) as described elsewhere [10]. Bromophenol blue indicator was added to the electrolyte for observation of pH changes using an optical microscope.

3. Results and discussion

A schematic view of the pH-P co-polymer is depicted in Fig. 2. The AETMA block contains a positively charged quaternary ammonium group that allows anchoring of the co-polymer chains onto the negatively charged surface (experimentally obtained through zeta potential measurements) of MnO_2 particles through electrostatic interactions. The AA block is pH-responsive and it is responsible for the protection or (re-) exposure of MnO_2 particles to the electrolyte.

The reversible mechanism of opening/collapsing of pH-P chains is based on the deprotonation/protonation of the carboxylic group of the AA block. Briefly, at higher pH values, the acid groups are deprotonated, and the chains expand due to charge repulsion. Upon acidification, protonation reduces the electrostatic repulsion, causing chains to collapse. At this stage, MnO_2 particles become shielded by the polymer and protected from the acid environment. As local acidification gradually vanishes (i.e., pH increases), the carboxylic groups deprotonate, and the polymer chains shift into an expanded conformation, re-exposing MnO_2 particles. These changes are possible thanks to the pKa of the polymer (value ~ 4.7, obtained from cloud point experiment), matching well with the conditions required for effective MnO_2 protection. This mechanism is schematically represented in Fig. 2.

The electrochemical response of the electrodes was evaluated using cyclic voltammetry within the regular potential window in 0.5 M Na_2SO_4 electrolyte (pH ~ 6). The voltammograms, displayed in Fig. 3 (a), reveal distinct electrochemical responses for MnO_2, MnO_2/pH-P, and pH-P electrodes. MnO_2 exhibits a quasi-rectangular-shaped voltammogram characterized by two broad peaks at 0.4 V and 0.6 V. These peaks are attributed to redox reactions occurring between Mn^{3+}/Mn^{4+} species, highlighting a pseudocapacitive behaviour. This effect is not so well defined in the MnO_2/pH-P electrode. Instead, a leaf-shaped voltammogram curve with two pronounced redox peaks at 0.50 and 0.45 V can be observed. The voltammogram of the pH-P electrode exhibits a very low current density (j_{max} ~ 10 mA g^{-1}), indicating an almost negligible electrochemical response. Due to this minimal electrochemical activity, the behaviour of the MnO_2/pH-P composite falls below that of the pristine MnO_2.

In addition to the differences in the shapes of the voltammogram, the MnO_2/pH-P composite displays lower current density and more pronounced redox peaks. This behaviour might be associated with two interconnected factors contributing to a mixed electrochemical behaviour. First, the presence of the polymer covers a fraction of the surface of MnO_2 particles, preventing their exposure to the electrolyte. This results in reduced current densities compared with the pristine MnO_2 where all particles are exposed. The second factor is related to a synergy between MnO_2 and pH-P materials during composite preparation. Functional groups containing N and O in MnO_2/pH-P contribute to the incipient redox peaks observed in the voltammogram, and to additional charge

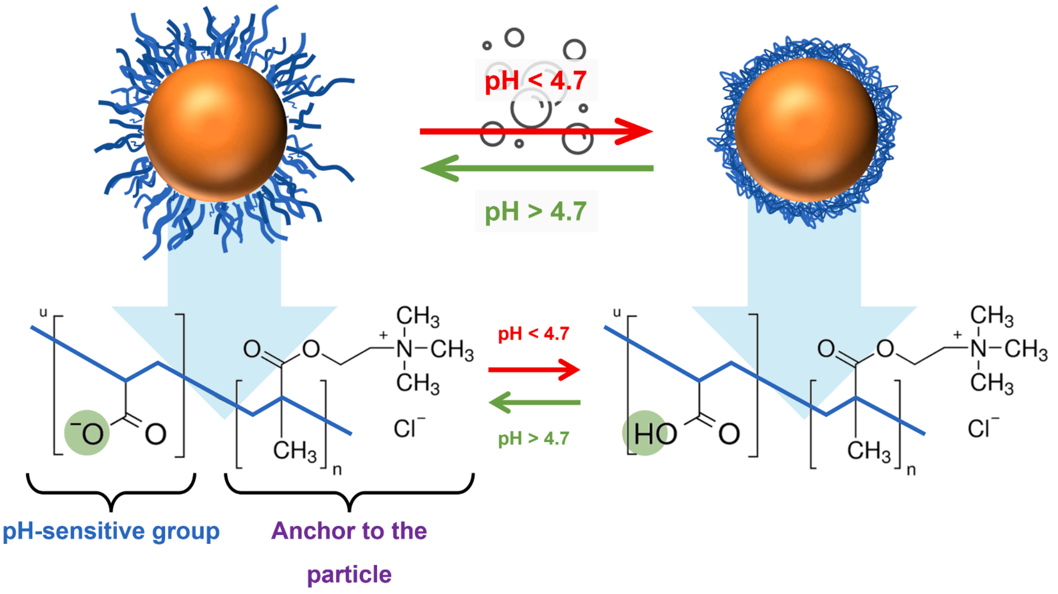

Fig. 2. Schematics view of opening/collapsing of pH-P onto MnO_2 particles.

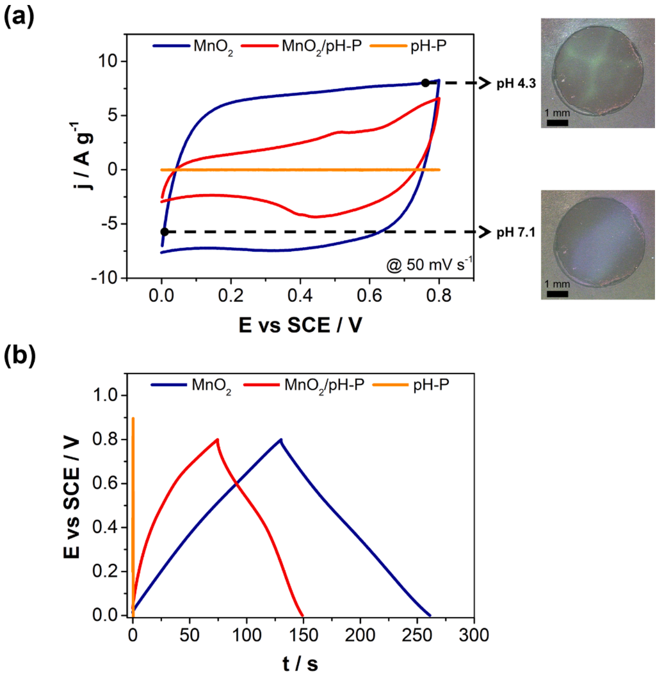

Fig. 3. Electrochemical response of MnO_2, MnO_2/pH-P, and pH-P electrodes: (a) cyclic voltammograms at 50 mV s^{-1}. Inset: optical micrographs of the electrode at upper and lower limits of the potential window; and (b) galvanostatic charge/discharge curves 1 A/g. Tests were performed in a potential range between 0.0 and 0.8 V in 0.5 M Na_2SO_4. Black dots in (a) correspond to the pH measurements at the electrode/electrolyte interface using SIET.

storage. These findings were corroborated by the charge/discharge curves depicted in Fig. 3 (b), in which the curves for the composite are not as symmetrical as the one observed for MnO_2. Specific capacitance values are 165.8 and 94.5F g^{-1} for MnO_2 and MnO_2/pH-P electrodes, respectively.

Close to the limits of the selected potential window, the acidification assigned to the beginning of OER potentially damages MnO_2 material [11]. To prove that this acidification can trigger conformational changes of pH-P during cycling, quantitative and qualitative pH determinations were performed using localized pH monitoring (SIET) and a pH indicator (optical microscopy). Quantitative SIET analysis revealed pH values of 4.3 and 7.1 close to the upper and lower limits of the potential window, Fig. 3 (a). Qualitative analysis showed a colour change from blueish (pH > 7) to yellowish (pH < 5), evidencing the pH variation near the surface of the electrode. Both results agree very well and prove that the pH conditions required for the polymer conformational change can be reached as OER onset approaches within the regular electrochemical potential window.

To simulate potential overcharge scenarios in real-world applications, MnO_2 and MnO_2/pH-P electrodes were polarized up to 1.8 V, inducing OER and localized acidification. Subsequently, these electrodes were subjected to further cycling in the regular potential window. The electrochemical stress protocol was repeated 10 times during a 7500 cycle test. Fig. 4 evidences the evolution of the capacitance retention for MnO_2 and MnO_2/pH-P electrodes throughout the test.

MnO_2 electrodes were used as control samples to study the protection capability of the polymer in the composite. The MnO_2 electrode

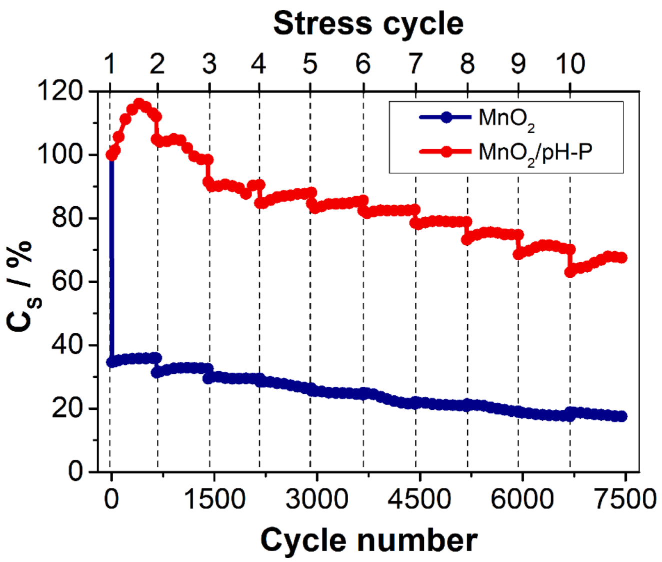

Fig. 4. Capacitance retention of MnO_2 and MnO_2/pH-P electrodes during 10 consecutive stages of OER electrochemical stress within a 7500 cycle test.

showed a sudden drop in capacitance attributed to damages caused by O_2 bubble release, including loss of material. Immediately, following the first OER, the capacitance decay was ~ 65 % from 165.8 to 57.3F g^{-1}. During the next stresses, the capacitance retention continuously decreased probably due to MnO_2 dissolution under acidic conditions. After 10 induced OER cycles, the retained capacitance reached ~ 18 % of its initial value, revealing a dramatic degradation of the electrochemical performance of the MnO_2 electrode.

Contrarily to the MnO_2 electrode, the MnO_2/pH-P composite showed an unexpected increase of capacitance immediately after the first induced stress. While we had initially anticipated stable capacitance values due to the protective role of the pH-sensitive polymer, an unexpected rise in capacitance occurred. Two factors may have contributed to this result. On one hand, as a polymer material, pH-P can act as a binder, enhancing adhesion between particles and the current collector. This ensures greater mechanical resistance against the impact of the O_2 bubbles. On the other hand, at early stages, the polymer conformation might involve both states. Since the polymer synthesis is performed at pH 3, without any further exposure to higher pH, in the fresh composite, the polymer chains are collapsed. When the electrode is immersed in 0.5 M Na_2SO_4 electrolyte, the outer surface is immediately wet by the neutral media that promotes the expansion of the exposed polymer. However, in more confined regions, wetting takes longer and some parts of the polymer chains may undergo the first OER cycle still in the collapsed conformation. Therefore, the increase in capacitance retention can be assigned to an additional polymer conformation change to the expanded state following OER, and further exposure of MnO_2 particles. This polymeric activation is believed to persist during the initial stages and can explain the oscillations in the capacitance until the third OER.

After the fourth induced stress, the recovery of capacitance became more stable with a 3 % capacitance increase in each cycle, a pattern that was consistently observed until the end of the test. Despite the self-protection provided by the change of conformation of the polymer, this could not entirely prevent MnO_2 dissolution because of the harsh OER conditions, leading to a slow capacitance decay. Nevertheless, the MnO_2/pH-P electrode retained ~ 70 % of its initial capacitance, demonstrating remarkable long-term stability after enduring 10 cycles of stress in contrast to the reference material which only retained 18 % of its initial capacitance. These preliminary findings point out the pH induced self-protective capability of the pH-P in the composite that effectively decelerates capacitance fade under OER stress conditions.

Based on these results, our concept leverages a new strategy in which the unavoidable and undesired local pH changes are used as the trigger for the self-protective mechanism. This approach creates a smart self-protecting strategy to enhance the capacitance retention and longevity of MnO_2 electrodes. The gains in capacitance retention under cycling and electrochemical stress offer important benefits in terms of electrode performance and reliability.

As an ongoing effort, we are actively optimising the polymer contents in the composite to increase its initial capacitance. Additionally, we are developing a basic pH-sensitive polymer capable of protecting MnO_2 particles upon alkalinization provoked by HER. The conjugation of acidic and basic pH-sensitive polymers within the same composite holds great potential for extending the lifetime of MnO_2 electrodes and paving the way for designing self-healing composites for electrodes used in aqueous electrolytes.

4. Conclusions

This work reports the enhanced capacitance retention of a composite material based on MnO_2 and a pH-responsive co-polymer. The groundbreaking finding is that local acidification, unavoidable when the potential approaches OER region, can be used as a trigger for a self-protection mechanism by a pH-sensitive polymer. We proved this concept by studying MnO_2 and MnO_2/pH-P electrodes under electrochemical stress provoked by OER on a 7500 cycle test. The MnO_2/pH-P composite displayed a remarkable capacitance retention of 70 % after enduring 10 induced OER stress stages. This result stands out when compared to the response of pristine MnO_2 which, despite its higher initial capacitance, only retained 18 % of capacitance under similar conditions. These original findings highlight the potential of the pH-sensitive polymer for designing self-healing materials for MnO_2 electrodes for aqueous electrochemical energy storage.

CRediT authorship contribution statement

A.C. Alves: Conceptualization, Methodology, Validation, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Luisa Chiavassa:** Methodology, Validation, Investigation, Writing – review & editing. **Tiago D. Martins:** Methodology, Validation, Investigation, Writing – review & editing. **Maryna Taryba:** Methodology, Validation, Investigation, Writing – review & editing. **Carlos Baleizão:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Funding acquisition. **Teresa M. Silva:** Conceptualization, Writing – review & editing, Supervision. **M.F. Montemor:** Conceptualization, Resources, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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