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Nitrate electro-sorption/reduction in capacitive deionization using a novel Pd/NiAl-layered metal oxide film electrode

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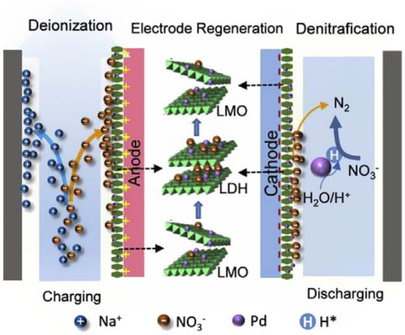
GRAPHICAL ABSTRACT

Pd/NiAl-LMO as CDI electrode can effectively electro-sorb NO_3^- and subsequently convert them to harmless N_2 in the electrode regeneration process.



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ABSTRACT

Capacitive deionization (CDI) is a promising candidate for the removal of nitrate (NO_3^-) from water, but the concentrated waste water inevitably produced in the electrode regeneration process would cause secondary pollution. In the present study, a Pd/NiAl-LMO film electrode was successfully prepared and used as an innovative NO_3^- electro-sorption/reduction electrode. Metallic Pd nanoparticles were uniformly doped into NiAl-LMO nanosheets, which created a loose porous nanostructure for NO_3^- electro-sorption and enabled catalytic activity for NO_3^- electro-reduction. Doping Pd nanoparticles into NiAl-LMO improved electron transport in the film electrode. The Pd/NiAl-LMO film electrode possessed larger specific capacitance and lower ion diffusion resistance than the pristine NiAl-LMO electrode. NO_3^- was electro-adsorbed by the Pd/NiAl-LMO electrode with concomitant reconstruction of the original hydrotalcite structure by the intercalation of NO_3^-, then the adsorbed NO_3^- was electro-reduced to N_2 by atomic H* during the electrode regeneration process. Our study provides not only a novel CDI electrode but also a new concept for a CDI process to achieve a more environmentally friendly outcome.

1. Introduction

Capacitive deionization (CDI), also referred to as electro-adsorption desalination, is a promising and fast-emerging electrochemical desalination method that has been extensively investigated over the last few years [1–3]. It employs electrodes to impose an electric field and adsorb ions from water during a charging step, followed by release of the ions to regenerate the electrodes by applying a reverse current or

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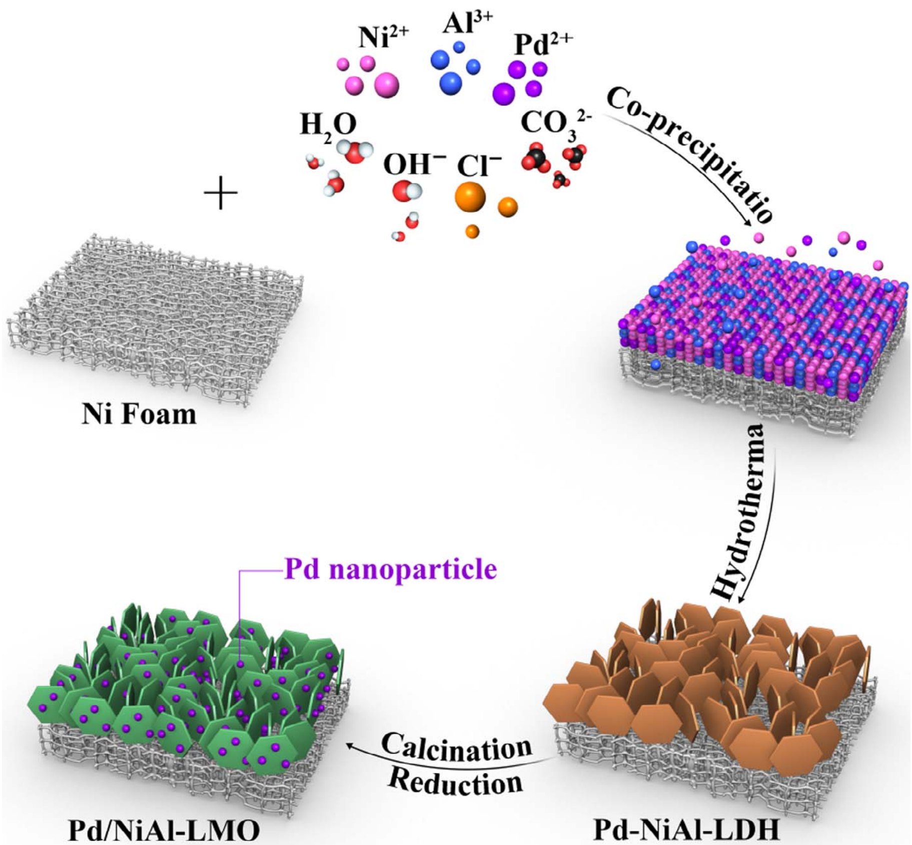

Fig. 1. Schematic illustration of the fabrication of the Pd/NiAl-LMO film electrode.

short-circuit during a discharging step. Electro-sorption was demonstrated to be effective in removing nitrate (NO_3^-) from water [4,5]. Pollution by NO_3^- is currently prevalent in groundwater [6], which leads to serious health risk since a high level of NO_3^- in drinking water (more than 10 mg N/L) can cause methemoglobinemia in infants and gastrointestinal cancer in adults [7].

NO_3^- removal by CDI has been investigated through development of new electrode materials [8,9] and novel cell architectures [10] to improve the performance in terms of efficiency. In these electro-sorption processes, however, the NO_3^- is simply concentrated onto the electrode surface and then discharged as a concentrated solution, which needs further treatment by denitrification to convert NO_3^- into harmless nitrogen gas before entering the environment. Unfortunately, until now, there has been no effort to develop a benign treatment for the concentrated wastewater, even though it is a crucial flaw in the environmental friendliness of CDI [1,2].

Layered double hydroxides (LDH) have always been represented by the formula $M_{1-X}^{2+}M_x^{3+}(OH)_2A_{x/n}^{n-}\cdot mH_2O$, which vividly reveals that LDH layers are positively charged due to the substitution of divalent metals by trivalent metals, with anions intercalated into the interlayer spaces to achieve charge balance [11,12]. Layered metal oxides (LMO) have been prepared by calcination of LDH, and can inherit the high active surface areas of LDH [12,13]. LMO can adsorb anions from water with concomitant reconstruction of the original layered structure [13,14], and have been used as effective absorbents for NO_3^- removal [15,16]. It has been reported that LMO have also been investigated as CDI electrode materials [12], which exhibited significantly higher capacity than carbon-based electrodes regarding electro-sorption of ions. In addition, LMO, with their high specific surface area and large anion adsorption capacity, have favourable properties as catalyst (such as noble metals) supports [17–19].

Pd-based catalytic reduction has exhibited high efficiency in the reduction of NO_3^- [20,21]. Previous studies revealed that LMO-supported Pd catalysts not only adsorbed NO_3^- effectively but also reduced NO_3^- to nitrogen by electrocatalytic reduction [22]. Moreover, it has been recently reported that the introduction of NiO into the supports can alleviate the poisoning of Pd catalysts [23,24]. Therefore, if Pd nanoparticles were doped into LMO (Pd/NiAl-LMO) and used as a CDI electrode, NO_3^- electro-sorption and electro-reduction could be expected to take place in the charging and discharging process, respectively. NO_3^- could be adsorbed on the NiAl-LMO surface under a positive potential, and subsequently reduced under a negative bias, which would enable the harmless removal of NO_3^- during electrode regeneration in the CDI process. Thus NO_3^- could be completely removed by the Pd/NiAl-LMO electrode from water without secondary pollution. The Pd/NiAl-LMO electrode would be a particularly promising candidate to cleanly remove NO_3^- through electro-sorption/reduction.

In the present study, a Pd/NiAl-LMO film electrode was successfully prepared and used as an innovative NO_3^- electro-sorption/reduction electrode. The morphology, structure and electrochemical properties of the Pd/NiAl-LMO electrodes were characterized to illuminate the key role of Pd nanoparticles in the CDI performance. The NO_3^- electro-sorption/reduction by the Pd/NiAl-LMO electrodes during the CDI process was investigated to optimize the electrochemical parameters and Pd loading amount. Our study provides not only a novel CDI electrode but also a new concept for a CDI process to achieve a more environmentally friendly NO_3^- removal.

2. Experimental

2.1. Synthesis of Pd/ NiAl-LMO film electrodes

Pd-NiAl-LDH film electrode was obtained by an in-situ hydrothermal method. Nickel foams (3*2*1) were used as the Pd-NiAl-LDH substrates. Solution A (100 mL), containing 0.12 mol $NiCl_2$, 0.04 mol $AlCl_3$ and a certain amount of $PdCl_2$, was firstly prepared. Solution B, (100 mL) containing 0.32 mol NaOH and 0.08 mol Na_2CO_3, were