
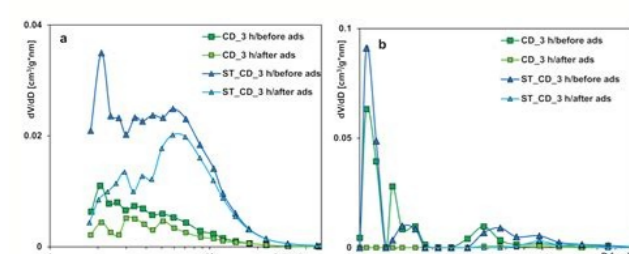


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A Chemical-Adsorption Strategy to Enhance the Reaction Kinetics of Lithium-Rich Layered Cathodes via Double-Shell Surface Modification

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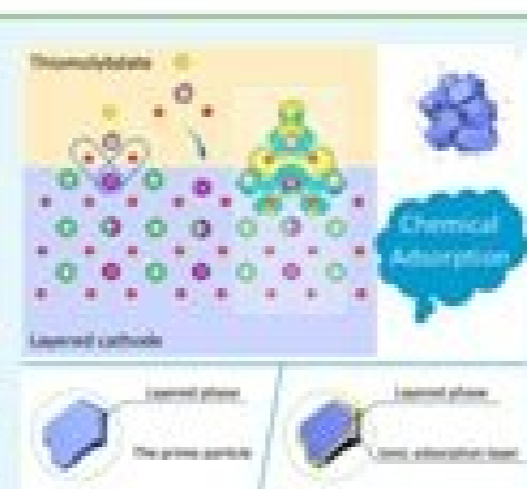
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Supporting Information

ABSTRACT: Sluggish surface reaction kinetics hinders the power density of Li-ion battery. Thus, various surface modification techniques have been applied to enhance the electronic/ionic transfer kinetics. However, it is challenging to obtain a continuous and uniform surface modification layer on the prime particles with structure integration at the interface. Instead of classic physical-adsorption/deposition techniques, we propose a novel chemical-adsorption strategy to synthesize double-shell modified lithium-rich layered cathodes with enhanced mass transfer kinetics. On the basis of experimental measurement and first-principles calculation, MoO₃S₂ ions are proved to joint the layered phase via chemical bonding. Specifically, the Mo–O or Mo–S bonds can flexibly rotate to bond with the cations in the layered phase, leading to the good compatibility between the thiomolybdate adsorption layer and layered cathode. Followed by annealing treatment, the lithium-excess-spinel inner shell forms under the thiomolybdate adsorption layer and functions as favorable pathways for lithium and electron. Meanwhile, the nanothick MoO₃·x(SO₃)₂ outer shell protects the transition metal from dissolution and restrains electrolyte decomposition. The double-shell modified sample delivers an enhanced discharge capacity almost twice as much as that of the unmodified one at 1 A g⁻¹ after 100 cycles, demonstrating the superiority of the surface modification based on chemical adsorption.

KEYWORDS: chemical-adsorption, double shell, surface modification, lithium rich layered cathode, DFT calculations



1. INTRODUCTION

As the advanced lithium-ion batteries are required to work at various conditions, both energy and power density are of vital importance in the materials engineering of cathodes. With a relatively high theoretical capacity and low cost, lithium-rich (Li-rich) layered cathode, or Li-rich layered oxides, Li₂MnO₄/LiTMO₂ (TM = transition metal elements), becomes the promising candidate as the cathode materials for the next-generation Li-ion batteries.^{1–3} As a member of the two-dimensional (2D) layered oxides, Li-rich layered cathode has the advantage of high specific capacity (>200 mAh g⁻¹). However, because of the 2D percolating network, lithium ions have to diffuse along specific crystal planes, known as the classic 1-TM channel.^{4,5} The lithium rich component suffers from low electron conductivity and poor lithium diffusion coefficient, leading to large electrode polarization. What's worse, interfacial resistance keeps increasing as side reactions proceed during cycling.⁶ Because of the sluggish kinetics, the practical capacity of Li-rich cathode decreases rapidly at high current rates.

To enhance the reaction dynamics, surface engineering has been developed as a major orientation on improving the electrochemical properties of layered cathodes.^{7–10} Basically, fast

electron and lithium transfer kinetics is one of the key factors in achieving rapid electrochemical reaction dynamics. The modification techniques are largely related to the physicochemical properties of the modification sources. For a long period of time, physical adsorption, precipitation and deposition dominate in surface engineering of lithium cathodes. Most of the metal oxides or phosphate coating by physical deposition cannot effectively meet the requirements for fast mass transfer. To settle the problem, Wu et al. first reported the spinel coating on the Li-rich cathode by dip and dry.¹¹ Other than 2D channels, 3D channels in spinels offer great enhancement in lithium-ion transfer kinetics, leading to an optimized rate performance. One should note that "dip and dry" is a kind of physical deposition technique and requires precise control. Ever since, surface modification with three-dimensional (3D) spinel phase has drawn great attention because of its flexibility and feasibility in surface engineering. A majority of related researches are focused on the carbon modified Li-rich

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PAPER

Computational study of the adsorption and dissociation of phenol on Pt and Rh surfaces[†]

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The adsorption of phenol on flat and stepped Pt and Rh surfaces and the dissociation of hydrogen from the hydroxyl group of phenol on Pt(111) and Rh(111) were studied by density functional calculations. On both Pt(111) and Rh(111), phenol adsorbs with the aromatic ring parallel to the surface and the hydroxyl group tilted away from the surface. Furthermore, adsorption on stepped surfaces was concluded to be unfavourable compared to the (111) surfaces due to the repulsion of the hydroxyl group from the step edges. Transition state calculations revealed that the reaction barriers, associated with the dissociation of phenol into phenoxy, are almost identical on Pt and Rh. Furthermore, the oxygen in the dissociated phenol is strongly attracted by Rh(111), while it is repelled by Pt(111).

1 Introduction

Due to environmental concerns and depletion of oil reserves, the interest towards biomass as a source for fuels has increased rapidly during the last decade. The main disadvantage of liquids derived from biomass, through processes such as pyrolysis, is that they include as much as 50 wt% oxygen.^{1,2} High oxygen content causes several undesired properties, such as low volatility, corrosiveness, thermal instability and tendency to polymerize under exposure to air.^{1,3} Thus oxygen needs to be removed, at least partially, to increase the energy value and stability of the fuel.

Oxygen-removal can be carried out with a hydrodeoxygenation (HDO) process in the presence of hydrogen on a catalyst that is conventionally a sulfided CoMo or NiMo catalyst on γ -Al₂O₃.² The sulfidation process of these catalysts contaminates the fuel by sulfur species. Loss of sulfur from the catalyst surface decreases its activity unless extra sulfur is added to the feed.² This results in increased contamination of the product. Another challenge is the γ -Al₂O₃ support that has been found to be unstable under HDO conditions and that catalyzes coke formation because of its acidity.

Due to disadvantages of sulfur-catalysts, research into sulfur-free catalysts has increased. It is expected that non-sulfided catalysts work at lower temperatures, which reduces the coke

formation and thus decreases the deactivation of the catalyst. Furthermore, the problems with the γ -Al₂O₃ support can be avoided if a different support material is used. One promising alternative for non-sulfided catalysts has been to use transition metal catalysts, such as Pt, Rh or Pd, on the ZrO₂ support.⁴

As biomass-based liquids are complex mixtures of hydrocarbons, their reactions are often studied using model components.^{2,4} Typical model components for wood-based liquids are phenol, anisole (methoxybenzene) and guaiacol (2-methoxyphenol), the chemical structures of which are illustrated in Fig. 1.

Although several computational studies discuss the behavior of benzene on Pt, Rh and Pd surfaces (reviewed by Jenkins⁵), only a few discuss the behavior of aromatic oxygen-containing components on these surfaces.^{6–8} For example, Bonalumi and co-workers⁷ studied the adsorption of anisole and its derivatives on the Pt(111) surface using density functional theory (DFT) cluster calculations. They concluded that the studied molecules are less strongly bonded to the surface compared to the parent molecule benzene. In the case of anisole, this effect is thought to be a result of steric hindrance of the methoxy group.⁸ Furthermore, Orita and Itoh studied phenol on Pd(111), illustrating that also this molecule adsorbs weaker compared to benzene.⁸

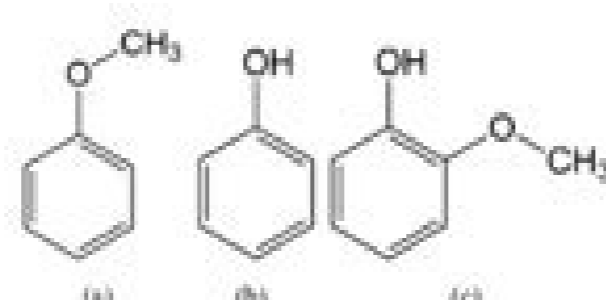


Fig. 1 Structures of (a) anisole, (b) phenol and (c) guaiacol.

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