



# Exploration of vanadium benzenedicarboxylate as a cathode for rechargeable lithium batteries



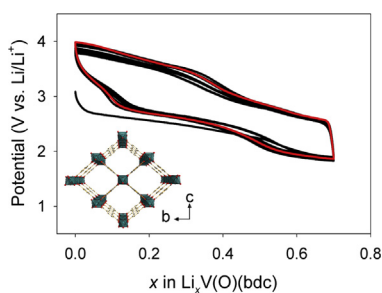
Watchareeya Kaveevivitchai, Allan J. Jacobson\*

Texas Center for Superconductivity and Department of Chemistry, University of Houston, Houston, TX 77204-5003, USA

## HIGHLIGHTS

- Microporous MOF, V(O)bdc, is used as a cathode material for lithium batteries.
- Lithium intercalation is reversible with good rate capability up to 10C.
- For  $x \leq 0.7$  in  $\text{Li}_x\text{V}(\text{O})(\text{bdc})$ , cells give  $82 \text{ mAh g}^{-1}$  with  $\sim 100\%$  coulombic efficiency.
- These properties are superior to those of the isostructural iron analog MIL-53(Fe).
- The V(O)bdc structure is found to be well maintained during Li insertion.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 22 September 2014  
 Received in revised form  
 6 November 2014  
 Accepted 20 December 2014  
 Available online 22 December 2014

### Keywords:

Vanadium benzenedicarboxylate  
 Metal-organic framework  
 Lithium intercalation  
 Electrode materials  
 Lithium batteries

## ABSTRACT

The electrochemical reaction with lithium of a vanadium-based metal-organic framework  $\text{V}^{\text{IV}}(\text{O})(\text{bdc})$  [MIL-47], which is isostructural to the iron compound MIL-53(Fe), was investigated. The large open channels which can accommodate small guest species, such as  $\text{Li}^+$  ions, together with the redox properties of the tetravalent vanadium ions make this material of potential interest as a rechargeable intercalation electrode for lithium batteries. The electrochemical properties were investigated in Li|1 M LiPF<sub>6</sub> in ethylene carbonate (EC) and dimethyl carbonate (DMC)|V(O)(bdc) cells between 4.0 and 1.5 V vs. Li/Li<sup>+</sup>. V(O)(bdc) cathodes can be reversibly cycled in Li cells with good rate capability and specific capacity. At a current density of C/12, Li/V(O)(bdc) cells can be cycled between  $0 \leq x \leq 0.7$  in  $\text{Li}_x\text{V}(\text{O})(\text{bdc})$  with  $\sim 100\%$  coulombic efficiency corresponding to  $82 \text{ mAh g}^{-1}$  which is a higher capacity than that found for MIL-53(Fe). The cell performance and electrochemical profiles at various current conditions are discussed. Structural evolution taking place during lithium intercalation was monitored by powder X-ray diffraction on phases of  $\text{Li}_x\text{V}(\text{O})(\text{bdc})$  ( $0 < x \leq 2$ ) chemically prepared by using n-BuLi. Previous studies of the reaction of lithium with metal-organic frameworks are briefly reviewed for comparison with the data presented for  $\text{Li}_x\text{V}(\text{O})(\text{bdc})$ .

© 2014 Published by Elsevier B.V.

## 1. Introduction

Recent research and commercial development of batteries have

focused on electrode materials with higher operating voltage and energy density, long cycle life, and rate capability for use in portable electronic devices, electric vehicles, and large-scale energy storage units for the power grid [1–4]. A wide range of compounds, such as LiMPO<sub>4</sub> (M = Fe, Mn, or Co) [5], Li<sub>3</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> [6], Li<sub>2</sub>MSiO<sub>4</sub> [7,8], LiMSO<sub>4</sub>F [9,10], LiMBO<sub>3</sub> (M = Fe, V, Mn, Co, etc.) [11], Li<sub>7</sub>Mn(BO<sub>3</sub>)<sub>3</sub>

\* Corresponding author.

E-mail address: [ajjacob@uh.edu](mailto:ajjacob@uh.edu) (A.J. Jacobson).

[12],  $\text{LiVOPO}_4$  [13,14],  $\text{LiVO}_4\text{F}$  [15,16], and  $\text{Li}_2\text{FeP}_2\text{O}_7$  have been examined as cathode materials for rechargeable lithium batteries [17–20]. In addition to these inorganic compounds, new organic materials, such as  $\text{Li}_2\text{C}_8\text{H}_4\text{O}_4$  [21],  $\text{Li}_2\text{C}_6\text{H}_4\text{O}_4$  [21],  $\text{Li}_2(\text{C}_6\text{H}_2\text{O}_4)$  [22],  $\text{Li}_2(\text{C}_{14}\text{H}_6\text{O}_4)$  [23],  $\text{Li}_4(\text{C}_6\text{O}_6)$  [24], and  $\text{Li}_4\text{C}_{24}\text{H}_8\text{O}_8$  have shown promise as electrode materials for Li-ion batteries [25–28].

Metal-organic frameworks (MOFs), assembled from inorganic building units (metal ions or clusters) and organic linkers, have also emerged as another class of crystalline electrode materials for rechargeable lithium batteries [29,30]. Due to the design and synthesis flexibility inherent in MOFs [31–33], in the past two decades many efforts have been made to address technological applications of these materials in areas, such as gas storage, separations, ion exchange, catalysis, selective molecular adsorption, optoelectronics, magnetic and photoluminescence responses, and drug delivery [34–39]. MOFs have attracted attention as possible candidates for new electrodes because they possess tunable, porous open channels that allow rapid insertion of species, and redox active metal centers. Both can be controlled by changing the organic ligand molecules and metal ions [40].

While porous organic–inorganic frameworks show a wide range of properties, MOFs still face a number of challenges in the area of redox chemistry, particularly because of their insulating nature [41–44]. Changes in the redox state of the metal centers are usually accompanied by changes in the coordination number of the metal ion, which can lead to a non-reversible degradation of the MOF structure [45,46]. Up to 2006, there had been only three reports of using MOFs as energy-storage electrodes for lithium batteries. None of them was successful. The first report was on electrochemical reduction of a microporous nickel phosphate by Li which resulted in the irreversible decomposition of the compound into a nanocomposite electrode made of Ni nanoparticles embedded in a  $\text{Li}_2\text{O}$  matrix [47]. A second example was the Ga–V phosphonate framework containing redox active oxovanadyl centers, with preliminary cycling data revealing that voltage as high as 5 V vs.  $\text{Li}/\text{Li}^+$  was needed to extract the inserted  $\text{Li}^+$  ions from the structure [48]. The third reported by Li and co-workers was the study of electrochemical Li intercalation of a Zn-based MOF [49]. The result showed a relatively high irreversible capacity during the first discharge and a much lower reversible charge–discharge capacity in the following cycles. The precursor decomposed into a Zn-based nanocomposite matrix containing  $\text{Li}_2\text{O}$ . The authors claimed that this material was “not suitable for application in reversible lithium storage” [49].

One way to bypass these poorly reversible conversion/decomposition reactions is to use MOFs that are based on early 3d transition metals to take advantage of the lower occupation of 3d electron orbitals (higher oxidation states of the metals), which leads to greater M–O bond stability with respect to charge variations, and to bring about some long-range electron delocalization via the stabilization of class II and III mixed valence states [50]. Recently, Ferey and co-workers synthesized a wide variety of 3d metal ( $\text{V}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Fe}^{\text{III}}$ ) carboxylates, which belong to a group of compounds with the general framework formula  $\text{MX}(\text{bdc})$ , based on chains of *trans* corner-sharing  $\text{MX}_2\text{O}_4$  ( $\text{M} = \text{V}$  [51,52],  $\text{Cr}$  [53],  $\text{Al}$  [54,55],  $\text{Fe}$  [56–58],  $\text{In}$  [59],  $\text{Ga}$  [60],  $\text{Mn}$  [61], and  $\text{Sc}$  [62,63], with  $\text{X} = \text{O}$ ,  $\text{OH}$ ,  $\text{F}$ ) octahedra cross-linked by 1,4-benzenedicarboxylate (bdc). The three-dimensional framework that results has one-dimensional rhombic channels. The first member of the compound series  $[\text{V}^{\text{III}}(\text{OH})(\text{bdc})(\text{H}_2\text{bdc})_x]$ , known as MIL-47as, loses the guest acid on heating in air, and simultaneously the framework  $\text{V}^{3+}$  ions are oxidized to  $\text{V}^{4+}$  forming  $\text{V}^{\text{IV}}(\text{O})(\text{bdc})$  or MIL-47, without changing the topology of the structure, thus providing the first evidence of chemically induced redox reactions within this system [51].

Jacobson and co-workers synthesized two iron members of the family, namely,  $[\text{Fe}^{\text{III}}(\text{OH})(\text{bdc})(\text{py})_{0.85}]$  and  $[\text{Fe}^{\text{II}}(\text{bdc})(\text{dmf})]$  ( $\text{py} = \text{pyridine}$  and  $\text{dmf} = \text{dimethylformamide}$ ), where the change in the iron oxidation state is brought about by replacing the  $\text{OH}^-$  bridging species by the neutral oxygen atom in  $\text{dmf}$  [57]. This provides the first example of a  $\text{M}^{\text{II}}$  analog with the bridging species along the inorganic chains being neutral. Such findings suggest a possibility of inducing mixed valence states in this MOF family.

In 2007, the first example of MOFs as promising intercalation electrodes in Li-based batteries was reported [50]. An iron compound with composition  $[\text{Fe}^{\text{III}}(\text{OH})_{0.8}\text{F}_{0.2}(\text{bdc})](\text{H}_2\text{O})$ , known as MIL-53, was used as a cathode for a Li-based electrochemical cell. Reversible Li insertion/extraction to the extent of  $\sim 0.6 \text{ Li}^+$  per Fe accompanied by reduction/oxidation of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , with a charge–discharge capacity of  $75 \text{ mAh g}^{-1}$  at a  $C/40$  rate (one equivalent Li in 40 h) without any alteration of the framework, was reported. An attempt to increase the electrochemical capacity was made through the adsorption of an electroactive molecule, 1,4-benzoquinone, into the MIL-53 framework [64]. The overall benefit of the quinone uptake was an increase in the electrode capacity from  $75 \text{ mAh g}^{-1}$  to  $93 \text{ mAh g}^{-1}$ , which could not be maintained for longer than 5 cycles. Even though insertion of 2 more  $\text{Li}^+$  per mole of 1,4-benzoquinone is possible in principle compared to the parent MIL-53(Fe), practically this could not be achieved due to the solubility of the guest molecule in the electrolyte.

Following the same approach, an iron-based MOF designated as MIL-68,  $[\text{Fe}^{\text{III}}(\text{OH})(\text{bdc})(\text{dmf})_{1.1}]$ , which has larger and more rigid (compared to the rhombic channels of MIL-53) triangular and hexagonal one-dimensional pores, was electrochemically investigated for lithium insertion. Surprisingly, only  $0.35 \text{ Li}^+$  per Fe could be inserted into the structure corresponding to a capacity of  $30 \text{ mAh g}^{-1}$  at a  $C/10$  cycling rate [65].

Lithium storage by a formate-based MOF,  $\text{Zn}_3(\text{HCOO})_6$ , was reported [66]. An incredibly high capacity of  $560 \text{ mAh g}^{-1}$  corresponding to 9.6 mol of Li per formula unit was obtained for up to 60 cycles at 0.11C within the voltage range of 0.005–3.0 V. The zinc formate framework was found to react reversibly with Li through a conversion reaction. The matrix involved during discharge–charge cycling was lithium formate rather than the typical  $\text{Li}_2\text{O}$ . Also, the same authors reported the electrochemistry of  $\text{Co}_3(\text{HCOO})_6$  and  $\text{Zn}_{1.5}\text{Co}_{1.5}(\text{HCOO})_6$  with lithium metal [66].

In other studies, Devic and co-workers used MOFs based on the redox active organic linker tetrathiafulvalene tetracarboxylic acid, (TTF-TC) $_4$ , as the positive electrodes in lithium batteries. The TTF-based compounds, namely,  $\text{M}_2(\text{TTF-TC})\text{H}_2$  ( $\text{M} = \text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ), exhibited similar behavior in solid state cyclic voltammetry and galvanostatic charge–discharge experiments, with a reversible capacity of  $30\text{--}50 \text{ mAh g}^{-1}$  at high current density (10C) in the voltage range between 2.3 and 3.75 V [67]. Another series of TTF-based MOFs,  $[\text{M}(\text{H}_2\text{O})_4]_2(\text{TTF-TC})(\text{H}_2\text{O})_4$  ( $\text{M} = \text{Ni}$ ,  $\text{Co}$ ) and  $[\text{Ni}_2(\text{H}_2\text{O})_5](\text{TTF-TC})(\text{H}_2\text{O})$ , were also investigated as positive electrode materials in lithium cells [68].

Honma et al. reported the use of Prussian blue analogs (PBAs),  $\text{A}_x\text{Mn}^{\text{II}}_y[\text{Fe}^{\text{III}}(\text{CN})_6] \cdot n\text{H}_2\text{O}$  ( $\text{A} = \text{K}$ ,  $\text{Rb}$ ), as electrode materials exhibiting reversible lithium insertion/extraction with a capacity of about  $60 \text{ mAh g}^{-1}$  at a constant current density of  $50 \text{ mA g}^{-1}$  [69]. The result suggests that the valence state of Mn ions is constant at 2+ and that the Fe ions are redox active during the charge–discharge process [70,71]. Okubo et al. demonstrated that the ion storage ability of the cyanide-bridged MOF,  $\text{K}_2\text{Mn}^{\text{II}}[\text{Mn}^{\text{II}}(\text{CN})_6]$ , can be enhanced by suppressing vacancy formation within the framework. Once the  $\text{K}^+$  ions are completely removed electrochemically, a vacancy-free PBA framework  $\text{Mn}^{\text{III}}[\text{Mn}^{\text{III}}(\text{CN})_6]$  can be fabricated. The vacancy-free PBA compound underwent reversible

Download English Version:

<https://daneshyari.com/en/article/7734112>

Download Persian Version:

<https://daneshyari.com/article/7734112>

[Daneshyari.com](https://daneshyari.com)