



Vanadium oxychloride as electrode material for sodium ion batteries



Ping Gao^a, Clemens Wall^a, Le Zhang^a, M. Anji Reddy^a, Maximilian Fichtner^{a,b,*}

^a Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstr. 11, Ulm 89081, Germany

^b Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), PO Box 3640, Karlsruhe 76021, Germany

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ABSTRACT

Layered vanadium oxychloride (VOCl) was tested as cathode material for rechargeable sodium ion batteries. Electrochemical characterization showed that the VOCl electrode can deliver a discharge capacity of 120 mAh g⁻¹ at a 0.5 C rate in a voltage range of 1.0–3.0 V vs Na/Na⁺. A capacity of 80 mAh g⁻¹ was obtained after 55 cycles at 1 C rate. A combination of intercalation and conversion type reaction of VOCl with Na has been identified by energy-dispersive X-ray spectroscopy (EDX) and *ex situ* X-ray diffraction (XRD). The results demonstrate the principle feasibility of using VOCl as cathode material for rechargeable sodium ion batteries.

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1. Introduction

Due to the growing demand for environmental-friendly batteries with high energy density and low cost, several battery chemistries beyond lithium ion batteries (LIB) have been proposed [1–5]. Sodium ion batteries (SIB) have recently attracted great interest, as sodium resources are abundant and cheaper than lithium [6,7]. The positive electrode materials of polyanion compounds (NaMPO₄, M = Fe, Mn, etc.) [8–10] or layered oxide compounds (NaMO₂, M = Ni, Co, Mn, etc.) have been widely investigated for the feasibility of Na intercalation [11–13]. The ionic radius of sodium is 1.02 Å larger than that of lithium. This leads to higher kinetic limitations of the intercalation of Na compared to Li. For instance, graphite anodes, which are commonly used in LIB systems, do not intercalate sodium to an appreciable extent and intercalation rather proceeds in partly disordered environments such as hard carbon [14–16]. Recently, high theoretical capacity compounds, which undergo a conversion reaction, e.g., FeF₃, have been proposed as cathodes for rechargeable LIB and SIB [17–20]. In a conversion reaction, multi-electron redox processes can lead to a high reversible capacity. A systematic discussion on the basic thermodynamic properties of SIB electrode materials based on conversion reaction has been reported recently [21]. A high discharge potential, attributed to low kinetic limitations, has been observed for CuCl and CuCl₂ as cathode

materials [21]. However, the dissolution of active material in the electrolyte caused a poor cycling performance.

Herein, we report the application of layered vanadium oxychloride (VOCl) as a new cathode material for rechargeable sodium ion batteries. The VOCl has an orthorhombic structure of buckled V–O bilayer sandwiched by chlorine layers with a space group of *Pmnm* (lattice parameter: *a* = 3.78 Å, *b* = 3.30 Å, *c* = 7.91 Å) [22]. A high theoretical capacity of 260 mAh g⁻¹ could be obtained in case of a full reaction of 1 VOCl with 1 Na. Moreover, contrary to most chlorides, the VOCl is air stable, which facilitates handling and processing of the material, and it is insoluble in the electrolytes tested so far. The electrochemical performance and sodium storage mechanism of the VOCl electrode was investigated with galvanostatic charge and discharge test, cyclic voltammetry (CV), EDX and *ex situ* XRD.

2. Experimental

VOCl was prepared by a solid–gas reaction, the process is described elsewhere [23]. VOCl/C cathode composites were prepared by ball milling a mixture of 80 wt% VOCl and 20 wt% carbon black using a silicon nitride vial and balls for 1 h at a speed of 200 rpm (ball-to-powder ratio, 30:1). Galvanostatic charge–discharge tests were conducted using 2032-type coin cells with a solution of 1 M NaClO₄ in propylene carbonate (PC) as electrolyte and sodium as counter electrode. The working electrode was prepared by coating a slurry containing 80 wt% VOCl composite, 10 wt% poly(vinylidene difluoride) (PVDF) binder and 10 wt% carbon black on a stainless steel substrate (diameter 12 mm). The mass loading of the cathode electrode was around 2.0 mg per cm² after drying at 373 K overnight. For the *ex situ* measurement, the cycled

* Corresponding author at: Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstr. 11, Ulm 89081, Germany. Tel.: +49 721 608 25340; fax: +49 721 608 6368.

E-mail address: m.fichtner@kit.edu (M. Fichtner).

VOCl-Na cell was carefully disassembled in the glove box and the VOCl electrode was rinsed with PC and then dried at 373 K in the oven overnight. Battery tests were performed with an Arbin BT2000 battery system at 298 K. Cyclic voltammetry (CV) measurements were conducted with a Biologic VMP-3 electrochemical workstation using three electrode Swagelok-type cells, whereby sodium metal was used as reference and counter electrode. The sweep rate was 0.1 mV s^{-1} in the potential range of 1.0–3.0 V. XRD patterns were recorded in transmission geometry using a STOE STADI-P diffractometer and a Cu K α radiation source (operated at 40 kV, 40 mA). Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) were carried out by using a ZEISS LEO 1530 instrument.

3. Results and discussion

The morphology and crystallite size of the as-prepared VOCl and the VOCl/C were investigated by SEM and XRD (Fig. 1). By ball milling, the rod-like shape of the particles was destroyed, and a uniform distribution of carbon black and VOCl particles was obtained (Fig. 1b). The XRD patterns of the as-prepared VOCl and the VOCl/C composite match well with the standard PDF card as shown in Fig. 1c. In the crystal, the V^{3+} ions are coordinated by four oxygen atoms and two chlorine atoms forming strongly distorted VO_4Cl_2 octahedrons in a layered structure as it is shown in Fig. 1d [24]. After ball milling, the peaks attributed to the VOCl phase were broadened which indicates a reduction of the crystallite size (Fig. 1c) [25]. Minor impurities of V_2O_3 were observed (Fig. 4) in VOCl/C composite, which could be caused by partial decomposition of VOCl during ball milling.

The electrochemical behavior of VOCl vs. Na was investigated by galvanostatic charge–discharge tests and CV measurements. Fig. 2a shows the charge and discharge curves of the VOCl electrode at 0.5 C in the voltage range of 1.0–3.0 V for the initial 10 cycles ($1 \text{ C} = 260 \text{ mA g}^{-1}$). An initial discharge capacity of 120 mAh g^{-1} was obtained, corresponding to 0.46 mol of sodium per mole VOCl. In the second cycle, the charge and discharge curves were similar to the first one and a coulombic efficiency of 92% was observed. The capacity loss during the first cycle may be ascribed to an irreversible process leading to an interface layer at the surface and/or the structural changes associated with a loss of the electrical contact of a part of the active material.

The features of the charge and discharge curves of the 2nd cycle to the 10th cycle were very similar, hinting at a retention of the reaction path during the charge and discharge processes in these cycles.

The cycling performance of the VOCl electrode cycled at 1 C is given in Fig. 2b. An initial discharge capacity of 117 mAh g^{-1} was observed. A discharge capacity of 80 mAh g^{-1} was maintained during 55 cycles, which corresponds to capacity retention of 68%, which was higher compared to the previously published data for CuCl and $CuCl_2$ as cathode for SIB [21]. The coulombic efficiency between 92% and 95% indicates side reactions of the material, probably with the electrolyte. Preliminary results suggest that charging and discharging the material in a smaller voltage window can improve the cyclic properties. It has to be clarified in further studies whether the side reactions could also be mitigated by changing the electrolyte. By coating the surface of VOCl or confining the VOCl into conductive porous material, the cyclic stability of the electrode may be improved further. Fig. 2c shows the charge–discharge curves of VOCl-Na at 1 C in different cycles. It exhibited a behavior similar to the one, which was cycled at 0.5 C as shown in Fig. 2a. However, the polarization increased during the cycling, resulting in a lower discharge potential.

Fig. 2d shows the initial cycles of CV curves of the VOCl electrode. Five redox couples at 2.65/2.70 V, 1.86/1.95 V, 1.48/1.67 V, 1.25/1.46 V, and 1.04/1.14 V (vs. Na/Na⁺) were observed in the first cycle. After the stabilization of the initial processes, three main redox peaks at 2.64/2.72 V, 1.86/1.97 V, and 1.42/1.46 V were observed from the 6th cycle to the 13th cycle as shown in the inset of Fig. 2d. From the results of CV, it can be concluded that the reaction of the VOCl electrode with Na proceeds in multiple steps with different intermediate reaction products, similar behavior has been observed before for other electrode materials in SIB [26,27].

To gain insight in the reaction mechanism, several analytical techniques were employed in various states of charge and discharge. In a first overview, SEM and EDX measurements were performed on the discharged VOCl electrode. Fig. 3 shows the SEM images of the VOCl electrode. Compared to the as-prepared VOCl electrode (Fig. 3a and b), sub-micrometer-sized particles can be seen on the surface of the discharged electrode, which may correspond to new phases formed during the electrochemical reaction (Fig. 3d). The elements V, O, Cl, F, and Na were observed in the discharged state (Fig. 3e) which provides

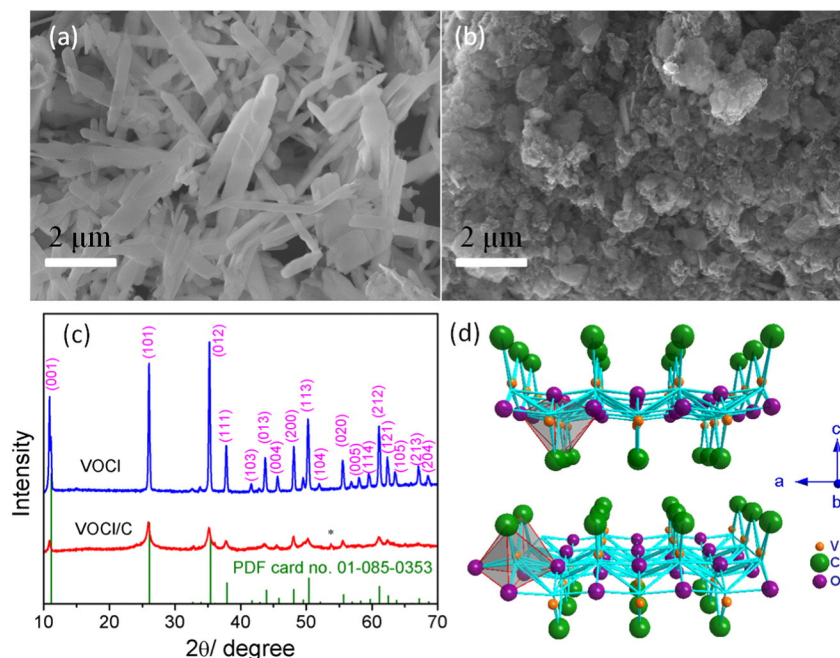


Fig. 1. SEM images of the as-prepared VOCl (a) and the VOCl/C composite (b), the corresponding XRD patterns (c), crystal structure of VOCl (d).

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