



Preparation and characterization of novel alkylviologens-intercalated vanadyl-vanadate (RV)V₃O₈

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ABSTRACT

Various n-alkylviologens-intercalated vanadyl-vanadate (RV)V₃O₈ were synthesized with the combination of redox and ions-exchange methods. The derivative compounds were characterized by X-ray diffraction (XRD), FT infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectroscopy (UV–vis DRS). The XRD results indicate that the interlayer spacing increases with the alkyl chain length of the alkylviologen cations. The FTIR data shows that alkylviologens were inserted into the interlayers of V₃O₈²⁻. XPS data reveals that the vanadium ions in the intercalation compounds are mostly in a pentavalent V⁵⁺ state with some partially reduced to the V⁴⁺ state. The intercalation compounds have the strong absorption character in the ultraviolet and visible light region. Magnetic susceptibility indicates that the (ethylviologen) V₃O₈ (EV3) is antiferromagnetic and possesses an ordered magnetic structure below 15 K. Above 15 K, EV3 exhibits paramagnetic behavior and a disordered magnetic structure.

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1. Introduction

Inorganic–organic intercalation materials have received substantial attention over the past several years because of their unique microstructures and properties [1–8], which have been applied in a variety of areas such as energy-storage applications [9], electrochemistry [10], proton-pump electrodes [11], sensors [12], heterogeneous catalytic processes [13] and photochemical redox reactions [14].

V₃O₈²⁻ anion, with semiconducting properties and layered structure, is a suitable host material for intercalation chemistry, since electrons or ions are easily transferred between the layers. The preparation of the controlled sinusoidal or planar layer structure in the intercalation compounds using V₃O₈²⁻ anion as host and their property investigations were one of much current research focus and has been extensively studied [15,16]. A variety of inorganic species have been obtained, for example: Li_{1+x}V₃O₈ [17], CoV₃O₈ [18], Mg(V₃O₈)₂ [19], Ca(V₃O₈)₂ [20] and (Li, Cu)_{1+x}V₃O₈ [21]. However, there is few reported about the intercalation of organic guest into V₃O₈²⁻, except for polyethylene oxide [22].

In the present research, we prepared a series of alkylviologens–V₃O₈ intercalation compounds, and in which alkylviologen cation ions with different alkyl chains were successfully introduced into the interlayers of V₃O₈²⁻ through the combination of redox and ion-

exchange procedures. At the same time, absorbance character in the ultraviolet and visible regions and magnetic susceptibility has been discussed.

2. Experimental procedure

2.1. Preparation of intercalation compounds

In a typical synthesis of these inorganic–organic intercalation compounds, two synthetic steps were followed: first, (NH₄)₂V₃O₈ was synthesized by using bulky divanadium pentoxide powders as a precursor in the presence of the hexamethylene tetramine as reductant were placed into a stainless steel reactor at a ratio of 1:1.2 by weight, and then 20 mL of 1:1 methanol/water (v/v) was added to the reaction reactor. The resultant mixture was sealed in the reactor and heated at 110 °C for 3 days in a controlled temperature oven. The black crystal trivanadium oxide (NH₄)₂V₃O₈ was obtained.

Second, (NH₄)₂V₃O₈ and the iodide salt of alkylviologen were blended in a molar ratio of 1–1.2 in water of 100 mL, then the reactant mixture was refluxed at 100 °C for 2–11 days. The resultant precipitate was filtered, washed with deionized water and acetone several times, and finally dried at room temperature. These synthesized intercalations compounds were represented by the general formula (RV)V₃O₈, and which was abbreviated to MV3(RV=methyl), EV3(RV=ethyl), PrV3(RV=propyl), BV3(RV=butyl) and PeV3(RV=pentyl) for

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$(\text{NH}_4)_2\text{V}_3\text{O}_8$ reacting with the iodide salt of methyl-, ethyl-, propyl-, butyl- and pentyl-viologen, respectively.

2.2. Characterization

Elemental analysis was completed on an Elementar Vario ELIII Elemental Analyzer (Elementar, Germany). The XRD patterns were generated on a D8-Advance diffractometer (Bruker, Germany) under the following conditions: Cu $K\alpha$ radiation, Ni filter; source voltage, 40 kV; source current, 40 mA. Fourier transform infrared (FT-IR) spectroscopy measurements were carried out with a Nicolet NEXUS 670 FT-IR spectrometer (Thermo Nicolet, USA) in the range of 400–4000 cm^{-1} using the KBr-disk technique at room temperature. The XPS spectra were recorded with a PHI 5000c ESCA System (Perkin Elmer, USA) working by using Mg- $K\alpha$ (1253.6 eV) radiation as the excitation source. Sample charge was corrected by setting the binding energy of adventitious carbon (C1s 284.6 eV). The XPS analysis was conducted at ambient temperature and pressure on the order of less than 10^{-7} Pa with an estimated error of ± 0.1 eV for all the measurements. Quantitative analysis of atomic ratios was accomplished by determining the elemental peak areas, following a Shirley background subtraction performing with the XPS-Peak 4.1 program. The DRS spectra were run in the range of 200–900 nm at room temperature using a JASCO V-550 spectrophotometer (Tokyo, Japan) equipped with an integration sphere. Variable-temperature magnetic susceptibility $\chi(T)$ data was obtained on 57 mg sample EV3 from 2 to 300 K in a magnetic field of 1 T on a Quantum Design PPMS-9 system (Quantum Design, USA).

3. Results and discussion

3.1. Synthetic method

The traditional synthesis methods of ammonium vanadylvanadate $(\text{NH}_4)_2\text{V}_3\text{O}_8$ was using vanadium pentoxide as starting oxide and sodium borohydride as reducing agent in a NaOH aqueous solution with excess NH_4Cl under argon atmosphere [23] or V_2O_3 was prepared by reducing V_2O_5 under H_2 at 900 °C, then V_2O_3 and NH_4VO_3 was ground intimately and sealed in Pyrex tube under a 10^{-4} Torr pressure, and then was heated slowly at 2 °C/min to 250 °C and soaked for 6–12 h to prepared $(\text{NH}_4)_2\text{V}_3\text{O}_8$ [24]. In our research, the hexamethylene tetramine was used as reductant and bulky divanadium pentoxide powders as a oxide precursor the process is easy to be controlled and the experiment conditions were milder. The prepared compound $(\text{NH}_4)_2\text{V}_3\text{O}_8$ shows planar structure [23,24], which is relatively easier to intercalate with the larger cations when using a method of ions exchange. The electrostatic action between the alkylviologen cations and the negative lamina of the layered $\text{V}_3\text{O}_8^{2-}$ is drive fore to form the novel inorganic–organic intercalation compounds with largely expanded d -spacing. The method used in the present work has many advantages, such as simple operation, high yield, efficiency and excellent atom economy.

The elemental analysis (C, N, H) data of the synthesized alkylviologen derivatives is shown in Table 1. C and H content increases with the increasing alkyl chain length of alkylviologen cation ions, and N content remains no obvious change. The experimental data of the intercalation compounds was close to the theoretical value of each compound (Table 1).

3.2. Crystal structure

The XRD patterns of $(\text{NH}_4)_2\text{V}_3\text{O}_8$ and its intercalation products with n -alkylviologens are shown in Fig. 1. A series of diffraction

Table 1

Elemental chemical analysis data of intercalation compounds.

Intercalation compound	C (%)	H (%)	N (%)	Molecular formula
MV3	29.6(30.9)	2.8(3.0)	5.8(6.0)	$(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{V}_3\text{O}_8$
EV3	32.6(34.0)	3.4(3.7)	5.4(5.7)	$(\text{C}_{14}\text{H}_{18}\text{N}_2)\text{V}_3\text{O}_8$
PrV3	35.4(36.7)	4.1(4.3)	5.1(5.4)	$(\text{C}_{16}\text{H}_{22}\text{N}_2)\text{V}_3\text{O}_8$
BV3	38.1(39.2)	4.5(4.8)	4.9(5.1)	$(\text{C}_{18}\text{H}_{26}\text{N}_2)\text{V}_3\text{O}_8$
PeV3	40.2(41.5)	4.9(5.2)	4.5(4.8)	$(\text{C}_{20}\text{H}_{30}\text{N}_2)\text{V}_3\text{O}_8$

The numbers in parentheses are theoretically calculated values.

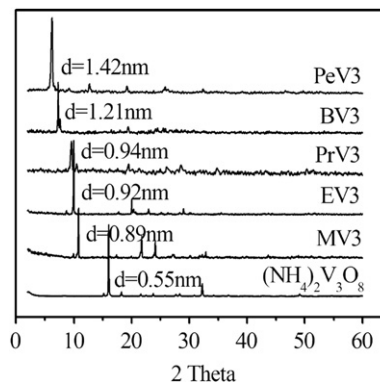


Fig. 1. XRD patterns of $(\text{NH}_4)_2\text{V}_3\text{O}_8$ and $(\text{RV})\text{V}_3\text{O}_8$.

peaks for every prepared sample illustrates that they possess the higher crystallinity. In contrast to a crystalline pattern of $(\text{NH}_4)_2\text{V}_3\text{O}_8$, the (0 0 1) reflection shift to a lower 2θ value in the diffractograms of the inorganic–organic intercalation compounds was observed [23–24]. This result implies that the interlayer space of the alkylviologen intercalation products undergo a large expansion after intercalation, and that the interlayer space increases with an increase of the number of carbon atoms in the n -alkyl chain from 0.89 nm for n =methyl- to 0.94 nm for n =propyl-, 1.21 nm for n =butyl- and 1.42 nm for n =pentyl-, indicating formation of lamellar intercalation compounds. A linear relationship between the interlayer distance and cationic sizes has not been observed. This phenomenon is different from research results on kaolinite–alkylamine intercalation compounds, in which the basal spacing between the layers of kaolinite increased linearly with the length of alkyl chains by 0.255 nm per carbon atom, and the alkylamine molecules in the interlayer space of kaolinite take a bilayer arrangement with their alkyl chains almost perpendicular to the layers of kaolinite [25,26]. However, our research results suggest that the alkylviologen molecules in the interlayer space might be arranged as monolayers between inorganic layers in all compounds with certain tilt angle, not perpendicular to the planar layers [27–29]. The reasons causing these differences can ascribe to the structural difference of the guest and/or host in intercalation compounds. Moreover, the XRD patterns of all prepared the intercalation products indicate that the integrity of the V_3O_8 interlayer structure was not destroyed during the processes of intercalation compounds preparation [26].

3.3. FT-IR analysis

Fig. 2 shows the FT-IR spectra of $(\text{RV})\text{V}_3\text{O}_8$ and the iodide salt of methylviologen (MVI_2). The IR spectra of all intercalation compounds were very similar (Fig. 2a), the bands at 1640, 1560, 1500 and 1450 cm^{-1} are attributed to the framework characteristic bands of conjugated aromatic rings in the guest molecules [30]. The antisymmetric and symmetric stretching bands of C–H

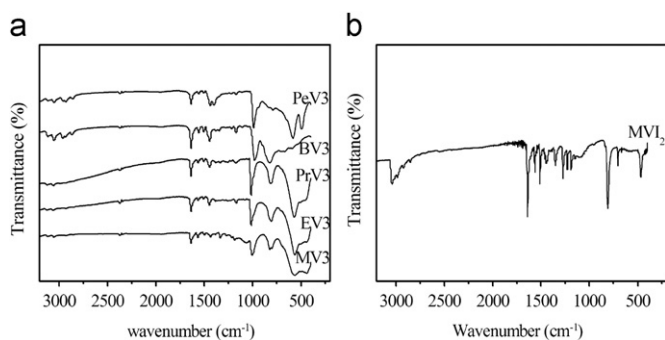


Fig. 2. FT-IR spectra of $(RV)V_3O_8$ and the iodide salt of methylviologen.

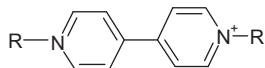


Fig. 3. The structure of guest with one positive charge.

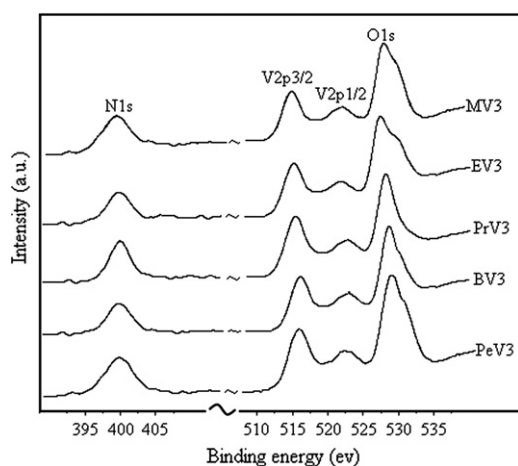


Fig. 4. XPS spectra of N1s, V2p and O1s for $(RV)V_3O_8$.

groups related to pyridine rings and alkyl chain appear at 3120, 3050, 2925 and 2855 cm^{-1} in the IR spectra of the intercalation compounds, and their band intensity become much stronger with the increase of carbon atom number in the alkyl chain [31].

Though the framework characteristic bands of conjugated aromatic rings in FT-IR spectra of intercalation compounds were no obvious shifts compared with that of MVI_2 (Fig. 2b), but the relative intensity of the bands showed obvious change. The intensity of the bands at 1635 and 1445 cm^{-1} increase evidently, whereas that of the bands at 1560 and 1505 cm^{-1} becomes substantially weaker, indicating the synergic effect between the host and guest in the intercalation compounds prolonged the life of the excited guest with one positive charge as represented in Fig. 3 [26,27].

3.4. XPS spectra

The XPS technique provides information on the surface layer of a sample. Fig. 4 presents the prominent XPS spectral features of N1s, V2p and O1s in the inorganic–organic intercalation compounds. The peaks of N1s, V2p3/2 and O1s are broad and asymmetrical, which hint that the nitrogen, vanadium and oxygen atoms of the surface layer of these intercalation compounds samples lie in different chemical environment. The binding energies (BE) and the full-width at half-maximum (FWHM) of the main peaks are shown in Table 2.

Table 2
O1s, V2p3/2 and N1s BE and FWHM for intercalation compounds.

Intercalation compounds	MV3	EV3	PrV3	BV3	PeV3
O1s					
BE (eV)	529.4	529.3	529.4	529.3	529.2
FWHM (eV)	2.48	2.51	2.52	2.54	2.82
V2p3/2					
BE (eV)	516.1	516.2	516.1	516.2	516.2
FWHM (eV)	2.81	2.79	2.76	2.83	2.85
N1s					
BE (eV)	400.7	400.6	400.6	400.7	400.7
FWHM (eV)	3.31	3.15	3.12	3.24	3.41

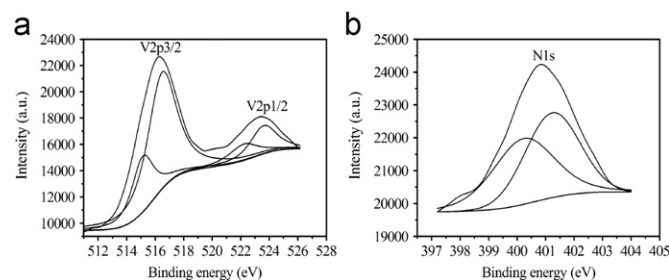


Fig. 5. Curve-fitting XPS spectra of V2p (a) and N1s (b) in EV3.

The XPS analysis was performed with the XPS-Peak 4.1 program and a Shirley function used to subtract the background. The V2p and N1s signals of EV3 can be deconvoluted into individual peaks as shown in Fig. 5. As the binding energy of the V2p3/2 core level depends on the oxidation state of the V cation, curve fitting of the V2p3/2 XPS signal can be used to detect the different oxidation states of vanadium cation on the surface layer of a vanadium compound sample [32,33]. In Fig. 5a, the broad peak of V2p3/2 is made of a maximum at 516.8 eV corresponding to the V^{5+} cation and of smaller peaks at 515.4 eV assigned to the V^{4+} cation [33]. The presence of vanadium with two oxidation states (V^{5+} and V^{4+}) is attributed to partial reduction of the vanadium ions V^{5+} by the iodine ion I^- during insertion of alkylviologen ions [34].

As shown in Fig. 5b, the profile of N1s peak can be deconvoluted into two components located at 399.4 and 401.2 eV, which reveals that N atoms in the intercalation compounds locate in two different chemical environments [35,36]. This may be resulted from transferring some electrons in the host vanadium–oxygen layers to the pyridine rings of the alkylviologen cations, which makes the nitrogen atom neutral and, forms the excited free cations with structure as shown in Fig. 3. The derived XPS results are consistent with those of FTIR, and both of them further confirm the possibility that the excited guest molecules as components of the intercalation compounds. At the same time, this result also suggests that chemical environment of the component elements in bulk phase and on the surface layer of the intercalation compound samples are the same.

3.5. UV–vis DRS analysis

The UV–vis DRS spectra of $(RV)V_3O_8$, the iodide salt of methylviologen (MVI_2) and V_2O_5 are shown in Fig. 6. The inorganic–organic intercalation compounds have strong absorption within ultraviolet and visible regions. The sharp absorption band around 215 nm may be assigned to the charge transfer transition from O to square-pyramidal coordination V^{IV} species [37]. The absorption band around 250 nm can be attributed to the electron transfer

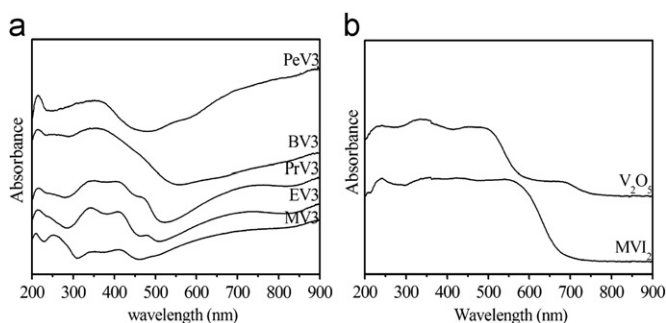


Fig. 6. UV-vis DRS spectra of $(RV)V_3O_8$, the iodide of methylviologen and V_2O_5 .

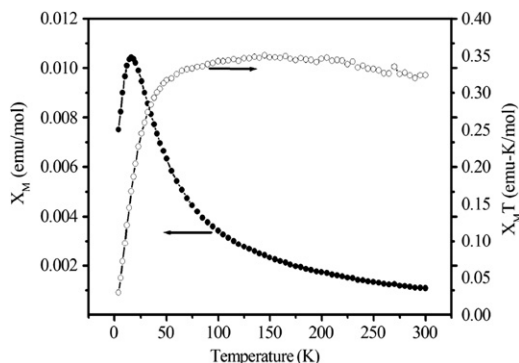


Fig. 7. Thermal dependence of χ_M and χ_{MT} for EV3.

within the alkylviologen cations [38], and the strong absorption band around 300–500 nm can be assigned to oxygen to square-pyramidal coordination V^V [39,40]. However, it is noteworthy that these intercalation compounds have stronger absorption in the range from 550 nm to 900 nm, which is in agreement with the characteristic absorption of electron transfer anticipated for alkylviologen cations [38], and further confirm that alkylviologen species exist in the intercalation compounds. Comparison with UV-vis DRS of V_2O_5 and MVI_2 in Fig. 6b, it is found that this wide and strong band also include the components from the $d-d$ transition of VO_2^+ ions and intervalence charge transfer of $V^{4+} \rightarrow V^{5+}$ besides being related to the electron transfer within the alkylviologen cations [40].

3.6. Magnetic susceptibility

A measurement result of the magnetic properties of the alkylviologen intercalation compound (EV3) is shown in Fig. 7 in the temperature range from 2 to 300 K. The molar magnetic susceptibility of EV3, χ_M , increased with decreasing temperature and reached a maximum 0.0106 emu/mol at 15 K. Below 15 K, the susceptibility continuously decreased with cooling, which suggests that the intercalation compound is antiferromagnetic and possesses ordered magnetic structure below 15 K and above 15 K exhibits paramagnetic behavior with ordered magnetic structure. The thermal variation of the molar susceptibility basically follows the Curie-Weiss law [$\chi_M = C_m / (T - \theta)$] with $C_m = 0.149 \text{ emu K}^{-1} \text{ mol}^{-1}$ and $\theta = -12 \text{ K}$. The effective magnetic moment (μ_{eff}) per vanadium determined from the equation $\mu_{eff} = 2.83(\chi_M \times T)^{1/2}$ is $1.09 \mu_B$, which is lower than $1.73 \mu_B$ that expected for the spin-only moment. This phenomenon may have resulted from the electron delocalization of V^{4+} in the host or the interaction of spin-orbital coupling. In addition, the alkylviologen cations may be beneficial to the electron delocalization of V^{4+} [41,42].

4. Conclusion

A series of novel inorganic-organic compounds were obtained by intercalating of various n -alkylviologens into layered $V_3O_8^{2-}$ host through the combination of redox and ions-exchange methods. The interlayer spacing of the inorganic-organic intercalation compounds increased and the structural regularity of these compounds decreased with increasing alkyl chain length in the alkylviologen cations. The investigation results suggest that the synergic effect resulting from the interaction of guest and host may prolong the life of excited guest molecules. The inorganic-organic intercalation materials have strong absorption within the ultraviolet and visible light region. Moreover, these compounds are antiferromagnetic, and possess ordered magnetic structure below 15 K, and above 15 K, exhibiting paramagnetic behavior with a disordered magnetic structure.

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References

- [1] K. Vallé, P. Belleville, F. Pereira, C. Sánchez, *Nat. Mater.* 5 (2006) 107.
- [2] E.R. Cooper, C.D. Andrews, P.S. Wheatley, P.B. Webb, P. Wormald, R. Morris, *Nature* 430 (2004) 1012.
- [3] D.L. Chen, Y. Sugahara, *Chem. Mater.* 19 (2007) 1808.
- [4] T. Takei, Y. Yonesaki, N. Kumada, N. Kinomura, *Langmuir* 24 (2008) 8554.
- [5] E.J. Yoo, J. Kim, E. Hosono, H.S. Zhou, T. Kudo, I. Honma, *Nano Lett.* 8 (2008) 2277.
- [6] L.F. Chen, J.C. Hu, R. Richards, *J. Am. Chem. Soc.* 131 (2009) 914.
- [7] T. Okada, T. Matsutomo, M. Ogawa, *J. Phys. Chem. C* 114 (2010) 539.
- [8] P. Sutter, J.T. Sadowski, E.A. Sutter, *J. Am. Chem. Soc.* 132 (2010) 8175.
- [9] P.G. Bruce, B. Scrosati, J.M. Tarascon, *Angew. Chem. Int. Ed.* 47 (2008) 2930.
- [10] Y. Ren, A.R. Armstrong, F. Jiao, P.G. Bruce, *J. Am. Chem. Soc.* 132 (2010) 996.
- [11] D.K. Karthikeyan, G. Sikha, R.E. White, *J. Power Sour.* 185 (2008) 1398.
- [12] M.A. Bizeto, A.L. Shiguihara, V.R.L. Constantino, *J. Mater. Chem.* 19 (2009) 2512.
- [13] E. Castillejos, P.J. Deboutiere, L. Roiban, A. Solhy, V. Martenez, Y. Kihn, O. Ersen, K. Philippot, B. Chaudret, *P. Serp, Angew. Chem. Int. Ed.* 48 (2009) 2529.
- [14] T. Nakato, H. Edakubo, T. Shimomura, *Micropor. Mesopor. Mater.* 123 (2009) 280.
- [15] G.J. Wang, Q.T. Qu, B. Wang, Y. Shi, S. Tian, Y.P. Wu, R. Holze, *J. Power Sour.* 189 (2009) 503.
- [16] S.N. Ichikawa, M. Hibino, T. Yao, *J. Electrochem. Soc.* 156 (2009) 299.
- [17] M. Dubarry, J. Gaubicher, D. Guyomard, N. Steunou, *J. Livage, Chem. Mater.* 16 (2004) 4867.
- [18] S.N. Ichikawa, M. Hibino, T. Yao, *Solid State Ionics* 179 (2008) 1688.
- [19] E. Levi, Y. Gofer, D. Aurbach, *Chem. Mater.* 22 (2010) 860.
- [20] S. Jouanneau, A. Verbaere, D. Guyomard, *J. Solid State Chem.* 172 (2003) 116.
- [21] P. Rozier, M. Morcrette, P. Martin, L. Laffont, J.-M. Tarascon, *Chem. Mater.* 17 (2005) 984.
- [22] G. Yang, W.H. Hou, Z.Z. Sun, Q.J. Yan, *J. Mater. Chem.* 15 (2005) 1369.
- [23] S. Petit, K. David, J.P. Doumerc, J.C. Grenier, T. Seguelong, M. Pouchard, *Solid State Chem. Cryst. Chem.* 1 (1998) 517.
- [24] G. Lin, J.E. Greedan, *J. Solid State Chem.* 114 (1995) 499.
- [25] K. Yoshihiko, S. Yoshiyuki, K. Kazuyuki, *Appl. Clay Sci.* 15 (1999) 241.
- [26] S. Passerini, D.B. Le, W.H. Smyrl, M. Berretoni, R. Tossici, R. Marassi, M. Giorgetti, *Solid State Ionics* 104 (1997) 195.
- [27] A. Bose, P.-G. He, C. Liu, B.D. Eilman, R.J. Twieg, S.-P. Huang, *J. Am. Chem. Soc.* 124 (4) (2002).
- [28] K.Q. Lai, A.G. Kong, F. Yang, B. Chen, H.M. Ding, Y.K. Shan, S.P. Huang, *Inorg. Chim. Acta* 359 (2006) 1050.
- [29] K.Q. Lai, Y.L. Wang, F. Yang, A.G. Kong, H.M. Ding, Y.K. Shan, *Acta Chim. Sin.* 64 (2006) 1456.
- [30] E.P. Kovalchuk, O.V. Reshetnyak, Ya.S. Kovalyshyn, J. Błażejowski, *J. Power Sour.* 107 (2002) 61.
- [31] N.V. Kosova, S.V. Vosel, V.F. Anufrienko, N.T. Vasenin, E.T. Devyatkina, *J. Solid State Chem.* 160 (2001) 444.
- [32] V.I. Bukhtiyarov, *Catal. Today* 56 (2000) 403.
- [33] G. Silversmit, D. Depla, H. Poelman, G.B. Marin, R.D. Gryse, *J. Electron. Spectrosc. Relat. Phenom.* 135 (2004) 167.
- [34] J. Mendialdua, R. Casanova, Y. Barbaux, *J. Electron. Spectrosc. Relat. Phenom.* 71 (1995) 249.
- [35] Y. Matsuo, T. Miyabe, T. Fukutsuka, Y. Sugie, *Carbon* 45 (2007) 1005.

- [36] R.J.J. Jansen, V.H. Bekkum, *Carbon* 33 (1995) 1021.
- [37] G. Genti, S. Perathoner, F. Trifiró, A. Aboukais, C.F. Aissi, M. Guelton, *J. Phys. Chem.* 96 (1992) 2617.
- [38] R.J. Mortimer, *Chem. Soc. Rev.* 26 (1997) 147.
- [39] I.L. Botto, M.B. Vassallo, E.J. Baran, G. Minelli, *Mater. Chem. Phys.* 50 (1997) 267.
- [40] L. Abello, E. Husson, Y. Repelin, G. Lucazeau, *J. Solid State Chem.* 56 (1985) 379.
- [41] L.L. Hung, S.L. Wang, H.M. Kao, K.H. Li, *Inorg. Chem.* 41 (2002) 3929.
- [42] Z.M. Dai, Z. Shi, G.-H. Li, D. Zhang, W.S. Fu, H.Y. Jin, W. Xu, S.H. Feng, *Inorg. Chem.* 42 (2003) 7396.