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## Materials for all-solid-state thin-film rechargeable lithium batteries by sol-gel processing

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**Abstract** A novel all-solid-state thin-film lithium battery has been fabricated by spin coating  $V_2O_5$  and  $LiClO_4$ - $SiO_2$  thin films on a stainless steel substrate. The  $LiClO_4$ - $SiO_2$  electrolyte has been synthesized using a new sol-gel route and it has been characterized by electrochemical impedance spectroscopy. The  $Li^+$  ion conductivity of the spin-coated thin film thus measured is in the order of  $10^{-6}$  S/cm, at 25 °C, which is sufficient for electrolytes in such thin-film batteries. The battery shows a typical discharge capacity of about 150  $\mu$ Ah/mg and satisfactory cathodic efficiency and cycle-life performance.

**Keywords** Thin Films · Lithium batteries · Sol-gel processing

### Introduction

All-solid-state lithium batteries with thin-film configurations are of considerable current research interest [1, 2, 3, 4, 5], especially since there is a strong demand for micro power sources which can be completely integrated into electronic circuits. The operational acceptability of such integrated devices has been enhanced in recent years by the low power requirements of modern electronic circuits and the high energy density of emerging lithium batteries [6]. Thin-film technology, on the other hand, is a matured research area by itself and thin-film battery technologists have a wider choice of

electrode and electrolyte materials than conventional battery technologists. As the electrode and electrolyte materials are fabricated as very thin films of a few microns thick, these films add only few ohms to the total internal resistance of the electrochemical cell. This in turn allows us to use battery materials with inherently low ionic conductivity as electrolytes, and using cathode materials without adding conventional conducting materials like graphite. The development of suitable solid electrolytes is a crucial step in realizing such batteries, as there are many well-developed cathode materials now commercially available. There is a very good choice of anode materials also, namely lithium metal itself, Li alloys with Al, Si, etc., lithiated carbon and lithiated transition metal (Co, Mn, V) oxides are all available for battery research. Major advantages of solid polymer electrolytes in lithium batteries are high specific energy and specific power, safe operation, flexibility in packaging and a low cost of fabrication [7]. The combination of a thin-film configuration and low current drain requirements in the nanoampere range allow the use of electrolytes with much lower conductivity than necessary for conventional devices. In addition, owing to the sophisticated nature of thin-film technology, a better control over the electrode-electrolyte interface behavior can be achieved in such thin-film batteries.

Lithium silicate-based materials are now used in making inorganic fire-resistant materials and as a binder between the active mass to the current collector in lithium batteries.  $Li_4SiO_4$  has also been used as an electrode material for high-temperature cells of composition  $Au/Li_4SiO_4/Au$  [8]. Lithium silicate-based materials are also used as breeder materials in nuclear fusion reactors [9]. In this study, we report the fabrication of all-solid-state thin-film batteries with the cell structure  $Li/LiClO_4-SiO_2/V_2O_5$ . The cathode and the electrolyte have been synthesized by sol-gel processing, while the battery was fabricated by spin coating the two layers followed by a thin layer of metallic lithium to complete the electrochemical cell. The ionic conductivity of the electrolyte has been measured using an AC impedance method [10].

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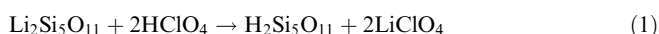
## Experimental

### Synthesis of vanadium pentoxide gel

Vanadium pentoxide gel was prepared using the condensation of polyvanadic acid solution obtained by ion exchange of a sodium metavanadate solution [11]. In a typical synthesis, 5 g of a cation exchange resin (Dowex 50 WX<sub>2</sub>, 50–100 mesh) were stirred well with 15 mL of 2 M HCl for about 2 h; the resin was then filtered and washed several times with deionized water, until the pH of the solution was above 6. It was then dried under vacuum. The resin was then stirred in 0.5 M sodium metavanadate (Aldrich) solution for about 3 h. The resulting red viscous solution of polyvanadic acid was filtered to remove the resin and kept for aging at room temperature. A spinable sol with high viscosity was obtained within a few days.

### Synthesis of lithium polysilicate gels

Lithium polysilicate was synthesized by hydrolysis and condensation of lithium silicate solution using perchloric acid [12]. This reaction leads to a gel in which LiClO<sub>4</sub> is dispersed:



In a typical synthesis, 0.2 M HClO<sub>4</sub> was stirred well with 0.1 M Li<sub>2</sub>Si<sub>5</sub>O<sub>11</sub> solution. The gel was found to form within 24 h and was monolithic and transparent.

### Fabrication of the cell

The V<sub>2</sub>O<sub>5</sub> sol was spin-coated onto a stainless steel current collector with a geometrical area of 3.14 cm<sup>2</sup> using a locally modified spin-coating apparatus at a speed of 2000 rpm for about 30 s. The spin-coated film was then dried at room temperature for 15 min in a nitrogen atmosphere, followed by heat treatment at 200–300 °C for about 2 h in an electric furnace. The V<sub>2</sub>O<sub>5</sub> film obtained showed a weight gain of 4 mg, which corresponds to a thickness of 3.8 μm. The LiClO<sub>4</sub>-polysilicate sol was subsequently spin-coated onto the finished cathode. The resulting film was dried for about 1 h under nitrogen at room temperature and then subjected to thermal treatment at 100 °C for about 5 h under a dynamic vacuum. This process gave a weight gain of 17.8 mg, which corresponds to a thickness of 3 μm. A commercially available (Good Fellow) lithium foil of 50 μm thick was used as the anode. The cell was then hermetically sealed with a top nickel-coated stainless steel current collector and a rubber gasket. The charge-discharge studies of the cell were then carried out galvanostatically at C/20 rate at a temperature of 25 ± 1 °C.

### Ionic conductivity measurements

Conductivity measurements of the LiClO<sub>4</sub>-polysilicate electrolyte were carried out in the form of a pellet of 2 mm thickness and 0.63 cm<sup>2</sup> geometrical area. The pellet was sandwiched between two pre-polished stainless steel electrodes. The AC impedance data were collected using a Hewlett-Packard analyser (HP 4192A). Measurements were carried out at various temperatures using a Buchi TO-50 temperature controller. At each temperature, both the real and imaginary components were recorded, while the driving frequency was scanned from 100 Hz to 10 MHz. Complex impedance values were plotted as a function of the real part and conductivity values were then evaluated using a semi-circle fitting of the experimental data. All the experiments were carried out under an argon atmosphere, maintained by a continuous flow of argon.

## Results and discussion

Among the various methods described in the literature for the synthesis of V<sub>2</sub>O<sub>5</sub>, the most reliable method

appears to be the hydrolysis and condensation of sodium metavanadate solution protonated with a cation exchange resin [13]. This method provides a clean route for the synthesis of colloidal self-prepared nano particles that can be stabilized in the form of a sol. These nano-structured sols are unique candidates to be used in a thin-layer cell, as they can be easily employed for spin coating to a suitable substrate [14]. Since the particle size can be controlled to be small enough in the nanometer range, uniform thin films can be fabricated and, as a result, high energy efficiency can be realized. The subsequent heat treatment also plays an important role in deciding the property of the V<sub>2</sub>O<sub>5</sub> film since crystallization into orthorhombic V<sub>2</sub>O<sub>5</sub> occurs only at 350 °C [15]. In the present study, the temperature was always kept below 300 °C to obtain amorphous V<sub>2</sub>O<sub>5</sub>, which is known to exhibit better electrochemical performance as a cathode material in rechargeable lithium batteries than crystalline V<sub>2</sub>O<sub>5</sub> [16]. Spin-coated V<sub>2</sub>O<sub>5</sub> thin films have also been used in electrochromic devices [17].

The use of polymer electrolytes allows the fabrication of safe batteries and permits the development of thin-layer batteries with design flexibility [18]. Various SiO<sub>2</sub>-based materials like lithium metasilicate (Li<sub>2</sub>SiO<sub>3</sub>) and lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) have been used in the past as composite electrolytes for lithium batteries. For example, the conductivity of LiI can be enhanced significantly by forming a two-phase mechanical mixture with submicron size SiO<sub>2</sub> particles [19]. Mechanically stable sol-gel lithium silicate electrolyte thin films with various mol% Li<sub>2</sub>O have been fabricated as thin films in the past using dip coating [20]. In the present study, we synthesized the LiClO<sub>4</sub>-SiO<sub>2</sub> electrolyte by the hydrolysis and condensation of lithium polysilicate (Li<sub>2</sub>Si<sub>5</sub>O<sub>11</sub>) with perchloric acid. Hydrolysis of lithium polysilicate with HClO<sub>4</sub> provides a unique way of synthesizing a polysilicate gel in which LiClO<sub>4</sub> is dispersed. The potential interest of Li<sub>2</sub>O-SiO<sub>2</sub> materials in electrochemical systems is their fast and stable ionic conductivity from room temperature to about 350 °C [20]. As counter ions, Li<sup>+</sup> ions are unique among all alkali metal ions in stabilizing the silica sol. Sols of very high Li<sub>2</sub>O:SiO<sub>2</sub> ratios are much more stable than the corresponding sols stabilized with Na<sub>2</sub>O [12]. In the present study, the Li<sub>2</sub>O:SiO<sub>2</sub> ratio was found to be optimum at 1:5. The concentrations of HClO<sub>4</sub> and Li<sub>2</sub>Si<sub>5</sub>O<sub>11</sub> were kept at 0.2 and 0.1 M, respectively. Above these concentrations the gel was found to form immediately after mixing without any control over the generation process; below this concentration the sol exhibits a very low viscosity and is not spinable even after aging for several weeks. Alkaline hydrolysis of lithium polysilicates with strong alkalis like LiOH can also be used for making the electrolytes films. However, we observed that acid hydrolysis provided a better gel than that formed using alkaline hydrolysis. In addition, from the chemistry of silica it is known that acid hydrolysis produces smaller particles compared to alkaline hydrolysis, which in turn is more suitable from an electrochemical point of view.

Figure 1 shows the room temperature impedance spectrum of the  $\text{LiClO}_4$ -polysilicate electrolyte sandwiched between two stainless steel electrodes in the frequency region from 100 Hz to 10 MHz. A nearly perfect semi-circle is obtained in this frequency region, with a slight dispersion at the low-frequency region. This behavior corresponds to the resistive part of the electrolyte with a capacitive part of two identical interfaces. A semi-circle fit of the data shown in Fig. 1 results in resistance values of  $5.7 \times 10^4 \Omega$ , yielding a specific conductivity of  $5.5 \times 10^{-6} \text{ S/cm}$ . This conductivity value is too low for an electrolyte to be used in a normal battery. However, in a thin-film battery, in which the thickness of the electrolyte is only few microns, it will add only a few ohms to the total resistance of the cell [21]. In the present cell, the electrolyte thickness is  $3 \mu\text{m}$ , the electrode area is  $3.14 \text{ cm}^2$  and the electrolyte conductivity is  $5.5 \times 10^{-6} \text{ S/cm}$ . Thus, the electrolyte will add only  $54.5 \Omega$  to the total cell resistance for every micron thickness of the electrolyte [22]. The variation of the specific conductivity of the electrolyte with temperature is shown in Fig. 2. Very good Arrhenius behavior with an activation energy of  $0.35 \text{ eV}$  is observed.

The potential interest in  $\text{V}_2\text{O}_5$  as a cathode material in such thin-film batteries is due to its high energy density and ease of fabrication. A single-step lithium insertion reaction has been reported for the material centred around  $3 \text{ V}$ , with a discharge capacity of about  $250 \mu\text{Ah/mg}$  and a Faradaic yield of  $1.8 \text{ F/mol}$  [22]. In addition, the poor electronic conductivity of the material does not present a serious problem in microbatteries in which the thickness of the layer is only few microns. Figure 3 shows a typical charge-discharge curve of the cell; the underlying intercalation-deintercalation reaction is now a well-established process [23]:

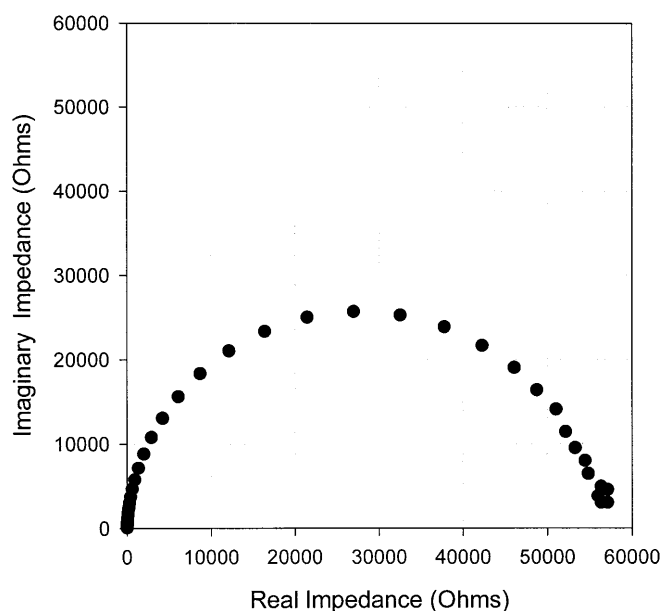
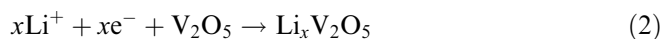


Fig. 1 Room temperature impedance spectrum of  $\text{LiClO}_4$ - $\text{SiO}_2$  composite electrolyte in the frequency region from 100 Hz to 10 MHz



with  $x$  being the degree of lithium insertion.

After the initial potential drop due to the cell internal resistance and depolarization, the discharge curve is more or less flat until the cut-off voltage. There is no step observed in these discharge curves, as reported for the case of  $\text{V}_2\text{O}_5$ -based materials [24]. The discharge curve

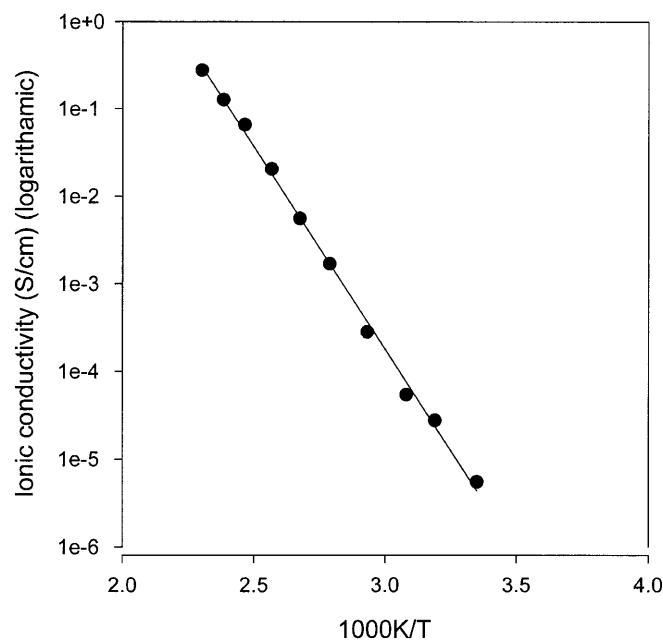


Fig. 2 Arrhenius plot of the conductivity of the  $\text{LiClO}_4$ - $\text{SiO}_2$  composite electrolyte

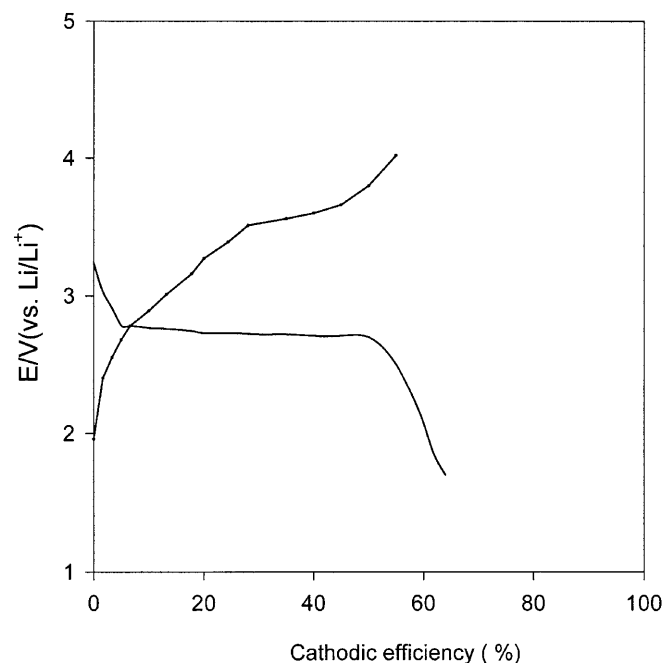
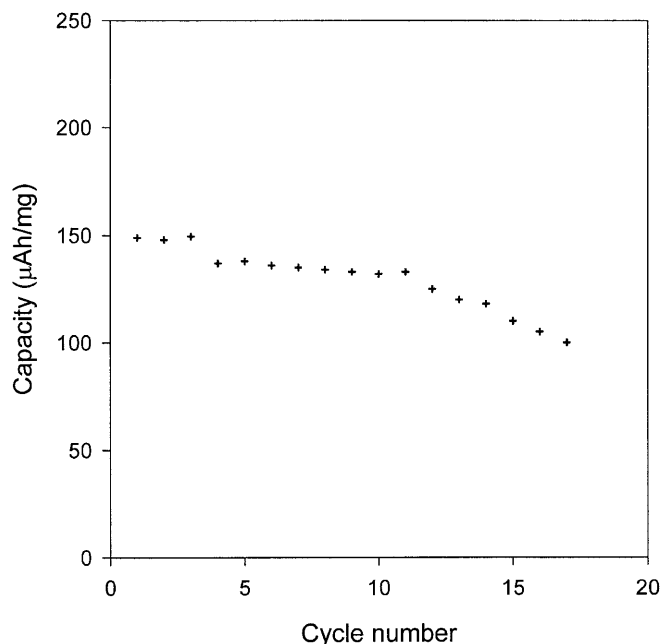


Fig. 3 A typical charge-discharge curve for the cell  $\text{Li/LiClO}_4$ - $\text{SiO}_2/\text{V}_2\text{O}_5$



**Fig. 4** Evolution of specific capacity as a function of cycle number for the cell  $\text{Li}/\text{LiClO}_4\text{-SiO}_2/\text{V}_2\text{O}_5$

shows a slow and continuous decrease of the voltage around an average value of 2.8 V. For a cut-off voltage of 2 V, a cathodic efficiency of 60% is observed, corresponding to the reduction process of  $\text{V}^{5+}$  to  $\text{V}^{4+}$  ions. The cell also shows a reasonable cycling efficiency, as shown in Fig. 4. The capacity is stable for the initial 10–15 cycles. More than 90% of the initial capacity is recovered after three cycles. The capacity is then found to be more or less steady up to 12 cycles. After this, a decline of capacity is observed.

## Conclusions

A novel sol-gel process combined with spin coating and a suitable heat treatment of the cathode and electrolyte layers has been developed for the fabrication of all-solid-state thin-film rechargeable lithium batteries. The lithium perchlorate incorporated polysilicate electrolyte obtained by the hydrolysis of lithium polysilicate with perchloric acid shows an ionic conductivity of  $5.5 \times 10^{-6}$  S/cm at 25 °C. The thin layer cell ( $\text{Li}/\text{LiClO}_4\text{-SiO}_2/\text{V}_2\text{O}_5$ ) fabricated has a specific capacity of

150  $\mu\text{Ah}/\text{mg}$  and shows reasonable cycling stability over 10–15 cycles.

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## References

1. Neudecker BJ, Dudney NJ, Bates JB (2000) *J Electrochem Soc* 147:517
2. Kumagai N, Baba M, Kobayashi H, Nakano O, Komaba S, Groult H, Devilliers D (2000) *ITE Lett Batteries New Technol Med* 1:43
3. Lee JK, Lee SJ, Baik HK, Lee HY, Jang SW, Lee SM (1999) *Electrochem Solid-State Lett* 2:512
4. Onishi K, Matsumoto M, Shigehara K (2001) *J Power Sources* 92:120
5. Liu P, Zhang JG, Turner JA, Tracy CE, Benson DK (1999) *Proc Electrochem Soc* 98:363
6. Linden D (1995) *Handbook of batteries*, 2nd edn. McGraw-Hill, New York
7. Bruce PG, Vincent CA (1993) *J Chem Soc Faraday Trans* 89:3187
8. Aceves JM, Anthony RW (1982) *J Chem Soc Faraday Trans* 78:2599
9. Pfeiffer H, Bosch P, Bulbulian S (1998) *J Nucl Mater* 257:309
10. Jacobs PWM, Lorimer JN, Russer A, Wasiucionek M (1989) *J Power Sources* 26:483
11. Lemerle J, Nejem N, Lefebvre J (1980) *J Inorg Nucl Chem* 42:17
12. Iler R (1979) *The chemistry of silica*. Wiley, New York
13. Livage J (1991) *Chem Mater* 3:578
14. Shouji E, Buttry DA (1999) *Langmuir* 15:670
15. Aldebert P, Baffier N, Gharbi N, Livage J () *Mater Res Bull* 16:669
16. Farcy J, Messina R, Perichon J (1990) *J Electrochem Soc* 137:1337
17. Shimizu Y, Nagase K, Miura N, Yamazoe N (1992) *Solid State Ionics* 53:490
18. Song JY, Wang YY, Wang CC (1999) *J Power Sources* 77:183
19. Owens BB, et al (1977) In: Geller S (ed) *Solid electrolytes*. Springer, Berlin Heidelberg New York, p 68
20. Mouchon RE, Klein LC, Picard V, Greenblatt M (1994) In: *Better ceramics through chemistry (VI)*. (Mater Res Soc symp proc 346) Materials Research Society, pp 189–200
21. Julien C (1998) In: Radhakrishna S (ed) *Trends in material science*. Narosa, London, p 24
22. Cocciantelli JM, Doumerc JP, Pouchard M, Broussely M, Labat J (1991) *J Power Sources* 34:103
23. Gabano JP (1983) *Lithium batteries*. Academic Press, New York
24. Delmas C, Brethes S, Menetrier M (1991) *J Power Sources* 34:113