



Short communication

Synthesis by sol–gel process and characterization of LiCoO_2 cathode materials

Z.S. Peng ^{a,*}, C.R. Wan ^b, C.Y. Jiang ^b^a Department of Chemistry, Capital Normal University, Beijing 100037, China^b Institute of Nuclear Energy Technology, Tsinghua University, Beijing 102201, China

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Abstract

The cathode material LiCoO_2 is synthesized by a sol–gel process. The structure and electrochemical properties are studied by DTA–TG, XRD, SEM, and electrochemical measurements. It is found that a homogeneous LiCoO_2 powder with purity and high electrochemical intercalation capacity can be obtained by the sol–gel process. © 1998 Elsevier Science S.A.

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1. Introduction

Secondary lithium batteries have been studied for the past two decades because they exhibit the highest specific energy among the rechargeable batteries. Nevertheless, the safety and rechargeability associated with use of metallic lithium prevent its widespread acceptance in the marketplace. Unsatisfactory results with lithium metal has directed research towards the development of so-called ‘rocking-chair lithium’ or ‘lithium-ion’ rechargeable batteries. These systems were first commercialized by Sony Energitic in 1990 [1] and used carbon as an anode. Promising candidate materials for cathodes in lithium-ion batteries are LiCoO_2 [1], LiNiO_2 [2], $\text{LiCo}_x\text{Ni}_{1-x}\text{O}_2$ [3] and spinel $\text{Li}_x\text{Mn}_2\text{O}_4$ [4–6].

As a result of the intense search for high specific energy cathode materials for use in lithium-ion rechargeable battery technology, LiCoO_2 has become the first, and one of the most promising for commercial application [1]. The

material displays many favorable attributes that include: good capacity, high specific energy, good power rates, low self-discharge, and excellent cycle life [7,8].

In most of these studies, LiCoO_2 has been synthesized using solid-state reactions that involve the mechanical mixing of oxide and/or carbonates, followed by high temperature firing and extended grinding. These synthetic conditions, which require long-range diffusion of the reactants and high temperature ($> 900^\circ\text{C}$), may result in non-homogeneity, abnormal grain growth, and poor control of stoichiometry.

In this study, we have adopted the sol–gel process to the synthesis of LiCoO_2 and its various modified forms. A powder of the resulting LiCoO_2 retains homogeneity on an atomic scale and may be calcined at low temperature to yield ultrafine particulate oxides. Using the sol–gel method, it is possible to obtain the phase-pure, ultrafine, crystalline rutile phase by employing temperatures as low as 550°C for several hours.

2. Experimental

Gel formation from organic acid and ethylene glycol solutions depends on the metalorganic agent. The best

* Corresponding author.

results were obtained with $\text{Co}(\text{CH}_3\text{COO})_2$ and LiCH_3COO . The gel was formed at 140°C by mixing $\text{Co}(\text{CH}_3\text{COO})_2$ and LiCH_3COO ($\text{Co}/\text{Li} = 1:1$ atom ratio) with citric acid in ethylene glycol solution. The gel was then vacuum dried at $170\text{--}190^\circ\text{C}$ to yield an organic polymer foam. Fine powders were produced by calcining the precursors in air at various temperatures for periods of a few hours.

The structural and morphological properties of the gel and oxide powders were characterized by several techniques. X-ray diffraction experiments were performed with a Rigaku Dmax/Rc diffractometer using $\text{CuK}\alpha$ radiation. The morphological changes during the calcination of precursors were observed using a scanning electron microscope (SEM). Thermal analysis measurements were performed in air at heating rates of $10^\circ\text{C}/\text{min}$.

The charge and discharge characteristics of the cathodes were examined in a laboratory cell. The cell comprised a cathode and a lithium metal anode that were separated by a separator (Celgard 2400 membrane). The cathode comprised 40 mg of active material and 8 mg of conducting binder (acetylene black-polytetrafluoromethylene composite). The mixture was pressed on to a nickel screen, and dried at 120°C for 24 h. The electrolyte solution was 1 M $\text{LiPF}_6/\text{EC} + \text{DEC}$. The EC and DEC were in a 1:1 volume. Cell fabrication was carried out in an argon-filled dry box. Cells were cycled in the range 4.3 to 3.0 V, and the typical charge and discharge current was 0.5 mA cm^{-2} except where otherwise specified.

3. Results and discussion

The pink transparent gel could be formed for various ratios of citric acid to total metal ions tested in this study. The transparency of the gel indicates that its composition is homogeneous. It is believed that the carboxylic groups on the citric acid form a chemical bond between the cations and polymeric chains, and these mixtures develop extremely viscous polymeric resins as they form a gel.

The TGA and DTA results of the gel precursor prepared with an equal molar ratio of citric acid to total metal ions are shown in Fig. 1. The weight loss of the gel precursor terminated at 400°C and two discrete weight-loss regions occurred at $85\text{--}190^\circ\text{C}$ and $270\text{--}400^\circ\text{C}$. The weight loss in the temperature range $85\text{--}190^\circ\text{C}$ corresponds to the removal of superficial ethylene in the gel precursor which is accompanied by an endothermic peak in the DTA curve at 184°C . The exothermic peak appears at about $300\text{--}350^\circ\text{C}$ and is due to the decomposition of the chelated precursors.

The X-ray diffraction (XRD) patterns for the gel-derived materials calcined at various temperatures for 10 h in air are given in Fig. 2. For the material calcined at 350°C , a significant amount of LiCoO_2 phase and a small number of impurity peaks are detected. This is quite consistent with the DTA result which shows the crystallization peak at 350°C . A single phase of high-temperature LiCoO_2 is formed when the material is calcined at 550°C . This result strongly suggests that the sol-gel preparation method requires a much lower calcination temperature and shorter

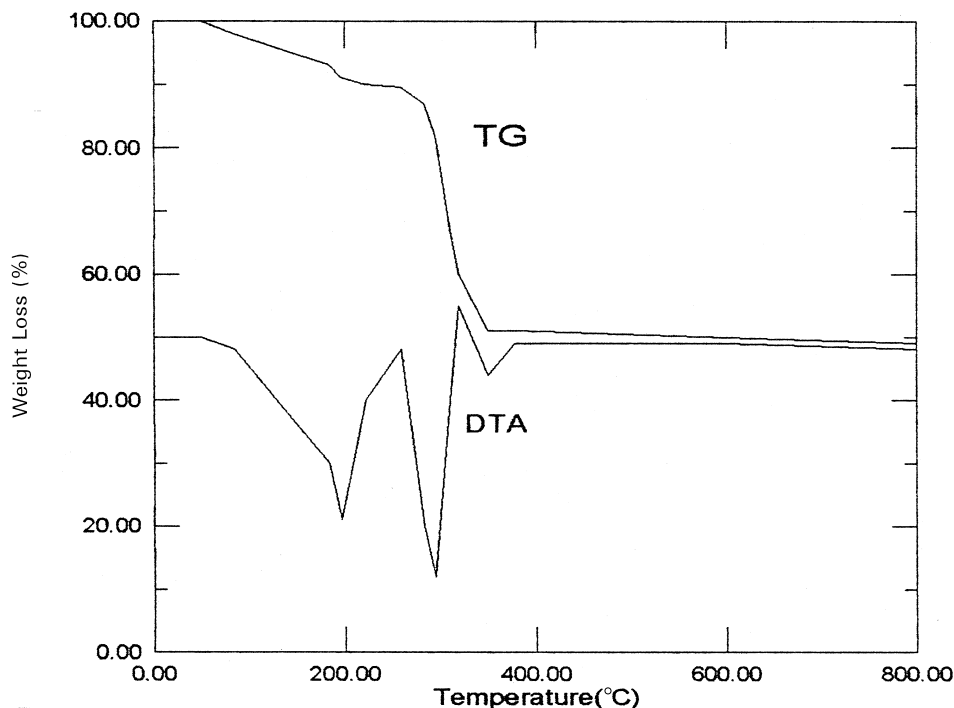


Fig. 1. Thermogravimetric and differential thermal analyses of gel precursors at a heating rate of $10^\circ\text{C min}^{-1}$.

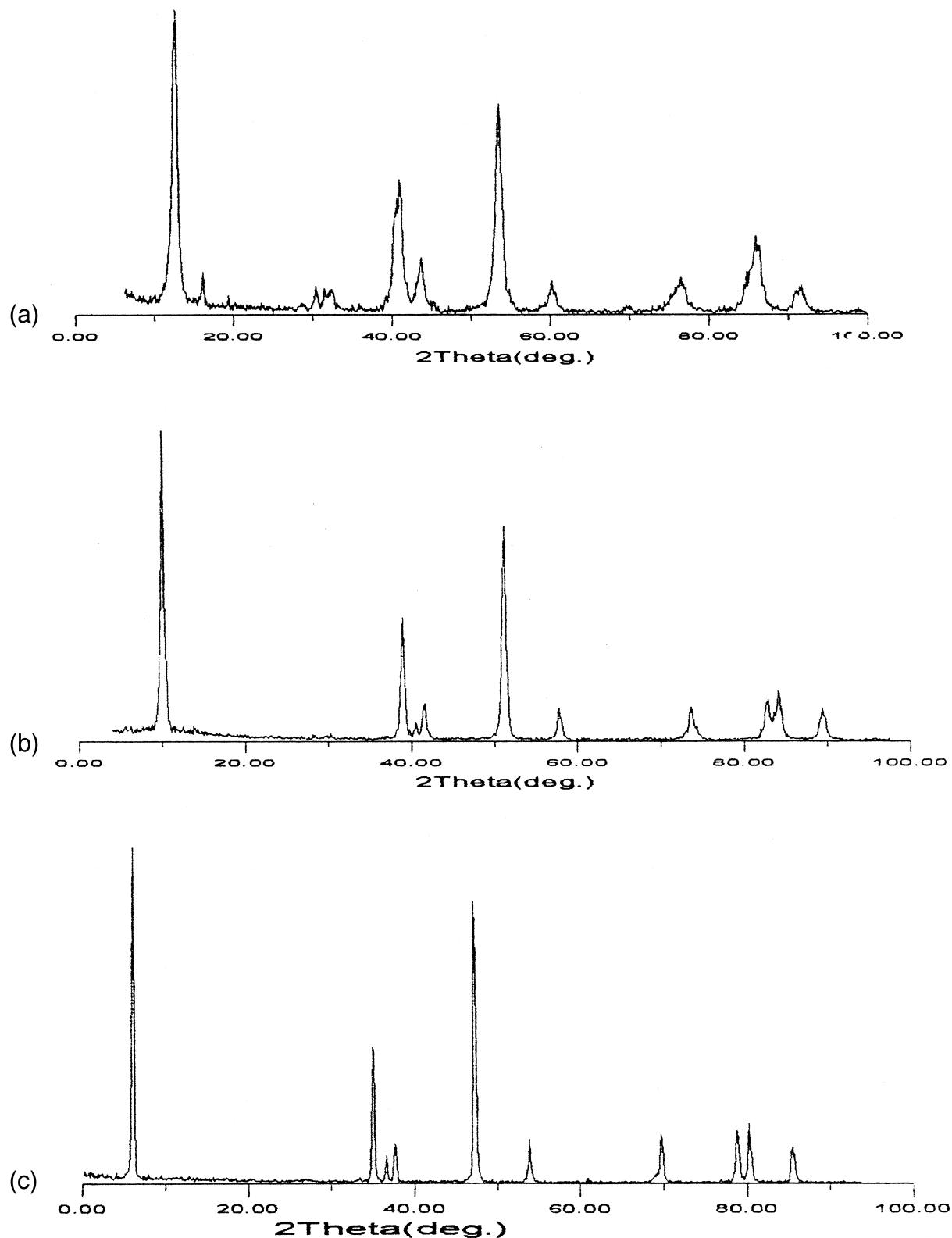


Fig. 2. XRD patterns of LiCoO₂ system fired to different temperatures (a) 350°C; (b) 550°C; (c) 750°C.

calcination time than the solid-state reaction where the calcination temperature is almost 900°C and the calcination time is more than 24 h.

A series of electron micrographs (Fig. 3) reveal the morphological changes that occur during the calcination of the polymeric precursor. As shown in Fig. 3a, the poly-

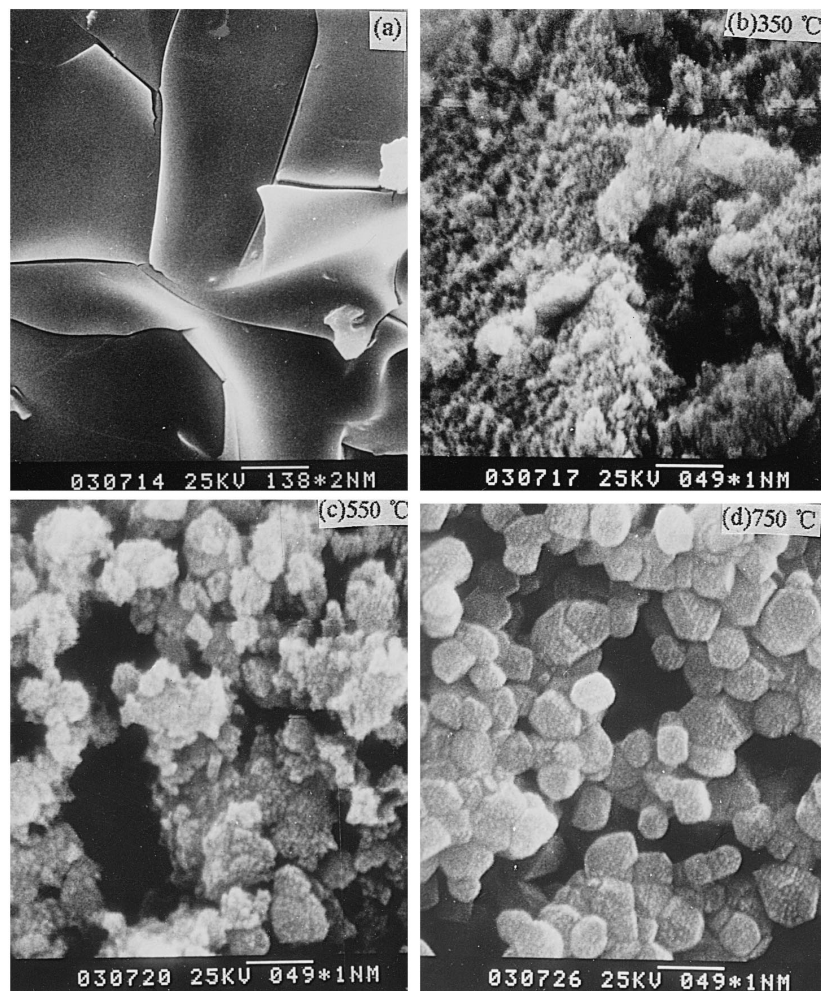


Fig. 3. SEM micrographs of powders calcined at (a) precursor before firing; (b) 350°C; (c) 550°C; (d) 750°C.

meric precursor appears smooth and featureless. Heating to about 350°C in air, however, degrades and chars the polymer and converts the organic component into CO_2 and H_2O . The abrupt formation of these gases bloats the material and greatly expands its structure to produce an ash-like morphology. The process also liberates heat, which can result in poor temperature control and overheating. The relation can be slowed by lowering the oxygen partial pressure and by spreading the precursor in a thin layer.

The desired layered oxides are obtained by further heating of the ash in air. Electron micrographs of powders calcined at 550 and 750°C for 10 h in air are shown in Fig. 3c and d, respectively. The surface of the powders calcined at 750°C contains monodispersed spherical fine particulates with an average particle size of about 30 nm. Both micrographs show that the powder particles are loosely aggregated and have diameters between 30–50 nm.

The specific capacity and cyclability of the various

samples were determined by cycling test cells at a constant current density of 0.5 mA cm^{-2} between 4.3 and 3.0 V. The charge and discharge characteristics of the first cycles of LiCoO_2 samples fired to different temperatures are shown in Fig. 4a–c. LiCoO_2 fired to 750°C initially delivered 154 mA h g^{-1} . The capacity slowly declined with cycling and remained at 140 mA h g^{-1} at the tenth cycle (Fig. 4d). For LiCoO_2 fired to 550°C, the initial capacity was 150 mA h g^{-1} . All of samples manifested excellent cyclability, except for the samples fired at 350°C which had impure phases.

The sol–gel process can undergo polyesterification when heated in a polyhydroxyl alcohol to form a solid polymeric resin through out which the cations are uniformly distributed. Thus, the resin retains homogeneity on the atomic scale and fine particulate oxides may be yielded through calcination at low temperature (500–700°C). The electrochemical and mechanical properties of the battery depends

on packing density, specific surface area, and homogeneity of LiCoO_2 powders [9,10], it is necessary to obtain sub-micron particles of uniform morphology with narrow size distribution and homogeneity. The LiCoO_2 powders with ultrafine nanometer particles performed by this sol-gel process could achieve higher energy capacity and excellent cycle life.

4. Conclusions

The sol-gel process is an attractive method to synthesize LiCoO_2 cathode materials for lithium-ion batteries, and requires a much lower calcination temperature and shorter calcination time than the solid-state reaction. Polycrystalline LiCoO_2 powder is found to be composed of

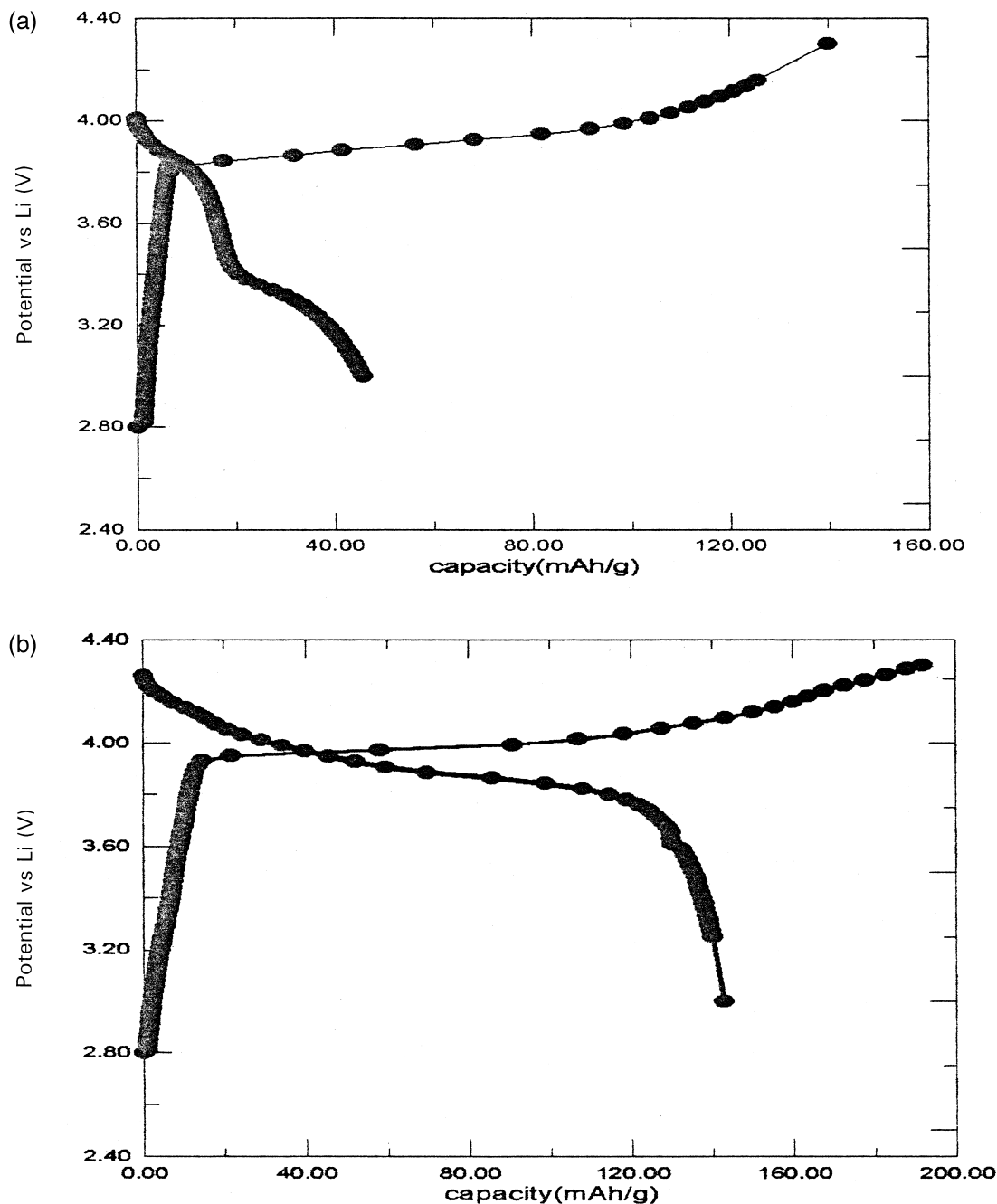


Fig. 4. Charge and discharge characteristics of the first cycles of LiCoO_2 fired to different temperatures: (a) 350°C; (b) 550°C; (c) 750°C; (d) graph of charge and discharge capacity vs. cycle numbers LiCoO_2 fired to 750°C.

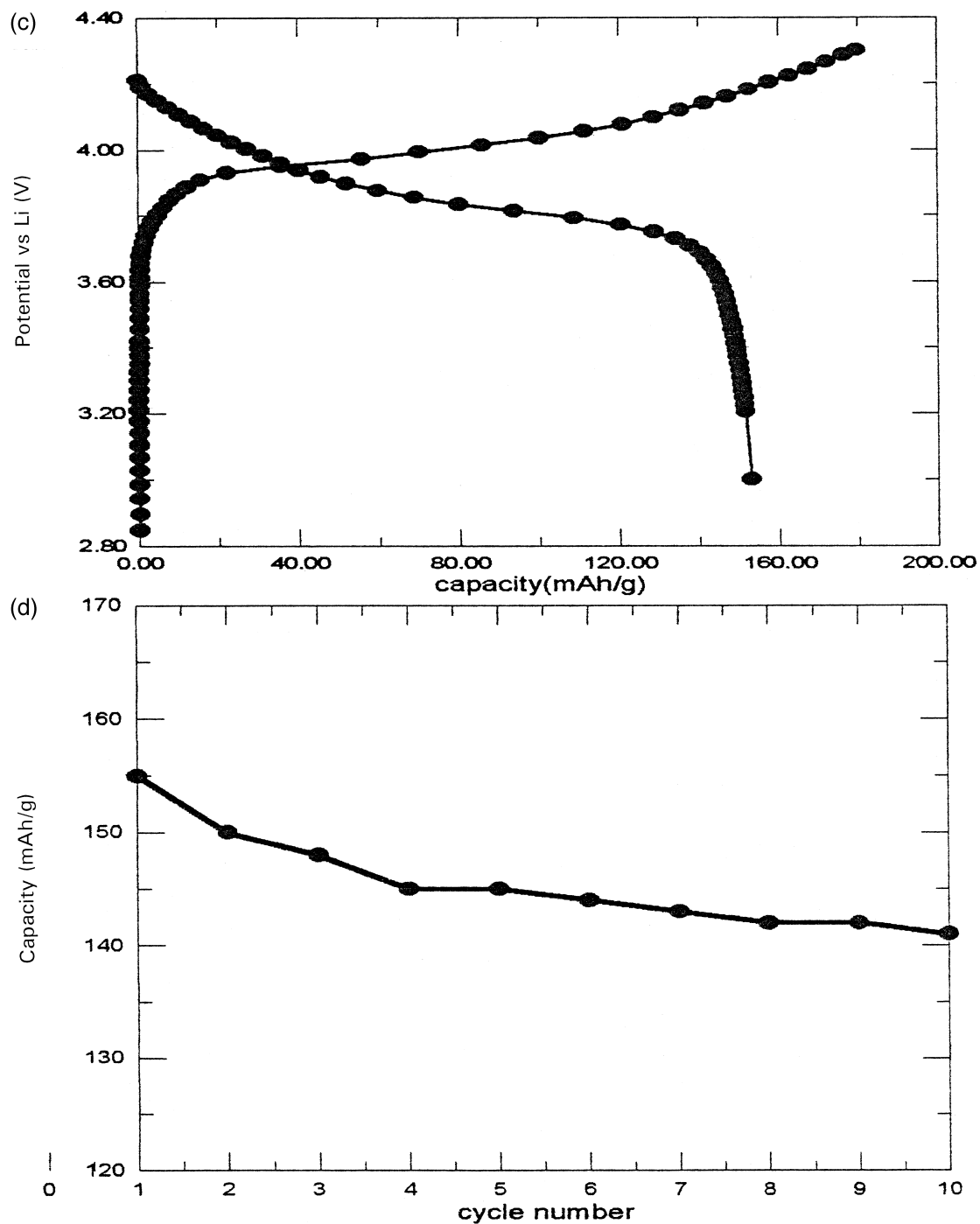


Fig. 4 (continued).

very uniformly sized, ultrafine particulates with an average particle size of 30 to 50 nm. Electrochemical studies show that the sol-gel synthesized materials display excellent performance.

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