

Synthesis and characterization of LiNiO_2 compounds as cathodes for rechargeable lithium batteries

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Abstract

Layered LiNiO_2 compounds are synthesized using a variety of conditions. Lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) and nickel oxide (NiO) are used as precursors. Heat treatment at 750°C in oxygen is found to be an optimum synthesis condition. Excess lithium ($\text{Li}:\text{Ni} = 1 \sim 1.1$ in molar ratio) is essential to produce LiNiO_2 compounds with good electrochemical performance. According to DTA/TG analysis, the LiNiO_2 can decompose to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$, which has a detrimental effect on the electrochemical reactivity of the LiNiO_2 compound. The kinetic parameters of LiNiO_2 electrodes are characterized by AC impedance spectroscopy. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: LiNiO_2 compounds; Lithium insertion/extraction; AC impedance spectroscopy

1. Introduction

Rechargeable lithium-ion batteries are state-of-the-art power sources for consumer electronics such as notebook computers, camcorders, and cellular phones because of their specific energy which is twice that of nickel/metal-hydride batteries. Lithium-ion batteries (sometimes called ‘rocking-chair’ batteries) are based on using intercalation compounds as electrodes in which lithium ions shuttle between cathode and anode hosts. Layered LiCoO_2 , LiNiO_2 and spinel LiMn_2O_4 are promising cathode materials for lithium-ion batteries and are under intensive investigation world-wide [1–4].

The spinel LiMn_2O_4 does not have an acceptable cycle life. This is because of the Jahn–Teller distortion which is observed near the end of the 4 V discharge plateau and the disproportion of Mn^{3+} ions into the electrolyte solution [5,6]. LiCoO_2 is currently used as a cathode material in commercial rechargeable lithium batteries due to its ease of preparation on an industrial scale and its stable electrochemical properties. It suffers from a disadvantage, however, that only half of its theoretical capacity can be used. It is also both toxic and expensive [7]. LiNiO_2 is an attractive cathode candidate because of the relatively abun-

dant natural resources of nickel and because this compound is environmentally benign. Nevertheless, it is difficult to synthesize stoichiometric LiNiO_2 with satisfactory electrochemical performance [8]. The electrochemical properties of LiNiO_2 are strongly dependant on the stoichiometry, crystal structure and cation disorder [9–11].

In view of the potential importance of LiNiO_2 as a cathode material for lithium-ion batteries, it is valuable to optimize the synthesis conditions. In this paper, the synthesis and electrochemical properties of LiNiO_2 compounds are reported. The thermal behaviour of LiNiO_2 compound is identified via DTA/TG analysis. The kinetic parameters of lithium nickelate electrodes are characterized by AC impedance spectroscopy.

2. Experimental

2.1. Synthesis of LiNiO_2 compounds

The LiNiO_2 compounds were synthesised via a solid-state reaction of precursors of $\text{LiOH} \cdot \text{H}_2\text{O}$ (99.95%, Aldrich) and NiO (Aldrich) with a molar ratio of $\text{Li}:\text{Ni}$ from 1–1.14. The reactants were thoroughly mixed by ball-milling and then pressed into pellets. The pellets were fired at different temperatures from 650 to 750°C in air or oxygen for 20–48 h.

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Table 1
Synthesis conditions and structural parameters of LiNiO₂ compounds

LiNiO ₂ samples	Molar ratio of Li:Ni in precursors	Calcination temperature (°C)	Atmosphere	Lattice constants (hexagonal)		Impurity phase	Bragg ratio $R_{(003)} = I_{(003)}/I_{(104)}$
				<i>a</i> (Å)	<i>c</i> (Å)		
A	1:1	650	air			Li ₂ O, NiO	
B	1:1	700	air			Li ₂ O, NiO	
C	1:1	750	air	2.8816	14.211		0.86
D	1:1	750	oxygen	2.8825	14.217		1.05
E	1.05:1	750	oxygen	2.8820	14.185		1.45
F	1.08:1	750	oxygen	2.8780	14.182		1.32
G	1.1:1	750	oxygen	2.8800	14.200		1.14
H	1.14:1	750	oxygen			Li ₂ O	

2.2. Structural characterization and thermal analysis of LiNiO₂ compounds

The structures of the synthesised LiNiO₂ samples were characterized by X-ray diffraction on a Philips PW1010 diffractometer with Cu-K α radiation. The lattice constants were calculated against an internal silicon standard. A simultaneous DTA-TG analyser (SETARAM, 92 model, France) was employed to determine the thermal behaviour of LiNiO₂ at high temperature.

2.3. Electrochemical test

Lithium test cells were constructed in an argon filled glove-box (Unilab, Mbraun, USA) in which the moisture and oxygen were controlled to under 1 ppm. The cathode mixtures, consisting of 85% active materials, 10% carbon black (Cabot Australasia, Australia) and 5% PVDF binder, were dissolved in dimethyl phosphate to obtain a slurry. The slurry was spread on to a aluminum foil with a scalpell and then dried at 180°C for 20 h. The area of the electrode was 0.75 cm². The anode was lithium foil (0.38 mm thick) pressed on to stainless-steel mesh. The electrolyte was 1 M LiPF₆ (lithium hexafluorophosphate) in a 2:1 mixture (by volume) of (ethylene carbonate (EC) and

dimethyl carbonate (DMC)). The cells were charged and discharged using a potentiostat (EG&GModel 393) combined with a Maclab interface and a Macintosh computer. Measurements of AC impedance characterisation were performed by means of a EG&G Princeton Applied Research Electrochemical Impedance Analyser (Model 6310) driven by Model 398 software. Each test cell for AC impedance consisted of three electrodes. Lithium metal was used as both the counter electrode and reference electrode. The AC amplitude was 5 mV and frequency range was 100 KHz to 0.1 Hz.

3. Results and discussion

3.1. Synthesis, XRD data and DTA/TG of LiNiO₂ compounds

The stoichiometric LiNiO₂ compound belongs to the rhombohedral system (SG:R3m) in which Li⁺ and Ni⁺ ions occupy the octahedral 3*a* and 3*b* sites, respectively, of fcc packing. Such structure provides a two-dimensional channel for lithium ion intercalation and de-intercalation. The hexagonal parameters are *a* = 2.8806 Å and *c* = 14.2050 Å [11]. Table 1 shows the synthesis conditions

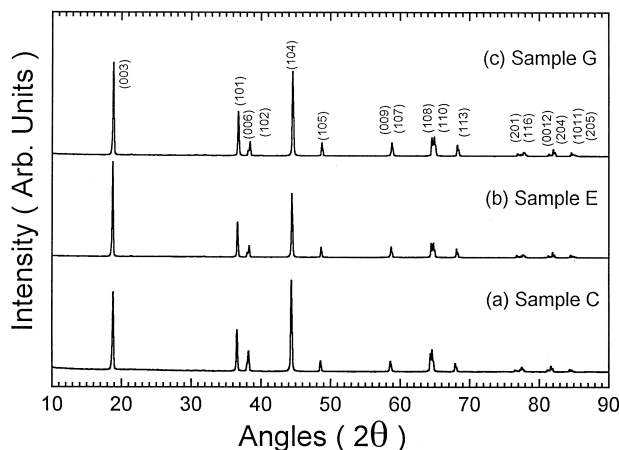


Fig. 1. X-ray diffraction patterns of LiNiO₂ compounds: (a) sample C; (b) sample E; (c) sample G.

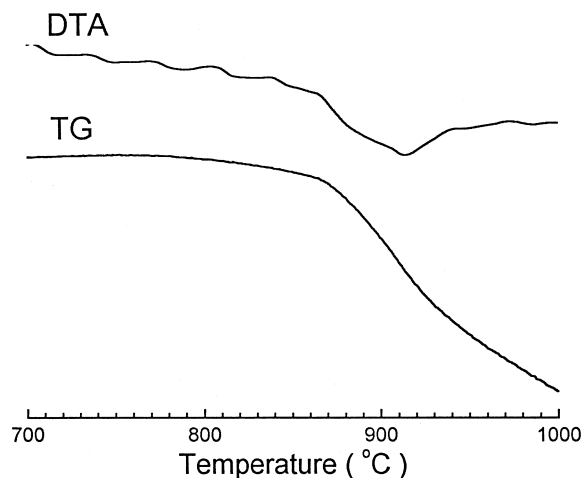


Fig. 2. DTA/TG curves of LiNiO₂ compound.

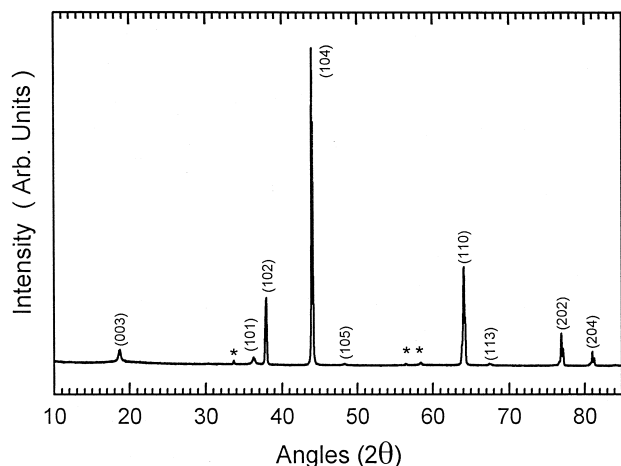


Fig. 3. X-ray diffraction pattern of quenched $\text{LiNiO}_2(\text{Li}_2\text{Ni}_8\text{O}_{10})$. Peaks for Li_2O marked by asterisks.

and structural parameters of the LiNiO_2 samples. The samples synthesized at 650 and 700°C in air (sample A and B) contained impurity phases of Li_2O and NiO. The

reaction proceeds through solid-state diffusion. The two components were not thoroughly reacted at these lower temperatures. The impurity phase of Li_2O was also detected in sample H. The Li_2O impurity contained in the LiNiO_2 compound could be leached into water, but this process affects the electrochemical performance of LiNiO_2 compounds adversely due to chemical delithiation through the following cation-exchange reaction [8]:



Consequently, samples A, B, and H were eliminated from further electrochemical tests. Typical X-ray diffraction patterns of LiNiO_2 compounds synthesized under the different conditions given in Table 1 are presented in Fig. 1. The intensities of peaks (003) and (104) differ for different samples. It has been reported [12,13] that the Bragg intensity ratio $R_{(003)} = I_{(003)}/I_{(104)}$ can be used as a reliable quantitative criterion for the stoichiometry of $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$ compounds. It is possible, however, that the texture of the powder can also influence the intensity of the diffraction peak. X-ray diffraction samples for the same LiNiO_2 com-

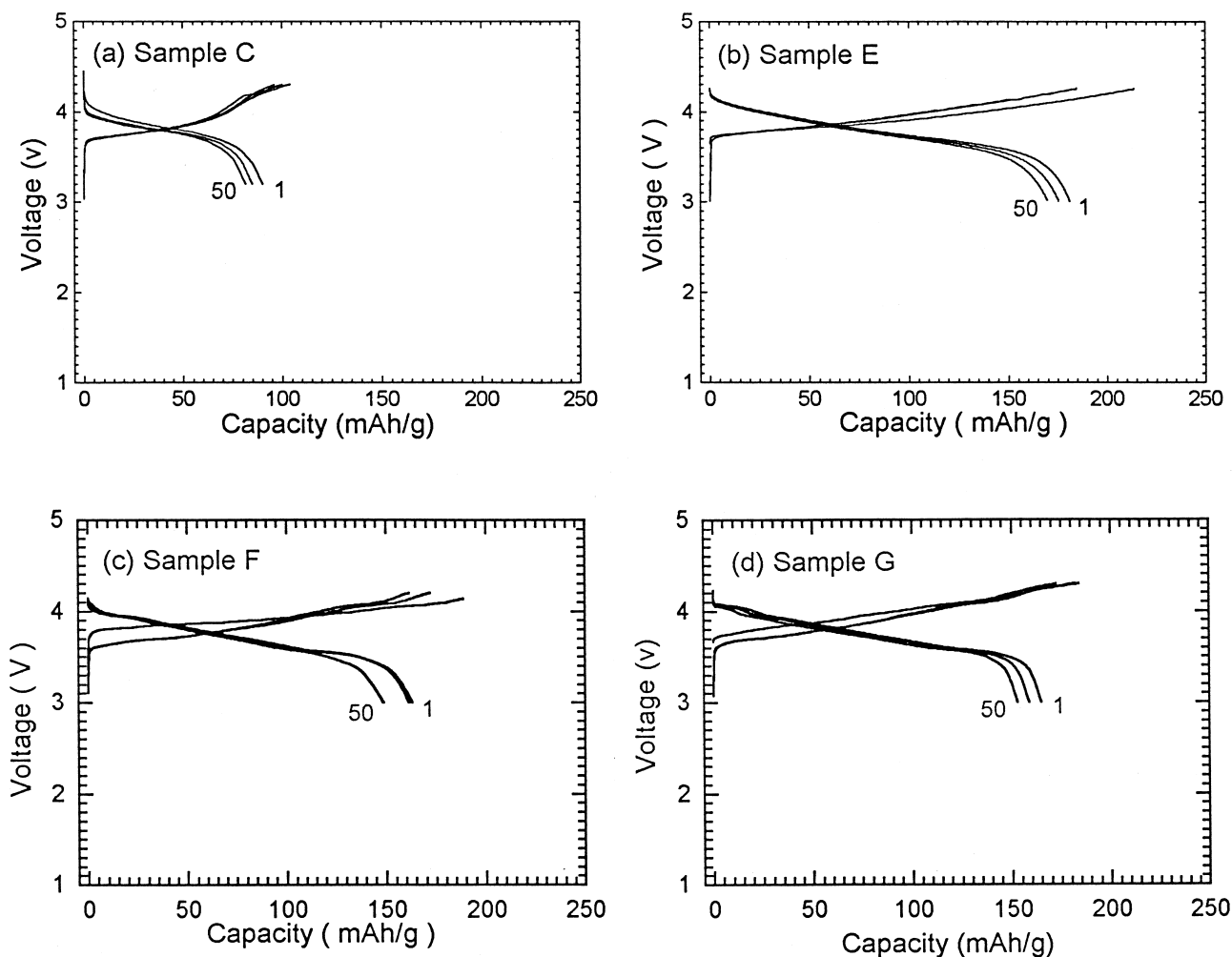
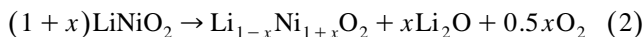


Fig. 4. Charge–discharge profiles of different LiNiO_2 electrodes: (a) sample C; (b) sample E; (c) sample F; (d) sample G.

powder were prepared in different ways which were designed to change the texture of the powder particles. The intensities of the (003) and (104) peaks changed slightly with the preparation method. On the other hand, the exact chemical composition of the LiNiO_2 compound is not the main factor which determines the electrochemical performance when the Li:Ni ratio is close to unity. Therefore, for optimum preparation conditions, examination of the electrochemical properties is needed rather than reliance on the XRD data.

The thermal behaviour of the LiNiO_2 compound was determined by DTA/TG analysis. The results are shown in Fig. 2. There is an endothermic peak on the DTA curve. The onset temperature is 860°C and the peak ends at 960°C . Within this temperature range, the sample loses weight continuously, which can be assigned to decomposition of LiNiO_2 to $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ and to oxygen evolution. Because only oxygen can be evolved from the LiNiO_2 compound at high temperature, it is proposed that the decomposition of LiNiO_2 can be expressed as:



Based on Eq. (2), the decomposition of LiNiO_2 at high temperature can be suppressed in an oxygen atmosphere. The excess lithium in the precursors can compensate for the loss of the volatile LiOH at high temperature. The decomposition product $\text{Li}_{1-x}\text{Ni}_{1+x}\text{O}_2$ has a disordered cation distribution with nickel ions partially occupying the lithium sites in the layered structure. These nickel ions impede the diffusion of lithium ions [14,15]. Thus, the electrochemical properties of such disordered LiNiO_2 are very poor. Consequently, the synthesis temperature for LiNiO_2 should be kept below 860°C in order to avoid any decomposition and oxygen evolution.

Sample D of LiNiO_2 was fired at 900°C for 24 h and then quenched into liquid nitrogen. With this procedure, the state of LiNiO_2 at high temperature was preserved at room temperature. The XRD pattern of the quenched LiNiO_2 compound is shown in Fig. 3. The compound was identified as hexagonal $\text{Li}_2\text{Ni}_8\text{O}_{10}$ (JCPDS-23-362). This confirms Eq. (2) and that the structure of LiNiO_2 changes during the heat treatment at high temperature.

3.2. Electrochemical characterisation

The charge–discharge tests of Li/LiNiO₂ cells were carried out in the voltage range 3 to 4.25 V at a constant current density of 0.25 mA cm^{-2} . The cycling profiles of different LiNiO_2 samples are shown in Fig. 4. Sample E displayed the best electrochemical activity. It delivered an initial charge capacity of 214 mA h g^{-1} and a discharge capacity of 181 mA h g^{-1} . During the first cycle, about 32 mA h g^{-1} of the specific capacity is irreversible. From the second cycle onwards, the reversibility of the electrode is quite excellent. After 50 cycles, the electrode still delivered 170 mA h g^{-1} of specific discharge capacity at a rate

of capacity loss of 0.122% per cycle. Sample C, which was synthesized in air, gave a first discharge capacity of only 90 mA h g^{-1} , which reflects its poor electrochemical reactivity. Samples F and G also demonstrated satisfactory discharge capacities, viz., 140 to 160 mA h g^{-1} . The average discharge voltage of the LiNiO_2 electrode for all the samples tested was about 3.7 to 3.8 V. This voltage is slightly lower than that of LiCoO_2 and LiMn_2O_4 and is beneficial for the stability of the organic electrolyte.

The electrochemical properties of quenched LiNiO_2 ($\text{Li}_2\text{Ni}_8\text{O}_{10}$) as a cathode in the lithium cells were examined. The quenched LiNiO_2 ($\text{Li}_2\text{Ni}_8\text{O}_{10}$) electrode was found to have no initial electrochemical reactivity. The $\text{Li}_2\text{Ni}_8\text{O}_{10}/\text{Li}$ cell could be quickly charged to 4.25 V and discharged to 3 V in a few minutes. No charge–discharge capacity was delivered by this test cell. The $\text{Li}_2\text{Ni}_8\text{O}_{10}$ structure can be written as: $(\text{Li}_{2/5}\text{Ni}_{3/5})_{3a}(\text{Ni})_{3b}(\text{O}_2)_{6c}$ in which nickel ions partially occupy the 3a sites lithium ions in the hexagonal array. Lithium ions cannot move in such a disordered structure even though it is iso-structural with layered LiNiO_2 . Further investigation is required to understand this phenomenon.

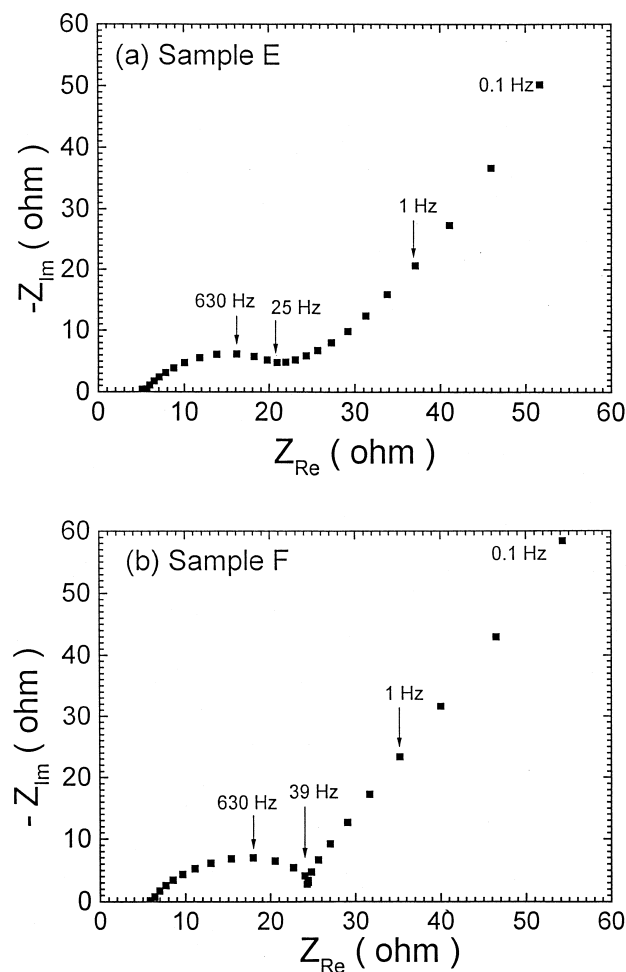


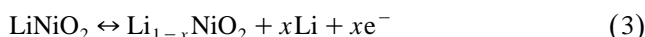
Fig. 5. AC impedance spectroscopy of LiNiO_2 electrodes: (a) sample E; (b) sample F.

Table 2
Kinetic parameters of LiNiO₂ electrodes in lithium cells

LiNiO ₂ samples	Ohmic resistance (Ω)	Charge-transfer resistance (Ω)	Double-layer capacitance (μF)	Exchange-current density (<i>I</i> ₀) (A cm ⁻²) × (10 ⁻³)
C	5.04	45.41	5.5	0.72
D	5.56	24.5	10.3	1.34
E	5.28	21.65	11.6	1.52
F	6.55	19.03	13.2	1.73
G	10.65	21.48	11.7	1.53

The results of the cycling test revealed that LiNiO₂ compounds prepared in an oxygen atmosphere can achieve better electrochemical properties than those synthesized in air. This is related to the fact that LiNiO₂ tends to decompose at high temperature due to the reduction of Ni³⁺ to Ni²⁺ at the lower partial pressure of oxygen. Oxygen can suppress the decomposition of LiNiO₂ and prevent structural disorder.

Lithium insertion into and extraction from LiNiO₂ compounds is already known to be a reversible topotatic reaction, i.e.,



The kinetic parameters of LiNiO₂ electrodes in lithium cells have been determined by AC impedance spectroscopy. Typical complex impedance diagrams (Nyquist plots) for LiNiO₂ compounds synthesized under different conditions are presented in Fig. 5. The semicircles are obtained, from which the ohmic resistance (*R*₀), double-layer capacitance, and charge-transfer resistance (*R*_{CT}) are calculated. The exchange-current density of each electrode can be deduced from the expression: $I_0 = RT/nFR_{CT}$ [16,17]. The straight line inclined to the real axis at 45° in the low frequency range of several Hz is the contribution of the Warburg diffusion impedance $Z_w = A\omega^{-1/2} - JA\omega^{-1/2}$. The end of the semicircle is distorted because of an overlap of the charge-transfer and diffusion processes. The kinetic parameters of the different LiNiO₂ electrodes are listed in Table 2. The LiNiO₂ compound synthesized in air has a high charge-transfer resistance (*R*_{CT}) which is not favourable for cell operation. The exchange-current density (*I*₀), deduced from the charge-transfer resistances (*R*_{CT}), is around 0.7 to 1.7×10^{-3} A cm⁻² for LiNiO₂ compounds prepared under the different conditions. These values are consistent with those previously reported [16,18] for the lithium insertion compounds.

4. Conclusions

The synthesis and electrochemical characteristics of LiNiO₂ compounds as cathodes for rechargeable lithium batteries have been investigated. The LiNiO₂ compound synthesized at 750°C in oxygen with excess Li (Li:Ni = 1.05) is found to be the optimum preparation condition in

this study. A cathode prepared from this compound can deliver approximately 180 mA h g⁻¹ of discharge capacity with good reversibility. It should be noted that this by no means represents the most appropriate synthesis condition for LiNiO₂ compounds. Thermogravimetric analysis revealed that the LiNiO₂ compound can decompose to Li_{1-x}Ni_{1+x}O₂ with poor electrochemical reactivity. The kinetic parameters of the LiNiO₂ electrode have been characterised by AC impedance. The LiNiO₂ compound synthesized in air has a high charge-transfer resistance (*R*_{CT}) and a low exchange-current density.

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