Short communication

# Thermal and electrochemical behavior of yttria-stabilized zirconia coated LiCoO$_2$ during overcharge tests

George Ting-Kuo Fey[*], Chiao-Ling Hsiao, Pandurangan Muralidharan

*Department of Chemical and Materials Engineering, National Central University, Chung-Li 32054, Taiwan*

A R T I C L E   I N F O

A B S T R A C T

Sol–gel synthesized yttria-stabilized zirconia (YSZ) ceramic powders were coated on LiCoO$_2$ cathode particles by a simple mechano-thermal process, calcined at 923 K for 10 h. The XRD patterns of YSZ-coated LiCoO$_2$ revealed a single-phase hexagonal $\alpha$-NaFeO$_2$-type structure with $R\bar{3}m$ symmetry of the core material without any modification. The surface of LiCoO$_2$ particles was coated with a uniform layer of YSZ that had an average thickness of ∼20 nm, as observed from TEM images. The different binding energies of O 1 s XPS data exhibited the presence of oxygen ions corresponding to the surface coated YSZ and LiCoO$_2$. The galvanostatic cycling studies for the coated materials suggest that 2.0 wt.% YSZ-coated LiCoO$_2$ delivered a stable capacity of 160 mAh g$^{-1}$ between 2.75 V and 4.4 V vs. Li and a good cycle stability of about 142 cycles. The impedance growth was slower for LiCoO$_2$ surface coated with YSZ, when cells were charged at 4.4 V and 4.5 V. DSC results illustrated that the oxygen evolution exothermic peak at about 458 K was significantly smaller for YSZ-coated cathode materials.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Layered LiCoO$_2$ is the most stable cathode material used in lithium-ion cells due to its excellent reversibility, high energy density, cycle stability and ease of preparation [1,2]. A practical level of (de)lithiation is only 0.5 mol of lithium from LiCoO$_2$ within the voltage range of 3.0–4.2 V vs. Li$^+$/Li, which delivers the maximum theoretical capacity of 137 mAh g$^{-1}$ [3]. Recently, major research has been focused on achieving higher capacity by charging beyond 4.2 V, but this led to failures due to some of the limitations of layered LiCoO$_2$, such as structural degradation, dissolution of Co$^{4+}$ ions into the acidic electrolyte and faster impedance growth [4,5].

In order to overcome these limitations of bare LiCoO$_2$, a new alternative technique has been developed that safeguards the surface of the cathode by coating it with electrochemically inactive oxides, and protecting the active oxides (3d metal ion) particles from direct contact with the acidic electrolyte, in order to deliver stable capacities when cycled beyond 4.2 V. ZrO$_2$ [4–7], Al$_2$O$_3$ [5–8], TiO$_2$ [6–7,9], SiO$_2$ [5,10], Co$_3$O$_4$ [11], CeO$_2$ [12], AlF$_3$ [13], and La$_2$O$_3$ [14] coated cathode materials demonstrated enhanced capacity and cycle stability. In addition to these coating materials of single metal oxides, we have examined the behavior of the mixed metal oxide, MgAl$_2$O$_4$ [15], as a coating material, which is mechanically robust and chemically inert with a high refractory spinel structure. The precursor materials and the method [4–14] adopted for coating play a vital role in forming a uniform and adhesive coating on the cathode materials with low temperature syntheses. Since YSZ is also a mixed metal oxide with a behavior similar to MgAl$_2$O$_4$, we are interested in using YSZ as a coating material for surface modification of LiCoO$_2$ in this work. Wang et al. [16] reported that the adhesion of 8 mol% YSZ to the La$_x$Sr$_{1-x}$MnO$_3$ (LSM) cathode for a solid oxide fuel cell significantly enlarges the three-phase boundaries area and leads to a pronounced improvement in electrochemical performance, thermal and chemical stability, and electronic conductivity, in addition to relatively good compatibility of the YSZ/LSM composite electrode. The benefits from coating with YSZ focused our attention towards preparing various wt.% YSZ-coated LiCoO$_2$ cathode materials by a mechano-thermal process in order to gain a deeper insight into the electrochemical cell performance and thermal stability when charged at higher voltages.

## 2. Experimental

(Y$_2$O$_3$)$_{0.08}$(ZrO$_2$)$_{0.92}$ ceramic powders were synthesized by a sol–gel process [17]. The solutions of Zr(OC$_4$H$_9$)$_4$ and Y(NO$_3$)$_3$.6H$_2$O in *iso*-propanol were mixed to form the YSZ gel precursor and heated at 1073 K for 10 h at a heating ramp of 2 K min$^{-1}$ to yield YSZ ceramic powders.

The YSZ-coated LiCoO$_2$ cathode was synthesized by a mechano-thermal process with 0.1, 1.0, 2.0 or 2.5 wt.% of YSZ ceramic powder.

Chemicals used were $LiCoO_2$ powder (commercial product of FMC) and YSZ (prepared by a sol–gel method). The 0.04 g of YSZ (2 wt.%) and 2.0 g of $LiCoO_2$ were each dispersed in 25 ml ethanol by a 1 h sonication, and stirred for 10 h and 3 h, respectively. The YSZ solution was added dropwise to the dispersed $LiCoO_2$ solution after sonication for 1 h and stirred for 10 h at 298 K, followed by heating at 343 K with continuous stirring. After the removal of excess ethanol, a thick black slurry was formed. The obtained slurry was dried in an oven at 383 K for 12 h to form a dry black powder, which was heated at 923 K for 10 h in air at a heating ramp of 4 K min$^{-1}$ to form a thin layer of YSZ-coated on $LiCoO_2$.

Structural analysis was carried out using a powder X-ray diffractometer (XRD), Siemens D-5000, Mac Science MXP18, equipped with a nickel-filtered Cu-K$_\alpha$ radiation source ($\lambda = 1.5405$ Å). The diffraction patterns were recorded between scattering angles of 15° and 80° in steps of 0.05°. The coated layer morphology of the particle was examined by a JEOL JEM-200FXII transmission electron microscope (TEM) equipped with a LaB$_6$ gun. X-ray photon spectroscopy (XPS) and the depth profiles were recorded by an electron spectroscopy for chemical analysis (ESCA) instrument (VG Scientific ESCALAB 250) with monochromatic Al-K$_\alpha$ radiation 1486.6 eV. The survey spectra were scanned in the range 0.00–1400.00 eV binding energy (BE) in 1.00 eV steps.

The cathodes for electrochemical studies were prepared by a doctor-blade coating method as described in our previous work [11]. The coin type cells of the 2032 configuration were assembled in an argon-filled VAC MO40-1 glove box. The prepared circular disk of YSZ-coated $LiCoO_2$ was used as the cathode, lithium metal (Foote Mineral) as the anode and a 1 M $LiPF_6$ in 1:1 by volume ethylene carbonate/diethyl carbonate (EC/DEC) (Tomiyama Chemicals) as the electrolyte with a Celgard membrane as the separator. The cell charge-discharge cycles were preformed at a 0.2$C$ rate between 2.75–4.4 V, 2.75–4.5 V and 2.75–4.6 V, at 293 K, in a multi-channel battery tester (Maccor 4000).

Thermal stability analysis was carried out on a Perkin-Elmer DSC 7 differential scanning calorimetry (DSC) for pristine $LiCoO_2$ and YSZ-coated $LiCoO_2$. The measurements were performed in a nitrogen atmosphere between 323 K and 623 K, at a heating rate of 3 K min$^{-1}$. The samples for the DSC investigations were prepared as described in our previous work [11].

## 3. Results and discussion

Fig. 1a and b show the XRD patterns of 2.0 wt.% YSZ-coated $LiCoO_2$ heated at 923 K for 10 h in air and pristine $LiCoO_2$, respectively. The diffraction patterns recorded for various wt.% YSZ coated materials conform to a single-phase hexagonal $\alpha$-NaFeO$_2$-type structure of the cathode material. The absence of secondary phase peaks in the entire range of the diffraction patterns corresponding to YSZ may be due to very low concentrations. Thus, the XRD patterns of the YSZ coated particles show no basic change in the $a$ and $c$ lattice parameters, the $2\theta$ values of the peaks and their $I(0\,0\,3)/I(1\,0\,4)$ ratios, which indicates that YSZ does not alter the structure of the core material when heated at 923 K.

Fig. 2 shows a TEM image of a 2.0 wt.% YSZ coated $LiCoO_2$ particle. The coating was a translucent thin compact layer of YSZ over the $LiCoO_2$ particles that had an average thickness of ~20 nm. The TEM image revealed that the YSZ coating remained on the surface of the core particles upon calcination at 973 K, due to the propensity of YSZ to form an adhesive compact layer [16].

Fig. 3 shows the XPS spectra of O 1s, at surface and a depth of 20 nm, for YSZ coated $LiCoO_2$. In Fig. 3, there is an unsymmetrical broad peak at a surface level with BEs of O 1s at 531.69 and 530.69 eV, which may be assigned to the oxygen bonded to
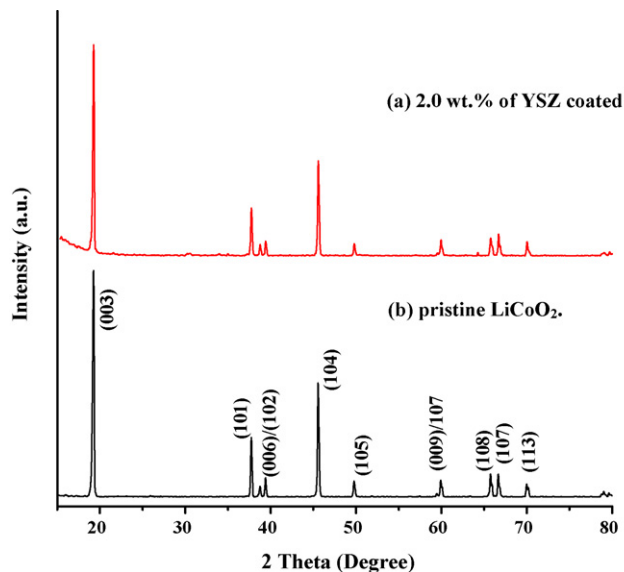


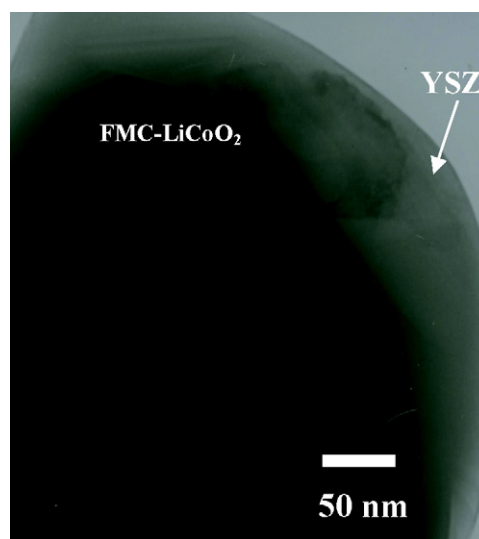Fig. 1. X-ray diffraction patterns of (a) 2.0 wt.% of YSZ-coated and (b) pristine $LiCoO_2$.



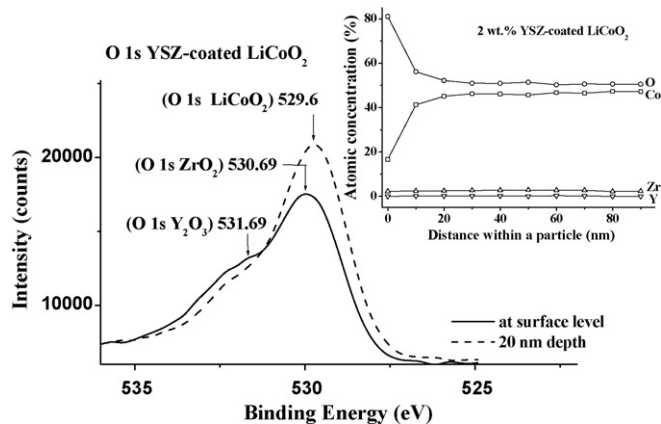Fig. 2. TEM image of a 2.0 wt.% YSZ-coated $LiCoO_2$ particle.



Fig. 3. XPS spectra of O 1s for a 2.0 wt.% YSZ-coated $LiCoO_2$ particle. The inset is the depth profile of a 2.0 wt.% YSZ-coated $LiCoO_2$ particle.
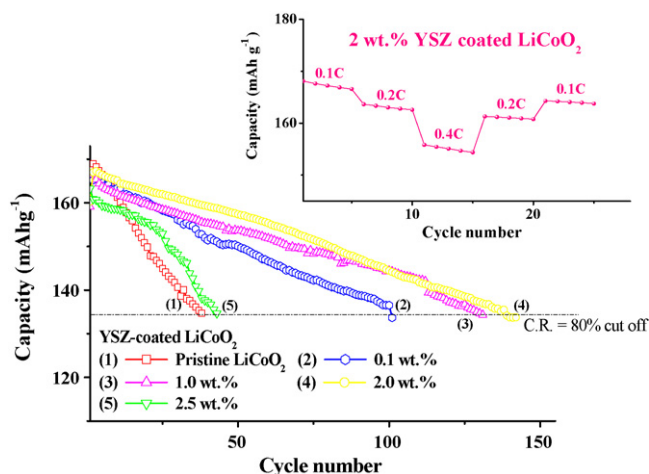
**Fig. 4.** Cycling performance of pristine and various wt.% YSZ-coated LiCoO₂; charge–discharge: 2.75–4.4 V; 0.2C rate. The inset shows charge-discharge at 0.1C, 0.2C and 0.4C rates.



**Fig. 5.** Cycling performance of 2.0 wt.% YSZ-coated LiCoO₂; charge–discharge: 2.75–4.4 V; 2.75–4.5 V; 2.75–4.6 V at a 0.2C rate.

Y and Zr ions, respectively [18]. The O 1s XPS profile at 20 nm depth showed that the unsymmetrical peak shifted to a lower BE at 529.6 eV with a low intensity shoulder peak. The low intensity shoulder peak at a 20 nm depth corresponds to the O 1s bonded with Y and Zr ions, which can be attributed to the coated material remaining principally on the surface. The high intensity BE peak at 529.6 eV corresponds to O 1s bonded with Co-ions in the lattice of the core material [18]. The peaks positioned at 531.69 eV and 530.69 eV at the surface and 529.6 eV at a 20 nm depth are evidence that the coated material remains on the surface. As a result, there is no influence on the chemical state or the BEs of the different ions in the YSZ coated LiCoO₂ sample. The inset of Fig. 3 shows the O, Co, Zr and Y atomic concentrations of distribution in YSZ coated LiCoO₂ with a depth profile of the particle. The concentration of cobalt increased to a depth of ∼20 nm and then leveled off. The high concentration of oxygen at the surface of the oxide is reasonable due to the presence of YSZ oxygen content. The concentrations of Y and Zr were lower than three atomic percent at the surface level. Beyond that, there was a gradually decrease in the yttrium and zirconium concentration with the depth of the particle.

Fig. 4 compares the cycle performance of pristine LiCoO₂, 0.1, 1.0, 2.0 and 2.5 wt.% of YSZ coated LiCoO₂ between 2.75 V and 4.4 V. In order to study the efficiency of the various wt.% of YSZ coating on the cycle performance of Li⁺/Li, a preset cut-off value of 80% capacity retention was fixed and calculated with the first-cycle discharge capacity of the respective material. From Fig. 4, it is observed that the 0.1, 1.0 and 2.0 wt.% YSZ coated samples exhibited enhanced cycling stability compared with pristine LiCoO₂. Based on the cut-off regime, pristine LiCoO₂ (168 mAh g⁻¹) could sustain just 38 cycles. In Fig. 4, the number of cycles sustained by 2.0 wt.% YSZ coated LiCoO₂ (160 mAh g⁻¹) was 142 cycles compared to 0.1 wt.% (166 mAh g⁻¹) 1.0 wt.% (159 mAh g⁻¹) and 2.5 wt.% (163 mAh g⁻¹) coatings which sustained 101, 131 and 43 cycles, respectively. It is evident that the 2.0 wt.% YSZ coated sample exhibited good discharge capacity and cycling stability. The 2.0 wt.% coating level may be optimal to form a compact adhesive uniform layer that results in enhanced cycling performance by protecting the core material from direct contact with the acidic electrolyte. The coating also suppresses the tendency of Li₁₋ₓCoO₂ to lose Co and O ions from the lattice via chemical interaction with the acidic electrolyte and allows it to retain good cycle stability [4,5,7].
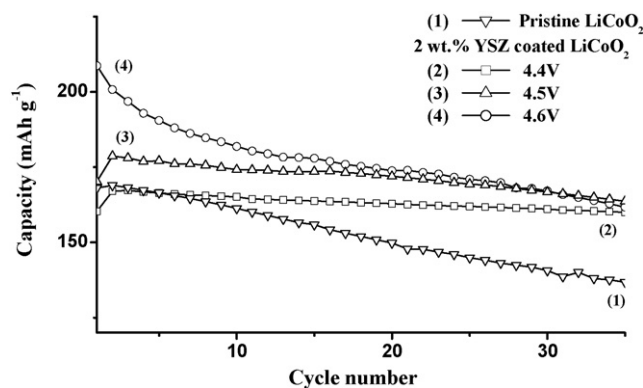
The inset of Fig. 4 shows the effect of YSZ coating on the rate capability for the cell cycled between 2.75 V and 4.4 V at different c-rates. The inset of Fig. 4 shows that for c-rates 0.1C, 0.2C and 0.4C, the discharge capacities were 168 mAh g⁻¹, 163 mAh g⁻¹ and 156 mAh g⁻¹, respectively, with smaller capacity fades. In a descending order of c-rates, 0.4C, 0.2C and 0.1 C, the cell was able to retrieve its capacities (inset of Fig. 4). Thus, the cell possessed a significant rate capability and it is evident that the channel for Li ion diffusion was probably not hindered by the surface coated layer of YSZ.

Fig. 5 shows the effect of YSZ coating on the cycling performance when charged at higher cutoff voltages for 35 cycles between 2.75–4.4 V, 2.75–4.5 V and 2.75–4.6 V at a 0.2C rate. The discharge capacity was relatively high at 208 mAh g⁻¹ for 2.75–4.6 V, but 170 mAh g⁻¹ for 2.75–4.5 V and 160 mAh g⁻¹ for 2.75–4.4 V. The pristine LiCoO₂ cathode cycled at 4.4 V showed a capacity of 164 mAh g⁻¹ and when the cell was charged at 4.5 V, exhibited a rapid capacity fade [4,5]. Better cycle stability was observed for the YSZ coated LiCoO₂ cell charged at 4.4 V and 4.5 V, rather than 4.6 V, and these results are comparable to the reports of Chen and Dahn [4,5]. They can be attributed to slower impedance growth on the surface of the core materials due to the presence of YSZ, which prevents the loss of 3d metal ions and oxygen when the cells are charged at higher voltages [4,5], whereas faster impedance growth is caused by some side reactions at the surface of pristine LiCoO₂. Aurbach et al. [19] reported that upon cycling, LiCoO₂ undergoes a major capacity fade due to the formation of surface films on the cathode. Edstrom et al. [20] conducted XPS studies, where the cathode surface was formed of organic species and their reactions with the lithium-salt anion were more dependent on electrode material type. It is particularly important to reduce the impact of the PF₆ anion and its related contaminants (HF and PF₅) on electrode surface chemistry by the implementing more stable inactive coating layer.

Fig. 6 shows the DSC curves for overcharged pristine LiCoO₂ and 2.0 wt.% YSZ coated LiCoO₂. The cathode material displays characteristic exothermic peaks due to their thermal decomposition of pristine materials at 447 K (44.6 J g⁻¹) and YSZ coated materials 458 K (25.3 J g⁻¹) which release oxygen. The coated sample showed a shift towards higher thermal decomposition by 11 K and the relative area under the peak was lower by a factor of three times over pristine LiCoO₂. Similar thermal stability was observed for the overcharged AlPO₄-coated LiCoO₂ cathode material in the electrolyte [21]. Hence, it could be concluded that YSZ coated LiCoO₂ has better thermal safety characteristics compared to the pristine LiCoO₂ cathode material.
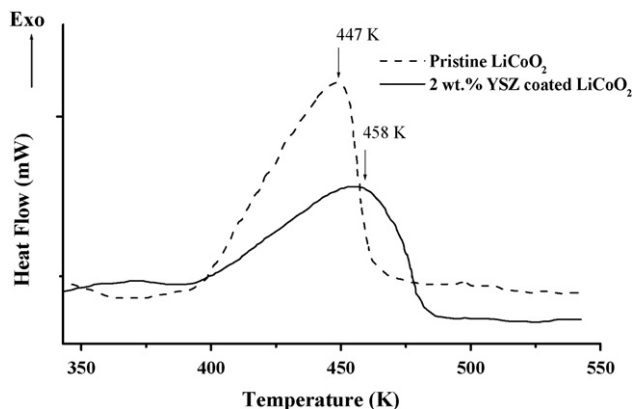
**Fig. 6.** DSC scans of pristine and 2.0 wt.% YSZ-coated $LiCoO_2$ after full charge at 4.4 V vs. Li for 20 h.

## 4. Conclusions

YSZ coated $LiCoO_2$ cathode materials were successfully synthesized by a mechano-thermal method. XRD patterns of the coated materials did not show any change in the lattice parameters, which confirmed that the coating oxide remained on the surface, a phenomenon also evident from the XPS spectra. The TEM image identified that YSZ formed a compact coating over the cathode particles. Cycling studies revealed an improvement in the cycle stability of 2.0 wt.% YSZ coated $LiCoO_2$, which is 3.7 times more stable than pristine $LiCoO_2$. The coated cathode material charged at the higher voltages of 4.4 V, 4.5 V and 4.6 V showed high discharge capacities and good cycle stability compared to pristine $LiCoO_2$. The YSZ-coated samples showed slower impedance growth on the surface of $LiCoO_2$ and prevented the loss of 3d metal ions and oxygen.

## References

[1] J.M. Tarascon, M. Armand, Nature (London) 414 (2001) 359.
[2] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novák, Adv. Mater. 10 (1998) 725.
[3] J. Cho, G. Kim, Electrochem. Solid-State Lett. 2 (1999) 253.
[4] Z. Chen, J.R. Dahn, Electrochem. Solid-State Lett. 5 (2002) A213.
[5] Z. Chen, J.R. Dahn, Electrochim. Acta 49 (2004) 1079.
[6] A.M. Kannan, L. Rabenberg, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A16.
[7] J. Cho, Y.J. Kim, T.J. Kim, B. Park, Angew. Chem. Int. Ed. 40 (2001) 3367.
[8] G.T.K. Fey, J.G. Chen, T.P. Kumar, J. Appl. Electrochem. 35 (2005) 177.
[9] G.T.K. Fey, C.Z. Lu, T.P. Kumar, Y.C. Chang, Surf. Coat. Tech. 199 (2005) 22.
[10] G.T.K. Fey, H.Z. Yang, T.P. Kumar, S.P. Naik, A.S.T. Chiang, D.C. Lee, J.R. Lin, J. Power Sources 132 (2004) 172.
[11] G.T.K. Fey, Y.Y. Lin, T.P. Kumar, Surf. Coat. Tech. 191 (2005) 68.
[12] H.W. Ha, N.J. Yun, M.H. Kim, M.H. Woo, K. Kim, Electrochim. Acta 51 (2006) 3297.
[13] Y.K. Sun, J.M. Han, S.T. Myung, S.W. Lee, K. Amine, Electrochem. Commun. 8 (2006) 821.
[14] G.T.K. Fey, P. Muralidharan, C.Z. Lu, Y.D. Cho, Electrochim. Acta 51 (2006) 4850.
[15] G.T.K. Fey, Z.F. Wang, C.Z. Lu, T.P. Kumar, J. Power Sources 146 (2005) 245.
[16] S. Wang, V. Jiang, Y. Zhang, J. Van, W. Li, J. Electrochem. Soc. 145 (1998) 1932.
[17] S.G. Kim, S.P. Yoon, S.W. Nam, S.H. Hyun, S.A. Hong, J. Power Sources 110 (2002) 222.
[18] http://www.xpsdata.com/XI_BE_Lookup_table.pdf.
[19] D. Aurbach, B. Markovsky, A. Rodkin, E. Levi, Y.S. Cohen, H.J. Kim, M. Schmidt, Electrochim. Acta 47 (2002) 4291.
[20] K. Edstrom, T. Gustafsson, J.O. Thomas, Electrochim. Acta 50 (2004) 397.
[21] J. Cho, T.G. Kim, C. Kim, J.G. Lee, Y.W. Kim, B. Park, J. Power Sources 146 (2005) 58.