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Improved high-rate performance of a supercapacitor electrode from manganese-oxide-coated vertically aligned carbon nanotubes prepared by a pulsed current electrodeposition method

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ABSTRACT

Although manganese oxide (MnO₂) can be incorporated with vertically aligned carbon nanotubes (VACNTs) to improve supercapacitor performance potentially, one of the hurdles that hampers this embodiment is a difficulty of coating MnO₂ on VACNTs homogeneously. As a way of overcoming this hurdle, we present here a facile method of pulsed current electrodeposition that turns out to exceed conventional methods in coating quality. Such improvement leads to a clear enhancement in gravimetric specific capacitance, reaching a state-of-the-art value of 243.3 F/g at a high scanning rate of 100 mV/s. In the course of this characterization, diffusion hindrance through a MnO₂ layer clogging over VACNTs is found out to limit the device performance at high mass loading. An empirical relationship is proposed to explain such phenomenon and demonstrates good application in various conditions. The optimized VACNTs/MnO₂ electrode also reveals outstanding high-rate performances.

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1. Introduction

Increasing demand of clean and renewable energy has set up a request for electrochemical storage. Though being able to operate rapidly, conventional double-layer-based supercapacitors (SCs) alone cannot often store sufficient energy [1]. Pseudocapacitive materials are considered to hold promise in boosting the SC energy density, approaching that of batteries [2]. Thanks to the high theoretical specific capacitance (C_m), environmental friendliness, rich earth abundance, and modest material cost, manganese oxide (MnO₂) has been drawing great attentions for use in SC electrodes [3,4]. Nevertheless, its poor conductivity ($10^{-6}-10^{-5}$ S/cm) remains a major obstacle that thwarts utilization of its full potential particularly in high-rate operation [3]. It has also been revealed that the increased resistance can severely deteriorate the performance of thickly MnO₂-coated SC electrodes [5].

A practical strategy is to develop a composite electrode in which MnO_2 is effectively dispersed into other highly porous and conductive materials, such as nanoporous metal [6], activated







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hindrance prevents precursor molecules from penetrating into the CNT forest deeply such that MnO₂ tends to clog over VACNTs instead of coating each CNT conformally [20,21]. The resulting electrode naturally suffers from poor performance caused by the non-ideal coating quality.

To resolve these issues, here we employ pulsed current deposition (PCE), a technique that have already been found instrumental to improve coating quality on an isolated CNT [41,42] or CNT mesh [14,29] but seldom on VACNTs [24]. We demonstrate that the PCE method can improve MnO_2 coating conformity by balancing the precursor ionic diffusion within the CNT forest. Consequently, the increased effectiveness of the pseudocapacitive layer renders the optimized composite electrode an unprecedentedly large specific capacitance particularly at high rate.

2. Experimental

2.1. Material synthesis

20-nm-thick Al and 3-nm-thick Fe were deposited via e-beam evaporation on $1 \text{ cm} \times 1 \text{ cm}$ Ni foils (Alfa Aesar, 99% metal basis, 0.025 mm in thickness) as catalyst. CNT growth using chemical vapor deposition (CVD) was then carried out in a hot-wall quartztube furnace (Lindberg Blue MTM Mini-MiteTM) at atmosphere pressure. Ni foils were loaded into the quartz tube and heated up to 750 °C at 30 °C/min, with 600 sccm of H₂ and 400 sccm of Ar flow rates. After annealing at this temperature for 20 min. additional $C_{2}H_{4}$ (250 sccm) was introduced to the furnace to initiate the VACNT growth with varving the nanotube height, or the VACNT mass. Upon completion of the growth step, the reactor was cooled in Ar atmosphere to room temperature. The mass of VACNT was determined by weighing it with a high-precision analytical microbalance (Mettler Toledo, XPE 105) before and after the growth. For simplicity, samples were named after their growth time, i.e., 1min-VACNTs, 3-min-VACNTs and 10-min-VACNTs. Typical growth rate was ~10 µm/min in terms of the forest thickness of or equivalently ~20 µg/min in terms of the mass of VACNT.

Electrodeposition of MnO₂ was carried out using a threeelectrode configuration in an electrochemical workstation (CH Instrument, CHI 660E). The VACNT-coated Ni foil was connected electrically to a Cu tape at the backside to external circuit and then encapsulated with an insulating polyimide (Kapton) tape, exposing approximately $0.8 \text{ cm} \times 0.8 \text{ cm}$ of effective area for a working electrode. A Pt wire was used as counter electrode, and a standard Ag/AgCl as a reference electrode. The solution for deposition was an aqueous mixture of 0.1 M Na2SO4 and 0.02 M MnSO4. Three different pulse widths (a 100% duty cycle in DCE with $t_{off} = 0$ ms, a 50% duty cycle with $t_{on} = t_{off} = 5$ ms in PCE 50%, and a 10% duty cycle with $t_{on} = 5$ ms and $t_{off} = 45$ ms in PCE 10%) were tested to optimize the electrodeposition condition. A deposition current of 5 mA was chosen particularly to ensure a high nucleation density without anodic oxygen evolution. For quick assessment, the mass of deposited MnO₂ was estimated from Faraday's law of electrolysis assuming 100% current efficiency. To obtain a better accuracy, the working electrode was thoroughly cleaned with deionized water and vacuum dried at 50 °C for 2 h before weighed.

2.2. Electrochemical and material characterization

Electrochemical measurements were conducted using the same setup except that the electrolyte was replaced by a Na₂SO₄ aqueous solution (1 M). Cyclic voltammetry (CV) scanning was performed in a potential range (V_t) from 0 V to 0.8 V at various scanning rates (ν). Total capacitance of the electrode (C_{total}), is calculated from eq. (1), in which *I* is the current.

$$C_{\text{total}} = \frac{\int IdV}{2V_t \nu} \tag{1}$$

Gravimetric specific capacitance (C_m) of the electrode is then defined by dividing the total mass m, which consists m_{CNT} and m_{MnO2} as the mass of VACNT matrix and MnO₂ loading, respectively. Areal specific capacitance (C_a) is calculated by normalizing to the working electrode area (A).

$$C_m = \frac{C_{\text{total}}}{m_{\text{CNT}} + m_{\text{MnO}_2}} \tag{2}$$

$$C_a = \frac{C_{\text{total}}}{A} \tag{3}$$

Galvanostatic charging and discharging (GCD) measurement was done in the same potential window but at different currents. C_m could also be obtained from eq. (4) during a discharging process after initial IR drop (V_{IR}).

$$C_m = \frac{2I \int_{t_c}^{t_c + t_d} V dt}{m(V_t - V_{IR})^2}$$
(4)

In this equation t_c and t_d are charging and discharging time, respectively, and thus Coulombic efficiency η is defined as:

$$\eta = \frac{t_d}{t_c} \tag{5}$$

Electrochemical impedance (EIS) was measured at a workingcounter electrode distance of ~4 cm and at frequency ranging from 0.1 Hz to 100 kHz at open circuit potential with an alternating amplitude of 5 mV.

Structure and morphology of the working electrode were characterized using scanning electron microscope (SEM, Hitachi, SU 8230). Quality of VACNTs and phase information of as-deposited MnO_2 were determined using a Raman spectroscope (Renishaw inViaTM) at 785 nm of an incident laser wavelength at 1% of the laser power. X-ray diffraction (XRD) spectrum of the sample was obtained with an X-ray diffractometer (Bruker, D8 Discover) using Cu K α radiation source (0.15418 nm in wavelength).

3. Results and discussion

Scanning electron micrographs of 10-min-VACNT/MnO2 samples reveal that at ~230 μ g of MnO₂ mass loading (m_{MnO2}) prepared via DCE, the top of the VACNT matrix is almost fully covered with granular MnO₂ (\sim 1 µm in size) (Fig. 1a). As proposed by a previous report [21], this clogging layer will block additional entrance of Mn^{2+} inside the CNT forest, leading to concentration drop and very little amount of coating near the bottom end (Fig. 1e). For samples prepared via PCE, on the other hand, MnO₂ growth pauses during a resting period (t_{off}) . With the same amount of deposition, smaller granules are formed (~500 nm in size) atop VACNTs, possibly leaving more (and larger) diffusion pathways. Moreover, Mn²⁺ ions can penetrate the CNT forest during the resting period, balancing the concentration polarization. As a result, more material is able to coat around CNTs (Fig. 1d, f), resulting in better coating quality. However, even with PCE, an obvious clogging layer still forms near the top few microns of the CNT forest at very high m_{MnO2} . With time, it is noticed that MnO₂ grows into granules (Figs. S2a-d), which eventually overlap with one another and almost fully block the top of VACNTs. A gradual decrease in the granule size is also observed from top to bottom (Fig. 1d), suggesting non-conformal



Fig. 1. (a, b) Top-view SEM images of 10-min-VACNTs/MnO₂ samples prepared by DCE (a) and PCE 10% (b), at ~230 µg mass loading. (c, d) Cross-section-view of the samples prepared by DCE (c) and PCE 10% (d), at ~575 µg mass loading. (e, f) Magnified view of (c) and (d) near the bottom end, respectively.

coating. The latter problem can be mitigated by switching to a shorter matrix (1-min-VACNTs, for example) with decreased ion diffusion lengths. In this way, MnO₂ granules can be formed into a nearly uniform size (~300 nm) along nanotubes (Fig. S2f).

To fabricate an effective SC electrode, it is of great importance to optimize C_m . SEM study expresses that too much deposition may only sacrifice device performance and waste material. To locate the optimal m_{MnO2} , a series of cyclic voltammetry (CV) experiments were performed. Fig. 2a shows typical CV scanning of a 10-min-VACNTs/MnO₂ sample prepared using PCE 10% (see the rest CV curves in Fig. S1). When pseudocapacitive MnO₂ is added to VACNTs, C_m, which is proportional to the area circled by the CV curve, rises monotonically with m_{MnO2} and saturates at ~235.2 µg. At the same time, the curve becomes distorted, behaving more "resistor-like" due to the increased thickness of MnO₂ coating. The Faradaic peaks (pointed by the arrow), originated from the intercalation (and deintercalation) of Na⁺ into MnO₂ [43-45], tend to shift outside the voltage window. When m_{MnO2} becomes too large, the incomplete Faradaic reaction likely weakens the trend of increasing in *C*_m.

We calculate C_m versus m_{MnO2} in Fig. 2c. For a sample prepared via DCE, the maximum value of C_m is found to be 101.7 F/g at mass loading of 311.3 µg. By introducing t_{off} (5 ms in PCE 50%) during deposition, maximum C_m upgrades to 128.9 F/g. Prolonging t_{off} to 45 ms (PCE 10%) leads to further improvement up to 138.9 F/g. This

finding matches with the improved coating quality (Fig. 1). Additionally, when shorter VACNTs are used, maximum C_m can be further increased; for 3-min- and 1-min-VACNTs/MnO2 samples, maximum C_m values are obtained at 198.8 F/g and 243.3 F/g with corresponding m_{MnO2} dropping to ~154.5 µg and ~50.7 µg, respectively. To make a fair comparison with reported MnO₂ based binary SC electrodes in aqueous electrolyte, C_m values at a fast scanning rate of 100 mV/s are listed in Table 1. It should be noted that some literatures report C_m by normalizing it to m_{MnO2} rather than the total mass (m_{total}). Such a metric might be misleading if "nonactive" mass (mass of CNT matrix, binder, and possibly the current collector in case a 3-dimensional metal foam is involved) takes up a significant portion of m_{total} . According to the tabulated values with correction to the best of our knowledge, C_m of our optimized electrodes exceeds the literature record [19] by ~21.6%. In terms of areal specific capacitance (C_a) , high-mass-loading electrodes (>20 mg/cm²) [8,31] provide much larger values than ours, despite that the corresponding C_m are smaller. This suggests that the material effectiveness in these electrodes is low.

Raman spectra confirms that crystalline phase of the asdeposited MnO_2 remains unchanged with the deposition condition (Fig. 2b). Therefore, better coating morphology, rather than phase, turns out to be responsible for the significant increase in C_m . In the two VACNTs/MnO₂ samples, peaks around 574 cm⁻¹ and 646 cm⁻¹ agree nearly perfectly with the literature value of Na⁺



Fig. 2. (a) Cyclic voltammetry of PCE 10% deposited 10-min-VACNTs/MnO₂ sample at 100 mV/s with respect to different MnO₂ mass loading, (c) dependence of MnO₂ mass loading on the gravimetric specific capacitance, and (d) capacitance of MnO₂ for various VACNTs/MnO₂ SC electrodes, with fitting using eq. (6). (b) Raman spectra of 10-min-VACNTs and 10-min-VACNTs/MnO₂ samples coated with either DCE or PCE 10%. Mass loading of these two samples are similar.

Table 1

Summary of specific capacitance at 100 mV/s of MnO₂ based binary supercapacitor electrodes using flat current collectors. Abbreviations: SCE, saturated calomel electrode; AC, activated carbon; Gr, graphene.

Reference	C_m (F/g)	Voltage range	Preparation method	$C_a (\mathrm{mF}/\mathrm{cm}^2)$
[5]	50	0.1-0.8 V vs. Ag/AgCl	MnO ₂ nanoflake and CNT co-filtration	50
[14]	77	-0.1-0.9 V vs. SCE	Voltage pulse deposition in CNT mesh	47
[19]	200	-0.1-0.8 V vs. SCE	DCE in CNT mesh with Gr additive	-
[21]	179	0-1 V vs. SCE	KMnO ₄ dropwise dipping in VACNTs	-
[27]	100	-0.1-0.9 V vs. SCE	KMnO ₄ and Mn ²⁺ reaction with CNT	-
[29]	75	0-0.8 V vs. Ag/AgCl	High voltage pulse deposition in CNT mesh	200
[31]	10	0-0.9 V vs. SCE	MnO ₂ CNT mixture at high loading	700
This work	243.3	0-0.8 V vs. Ag/AgCl	PCE 10% on 1-min-VACNTs	26.5
[8]	15	-0.3-0.6 V vs. Ag/AgCl	Potenialstatic deposition on AC	420
[12]	90	-0.4-0.6 V vs. Ag/AgCl	MnO_2 nanorods mixed with Gr nanoflakes	_

intercalated α -MnO₂ [46]. The α phase is considered preferable for the SC application given its large crystalline vacancies for cation intercalation [47]. D peak (1308 cm⁻¹) and G peak (1594 cm⁻¹) of VACNTs are determined according to the literature [48], and their intensity ratio (I_D/I_G) is calculated as 0.59 for as-grown VACNTs on a Ni foil. In a sample prepared via PCE and DCE, I_D/I_G rises to 0.98 and 1.54, respectively, indicating more defects and increased resistivity [49]. The relative intensity of MnO₂ observed particularly pronounced for the DCE sample (Fig. 2b) is likely attributed to a clogging layer of MnO₂ on top of VACNTs, in agreement with the SEM images (Fig. 1a, c). X-ray diffraction spectrum also suggests the α phase of as-deposited MnO₂ (Fig. S3).

To explore the nature of capacitance of $MnO_2(C_{MnO2})$, we extract

it by deducting the capacitance of raw VACNTs (C_{CNT}) from C_{total} . Unlike a literature [42] in which the authors have managed to deposit MnO₂ electrochemically on an isolated CNT and observed a linear relationship between C_{MnO2} and m_{MnO2} , we discover a nonlinear relationship in the case of MnO₂ coating on VACNTs (Fig. 2d). An empirical formula (eq. (6)) is proposed to fit this relationship nicely:

$$C_{\rm MnO_2} = C_0 \left(1 - \exp\left[-\frac{m_{\rm MnO_2}}{m_0} \right] \right), \tag{6}$$

 Table 2

 Summary of fitting parameters used in eq. (6) for VACNTs/MnO₂ samples.

-					
	VACNT growth time	Preparation method	$C_0(\mathbf{F})$	$m_0 (\mu g)$	$C_0/m_0 ({\rm F/g})$
	10 min	DCE	0.09695	522.6	185.5
	10 min	PCE 50%	0.09475	317.8	298.1
	10 min	PCE 10%	0.09437	286.7	329.2
	3 min	PCE 10%	0.09804	296.4	330.8
	1 min	PCE 10%	0.09993	322.5	309.9

$$C_{m,MnO_2} = \frac{dC_{MnO_2}}{dm_{MnO_2}} = \frac{C_0}{m_0} \exp\left[-\frac{m_{MnO_2}}{m_0}\right],$$
(7)

where C_0 represents the saturation capacitance, and m_0 is a fitting parameter related to the coating quality (see discussion below),

(b) (a) 5 mV/s 0 1 mA/cm² 10 mV/s 0.8 0.2 mA/cm² 200 20 mV/s 0.5 mA/cm² Specific capacitance (F/g) Potential vs. Ag/AgCI (V) 50 mV/s 1 mA/cm² 0.6 100 2 mA/cm² 5 mA/cm² 10 mA/cm² 0 0.4 -100 0.2 100 mV/s -200 200 mV/s 500 mV/s 0.0 1000 mV/s -300 0.0 0.2 0.4 0.6 0.8 ò 100 200 300 400 500 600 Potential vs. Ag/AgCI (V) Time (s) Current density (mA/cm² (c) (d)₃₀₀ 10 10° 101 Anodic current CV scan Cathodic current GCD scan 280 10 (b/j) 260 Peak current (A) cap acitance 240 220 10 cific 200 Spe 180 before 0.94 IR correction 160 10 10³ 10² 101 102 101 10³ Scan rate (mV/s) Scan rate (mV/s) (e) (f) Capacitance retention Coulombic efficiency 100 Capacitance retention (%) Coulombic efficiency (%) (g) 80 120 (ohm) ohm 60 Ņ. 80 40 40 20 5.5 5.6 Z' (ohm) 0 ٥ 1000 ò 2000 6 8 ġ 10 Cycle number Z' (ohm)

Fig. 3. Cyclic voltammetry (a), Galvanostatic charging and discharging spectra (b), peak current (c) and gravimetric specific capacitance (d) of a 1-min-VACNTs/50.7 µg MnO₂ sample prepared with PCE 10% in various scanning conditions. (e) Lifetime performance at 1 mA/cm² and (f) Nyquist plot with zoom-in view near horizontal axis (g) inset.

values of which are tabulated (Table 2) for all the VACNT/MnO₂ samples characterized. A suitable description for the specific capacitance of MnO₂ ($C_{m,MnO2}$) can be given by the derivative of C_{MnO2} with respect to m_{MnO2} (eq. (7)). It predicts that high m_{MnO2} decreases the effectiveness of $C_{m,MnO2}$, partly supported by MnO₂ clogging of VACNTs upon excessive m_{MnO2} supply (Figs. S2a–c). As sizes of the diffusion pathway shrink with MnO₂ coating thickness, diffusion of the precursor ions apparently drops [50], thwarting further coating of MnO₂ inside the CNT forest. The process is analogous to membrane fouling [51] except that the pore blocking granules may grow. Supported in part by the SEM images of Fig. 1, a large m_0 value in the via-DCE-prepared sample implies that pore blockade could happen faster and more easily. A detailed mechanistic understanding associated with eq. (6) calls for further investigation.

Similar values of *C*⁰ are found for all samples, hinting the same mechanism of hindrance. Particularly, C_{MnO2} of three PCE-10% samples nearly overlap with one another (Fig. 2d). The improvement of C_m for short VACNTs, therefore, largely comes from the use of light matrices. Additionally, at very small amount of deposition (setting $m_{MnO2} = 0$ in eq. (7)), one can obtain the ultimate $C_{m,MnO2}$ as C_0/m_0 , a value that is ideally unrestricted by hindered diffusion. For the 10-min-VACNT samples, the increasing trend of C_0/m_0 with respect to t_{off} clearly conveys that the via-PCE-prepared samples have better (more homogeneous) coating quality, outperforming the via-DCE-prepared sample in terms of $C_{m,MnO2}$. When the same PCE 10% method was applied on VACNTs in different lengths, interestingly, C_0/m_0 remains more or less unchanged, showing a clogging-independent $C_{m,MnO2}$ at ~310–330 F/g. It is noteworthy that our result closely matches with the value obtained from thin MnO₂ coating on an isolated CNT (310 F/g at 15 mV/s) [42]. Even with limitations at high mass loading, this result bolsters the potential of PCE in rendering high-quality coating into the indentations of a very high aspect ratio.

Noticeably, less amount of m_{MnO2} is needed to optimize lighter VACNTs. As C_{CNT} is usually much smaller than C_{MnO2} , we may neglect it from C_{total} for simplicity. By taking the first-order derivative of C_m with respect to m_{MnO2} as null and using eqs. (6) and (7), one can have:

$$1 + \frac{m_{\rm CNT} + m_{\rm MnO_2}}{m_0} = \exp\left[\frac{m_{\rm MnO_2}}{m_0}\right]$$
(8)

Although analytically unsolvable, we can plot both sides of eq. (8) as functions of m_{MnO2} and search for the intersection as a graphical solution (Fig. S3). For the three PCE 10% samples with slightly different m_0 values, smaller m_{CNT} shifts the straight line (left hand side) downwards and intersects the exponential curve (right hand side) at a small value of m_{MnO2} . The solution is in reasonable agreement with the experimental data. The master curve from eq. (8) can, therefore, be of great help to predict the optimal m_{MnO2} if m_{CNT} is given.

To fully demonstrate the versatility of the optimized electrode, a 1-min-VACNT sample coated with optimal loading (~50.7 µg) of MnO₂ was prepared in the PCE 10% method and characterized with various approaches. From Fig. 3a, Faradaic peaks from intercalation (cathodic, around 0.3-0.5 V vs. Ag/AgCl) and deintercalation (anodic, around 0.4-0.6 V vs. Ag/AgCl) are clearly seen at 5 mV/s and tend to smear out at higher rates (v). The peak current (i_p) can be fitted against v with a and b as fitting parameters:

$$i_p = av^b, (9)$$

where *b* should range theoretically between 0.5 and 1, with 0.5 standing for a diffusion-controlled Faradaic current and 1 for a surface-limited capacitive current [52]. A fitted value of 0.94 for both anodic and cathodic processes indicates a mostly capacitive nature for such an electrode (Fig. 3c), also verified by nearly straight and symmetric galvanostatic charging-discharging (GCD) curves (Fig. 3b). Certain decay in capacitance can be seen with the increased rate, as shown in Fig. 3d. The highest C_m achieved is 282.6 F/g at 5 mV/s and can retain a considerable value of 161.2 F/g at extremely high scanning rate of 1 V/s, or 204.4 F/g at a large current density of 10 mA/cm². The excellent property is attributed to synergy between MnO₂ and VACNTs, which manifests a low series resistance (R_s) as ~5.45 Ω from the horizontal intercept in the Nyquist plot (Fig. 3f). Compared with uncoated VACNTs (Fig. S5), the increase in R_s is insignificant, even at a relatively high mass ratio between MnO₂ and CNT (70:30). A tiny charge-transfer resistance (R_{ct}) of ~0.05 Ω can also be found from the initial unfinished semicircle (Fig. 3g). This R_{ct} is insignificant compared with the reported O(1) Ω values of MnO₂/CNT composites in the literature [17,27,28,32], implying quite fast and easy Na⁺ adsorption/intercalation by our electrode. In addition, after 2000 GCD cycles at 1 mA/cm² (~9 A/g), the sample still holds ~87% of initial capacitance at nearly unity η , proving great stability (Fig. 3e).

4. Conclusion

Pulsed electrodeposition of pseudocapacitive MnO₂ on VACNTs is established for SC performance characterization. We discovered that MnO₂ coating quality is vital to the SC performance and hindered diffusion of ions across the clogging layer on top of VACNTs is responsible for the drop of C_m at high m_{MnO2} . Our PCE approach proves quite effective in alleviating the clogging behavior. Although a state-of-the-art C_m at high rate has been obtained in this work, it should be pointed out that this capacitance value still falls short of an ideal one (a theoretical specific capacitance of MnO₂ of 1380 F/g [3]). Further improvement is still possible, should techniques such as atomic layer deposition (ALD) be there to allow for a truly conformal coating of MnO₂, with perhaps a larger optimal mass loading. Practically, given the excessive cost of the ALD process, our PCE method in the liquid phase may still find its place for largescale high-rate applications. Moreover, we foresee the possibility of extending PCE to a semi-conformal coating of various materials, e.g., oxides, onto VACNTs as a low-resistance platform for many other electrical and electrochemical applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2018.11.062.

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