

# Combinatorial arrays and parallel screening for positive electrode discovery

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## Abstract

Combinatorial techniques have been applied to the preparation and screening of positive electrode candidates for lithium batteries. This work describes the automated parallel synthesis of 64-electrode arrays using a Packard Multiprobe II liquid handling system. A cell was constructed with a single lithium reference-counter electrode and 64, three-millimeter-diameter working electrodes containing  $\text{Li}_x\text{Mn}_2\text{O}_4$  active material, PVdF-HFP binder and carbon black as a conducting additive. Eight duplicate electrodes, each of eight respective compositions, were deposited on the array and the mass fraction of carbon was varied in steps from 1 to 25%. The results showed a rapid increase in capacity at the percolation limit of 3% for most cells. Some groups of nominally identical cells showed random variations in capacity, especially at low carbon loadings. The overall result is a demonstration of advantages of the combinatorial concept, which were time-saving and an improved statistical significance of the results compared with on-off experiments.

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## 1. Introduction

Combinatorial synthesis has become an important technique for the discovery of new organic compounds with applications in the pharmaceutical industry. Using automated liquid handling equipment for parallel, multi-step syntheses, large “libraries” of compounds can be generated for rapid screening of biological activity. During the past 10 years, combinatorial chemistry has evolved in to a vibrant new discipline represented by several books [1], journals [2] and websites [3].

It is only in more recent times that the techniques of rapid array synthesis and screening have been applied to the discovery of catalysts and other materials [4]. Combinatorial approaches to electrochemical materials have been described by Reddington et al., who used an optical method to screen arrays of candidate materials as catalysts for methanol oxidation [5]. However, the present authors are unaware of any reports of combinatorial techniques being applied to battery materials except for an X-ray diffraction study [6] and the two other combinatorial papers that were presented at this lithium battery meeting [7,8].

Combinatorial synthesis is, in fact, particularly suited to the study of battery materials because here we have a group of materials where ternary, quaternary and even more complex compositions are often synthesized in efforts to meet the ever-increasing demands of new applications [9]. Furthermore, parallel screening is very appropriate because of the requirement for slow cycling in the characterization of battery electrodes; typical cycle times are a few hours rather than the few seconds typically encountered in other electrochemical areas. Until recently, however, multichannel battery cycling equipment has been expensive in terms of both capital equipment costs and laboratory space. Although such equipment is justified in the testing of complete battery modules, benchtop instruments are more appropriate for parallel screening of materials. Therefore, we will demonstrate the benefits of miniaturization of electronic equipment which have only recently become available.

The overall aims of our program are to develop automated synthesis methods to construct libraries of battery electrode materials, and to develop parallel screening methods for predicting performance in devices. Ultimately we will have available a variety of synthesis methods, such as sol-gel, chemical and physical vapor deposition. Similarly, we intend to have parallel screening of crystallography and morphology in addition to the usual electrochemical cycling

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parameters in the longer term. However, our initial objectives in this work were as follows:

- To develop a parallel fabrication procedure for an array of positive electrodes.
- To construct a suitable multi-channel cell to accommodate the array.
- To measure cycling performance simultaneously for all 64 working electrodes and compare with results obtained by conventional methods.

In order to satisfy the first and third aims, we chose a simple ternary system to demonstrate the concept with the composite electrode:

$\text{Li}_x\text{Mn}_2\text{O}_4|\text{PVdF}|\text{HFP}|\text{carbon black}$

In this case, a range of composite electrodes with different carbon loadings can be prepared simply by mixing different proportions of two dispersions in a suitable solvent. After deposition on the current collector array, simple drying is enough to fabricate the electrodes without heating or any further processing. The effect of carbon black is to facilitate electronic conductance from the current collector to the particles of active material bound together by PVdF–HFP. The composition dependence of the effect is well known [10]; the amount of carbon black required for percolation of the electronic conduction network can be very small, and the electronic conductivity rises very rapidly with volume fraction above the percolation threshold. Similarly, the high rate performance of the electrodes also improves dramatically with the percolation of the electronic conduction network [11].

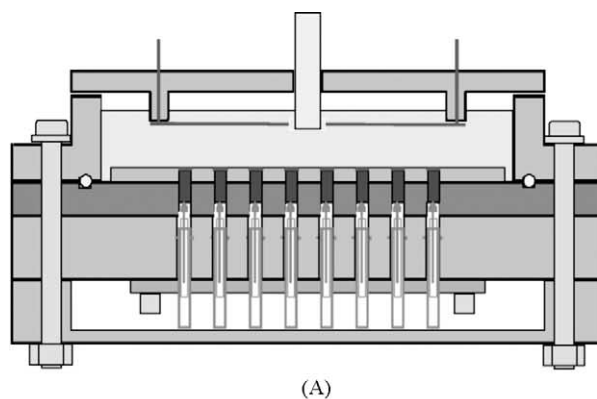
## 2. Experimental

### 2.1. Fabrication of the current collector array and multi-channel cell

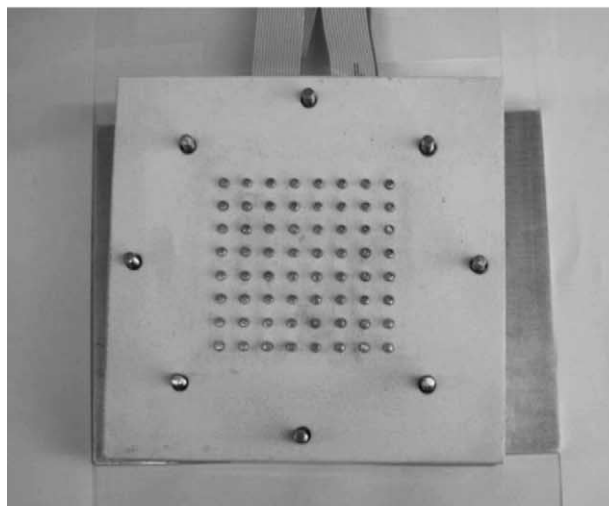
A multi-channel cell array was constructed to a design similar to that used in our fuel cell catalysis program. This consisted of 64 inert current collectors inserted as a square array into an insulating substrate (Fig. 1(A)). In the present work, the current collectors were constructed of aluminum, which passivates well under the conditions of positive electrode cycling. The multi-electrode plate was designed to be part of the complete cell (Fig. 1(B–C)) which also included a top plate, which exerted uniaxial pressure on the lithium counter-reference electrode and a glass fiber separator soaked in 1 M  $\text{LiPF}_6$  in propylene carbonate as the electrolyte. A hermetic seal was provided by a nonconductive “O” ring compressed between eight nuts and bolts.

### 2.2. Ink preparation

Thin film electrodes were prepared from metered mixtures of two inks, one containing the active material mixed



(A)



(B)



(C)

Fig. 1. Cell views: (A) schematic; (B) electrode array from above; and (C) assembled cell.

with 10% by mass PVdF–HFP binder, and the other containing acetylene black (100% compressed, Chevron) mixed with 10% binder in solid contents. The respective solids were dispersed in sufficient cyclopentanone (CP) to give a suitable viscosity for electrode coating without blocking the syringes; thus 75% CP was used in the  $\text{LiMn}_2\text{O}_4$  and 90% CP in the carbon ink. These inks were then placed in sealed

containers and stirred continuously to ensure homogeneity (usually overnight) until required for electrode preparation.

### 2.3. Electrode preparation

The two ink vessels were placed on the deck of the “robot”—a Multiprobe II automated liquid handling system (Perkin-Elmer Life Sciences) and stirred throughout the procedure to ensure homogeneity. A polypropylene 96-well plate was used to hold the 64 inks after mixing in different proportions. During the mixing step a predetermined quantity of each ink was aspirated from the stock solution and placed into each individual well as programmed in a Microsoft Excel spreadsheet. Once both the inks had been deposited in a well, the robot performed two additional mixing steps by re-aspiration of the solution into a pipette and re-deposition into each well. Approximately  $1\ \mu\text{l}$  ( $\pm 10\%$ ) of ink was then transferred from each well to the corresponding electrode. The mass of active material deposited on each electrode was calculated by multiplying the volume dispensed by the mass concentration of active material suspended in the ink.

### 2.4. Electronic instrumentation

The technique for evaluating high rate performance in this work was cyclic voltammetry rather than galvanostatic or constant load discharge as is often preferred in industry. The reason for choosing potential control was simplicity of instrumentation, whereby the same potential, versus a common reference-counter electrode, could be applied simultaneously to all electrodes while measuring currents independently.

A 64-channel potentiostat was built in-house according to our standard ring-disc electrode potentiostat design, using the same potential control circuit but a separate current follower for each channel. An array of 16 quad operational amplifiers with four  $10\ \text{k}\Omega$  feedback resistors each was connected to a Talisman 64-channel A/D converter board plugged into a 1.6 GHz PC. This arrangement gave a conversion factor of  $10\ \text{V mA}^{-1}$ .

### 2.5. Combinatorial electrode cycling

A single channel of a Perkin-Elmer VMP potentiostat applied a common potential versus ground to the reference-counter electrode while the working electrodes in the array were held at ground potential by the current followers. A cyclic potential was applied between the open circuit potential, 3.2 and 4.5 V versus Li, initially at a scan rate of  $0.1\ \text{mV s}^{-1}$ . Current data were recorded at one reading every 10 s on each channel using software written in-house using Visual Basic. (Faster acquisition rates up to a possible 100 readings per second were possible, but undesirable because of the excessive data accumulated over many slow cycles).

### 2.6. Additional characterization of electrode composites

Thin film samples were made by a “doctor blade” method for the determination of electronic conductivity by the four-point probe method in order to check the percolation behavior of the carbon black used in the combinatorial study.

One centimeter diameter discs were cut from the film and cycled galvanostatically in hermetically-sealed stainless steel cells using the same electrolyte as in the combinatorial tests.

Scanning electron micrographs of samples deposited automatically were taken using a Philips XL30 Environmental SEM.

## 3. Results and discussion

Fig. 2 shows SEM results for samples with carbon black contents varying from 1 to 20%. Grey particles are assumed to be  $\text{LiMn}_2\text{O}_4$  and the light spots are probably the PVdF-HFP binder. The dark patches, attributed to carbon black, can be seen to increase across the series as expected.

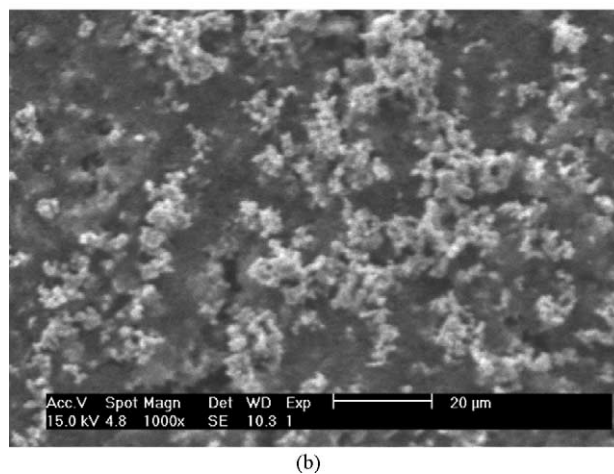
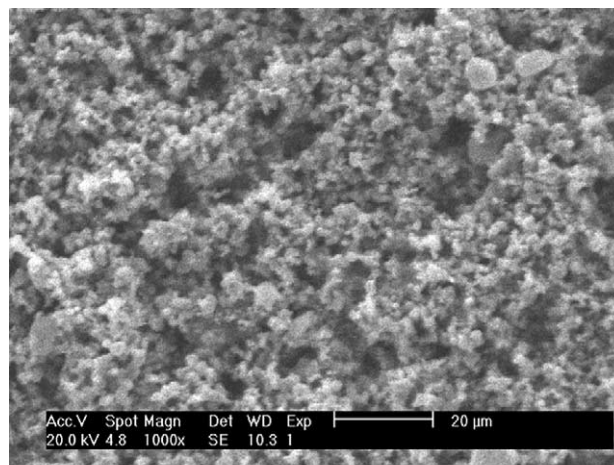


Fig. 2. SEM showing the carbon additive in: (a) 2 wt.% carbon; (b) 20 wt.% carbon.

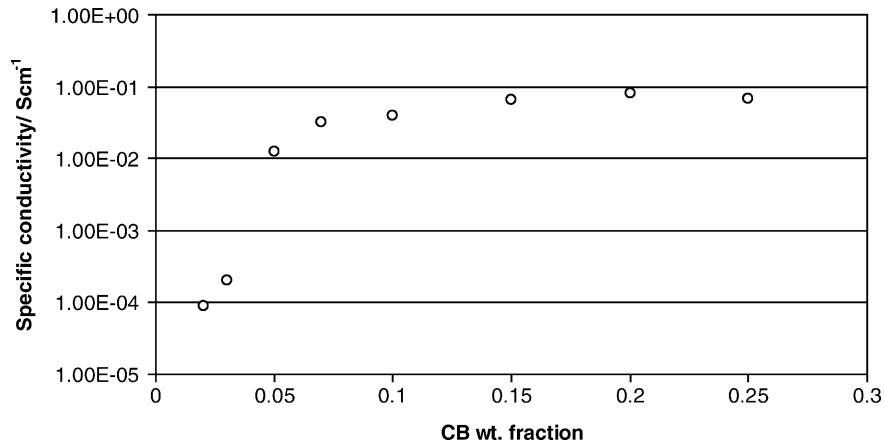


Fig. 3. Electronic conductivity vs. composition of composite electrode films.

However, the degree of agglomeration of carbon is surprisingly high, such that full contact between the carbon matrix and the electrode material is not achieved until 20% loading. Poor uniformity of the conducting additive may well be expected to give rise to anomalous cell cycling results.

The electronic conductivity of the composites is shown as a function of composition in Fig. 3. We note that the conductivity rose by two orders of magnitude between 2 and 5% carbon content, whereas, the increase in conductivity between 10 and 20% was only a factor of two.

Fig. 4 shows cyclic voltammograms taken simultaneously at a scan rate of  $0.1 \text{ mV s}^{-1}$ , corresponding to a discharge rate of about  $C/3$ , for eight, nominally identical electrodes containing 2% carbon. And the corresponding charge–voltage plots are obtained by integration. Each curve represents one cycle of one cell. In most cases, the current was still significant at the end of the anodic scan, showing that the active material was poorly equilibrated with the current collector. Only one, broad peak was shown in each half cycle, indicating that the active particles were not at equilibrium with each other. The specific charge values were also very low, and only reached maximum values after current reversal following the anodic scan. Fig. 5 shows the results for electrodes containing 3% carbon, where we note a better resolution of the voltammograms for about half of the cells. Also, half the cells showed specific charges close to the expected value of  $120 \text{ mAh g}^{-1}$ . The cells containing 20% carbon (Fig. 6), in most cases, showed two distinct peaks in the cyclic voltammogram as expected for this material. Also, the current fell to zero outside the active region between 3.6 and 4.4 V. The charge–potential plots showed proper equilibration at the end of each half cycle. Furthermore, the curves were geometrically similar in all cases, differing only by expansion along the charge axis.

The result of testing the same electrode compositions using a conventional method is shown in Fig. 7. This figure shows a clear electronic percolation effect at 3% by volume, confirming the combinatorial result.

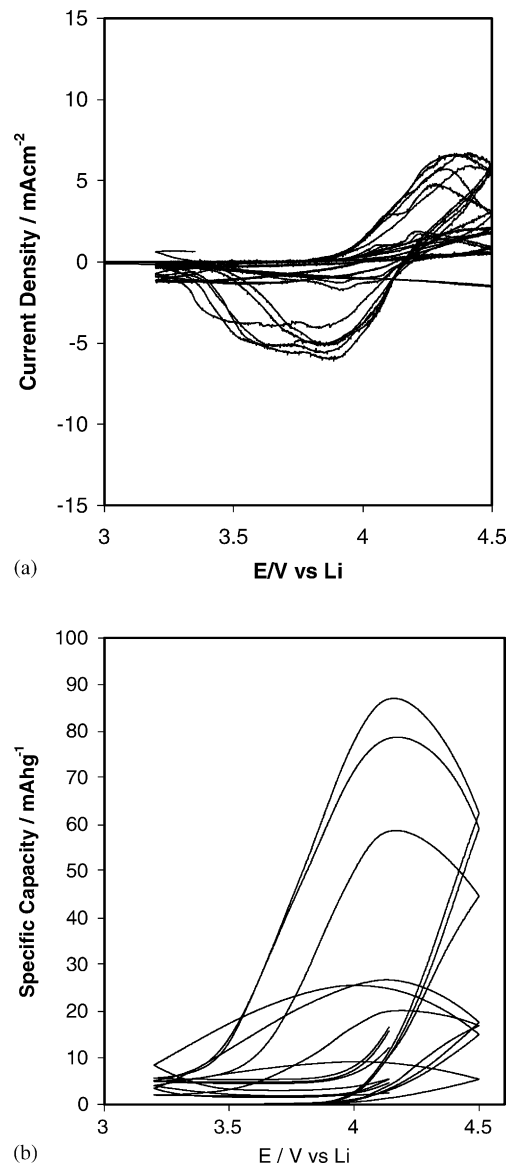


Fig. 4. Simultaneous cyclic voltammograms of electrodes containing 2% carbon.

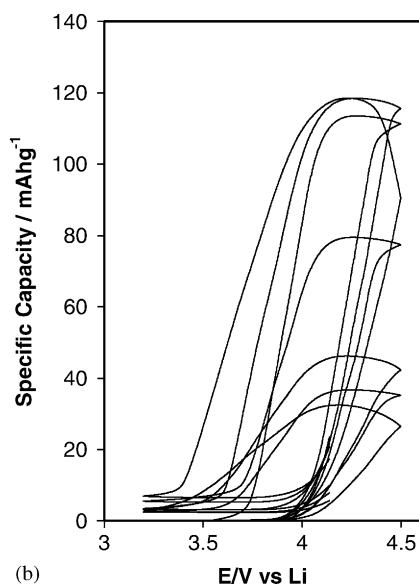
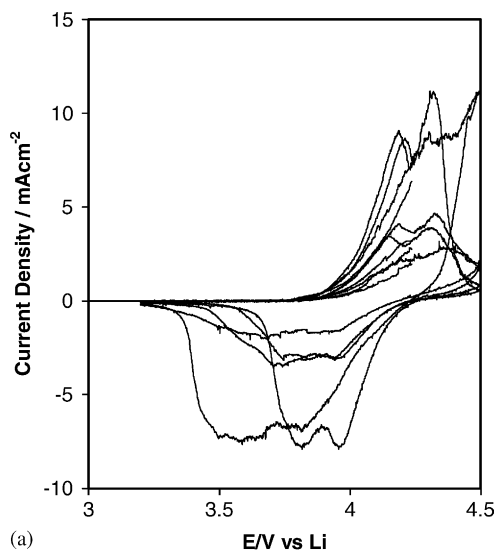


Fig. 5. Simultaneous cyclic voltammograms of electrodes containing 3% carbon.

The results immediately show that the combinatorial approach does indeed lead to a significant evaluation of electrode materials. The observation of a strong percolation effect at around 3% carbon loading is in agreement with results obtained from individually made cells. In this series of automatically prepared electrodes, a 20% carbon loading was required to obtain effective cycling of the material in most cases. An unexpected feature of these results is the nature of the scatter in results, which is probably due to non-uniform deposition of the active material and carbon during the automated electrode fabrication procedure. The specific charge plots were calculated by dividing the charge passed per element by the nominal active mass in each electrode. Therefore, the spread of values above and below the theoretical value for 20% carbon loading indicates a random error in the amounts of active material deposited on each

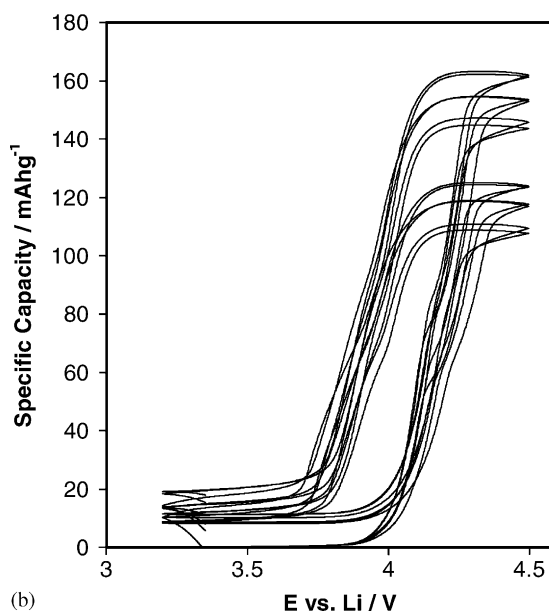
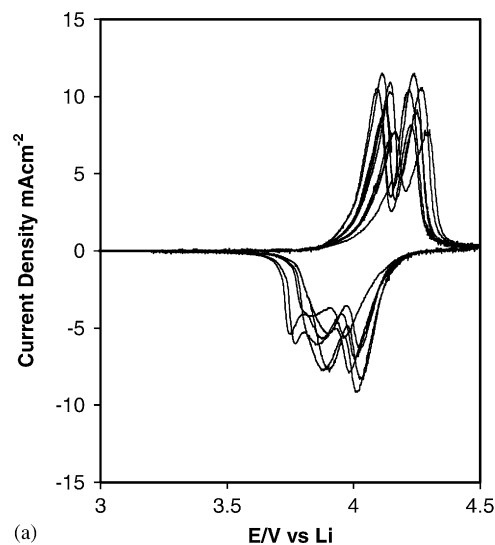


Fig. 6. Simultaneous cyclic voltammograms of electrodes containing 20% carbon.

element. In the examples with 3% loading, differences in shapes of voltammograms indicate differing extents of percolation of the electronic conductivity, presumably due to aggregation and non-uniform deposition of the carbon additive.

The outcomes of this investigation are an expectation of further developments of the combinatorial screening method and some guidelines for future experimental designs. The spread in behavior observed for nominally identical samples is a point for concern. Two sources of error are being investigated, errors in liquid metering and insufficient homogenization of the feed solutions. Both of these errors are increased with decreasing sample size, and in this respect the choice of array element size of 3 mm must be considered fortunate. Lower values would have produced unacceptable error margins, whereas, higher values would have defeated



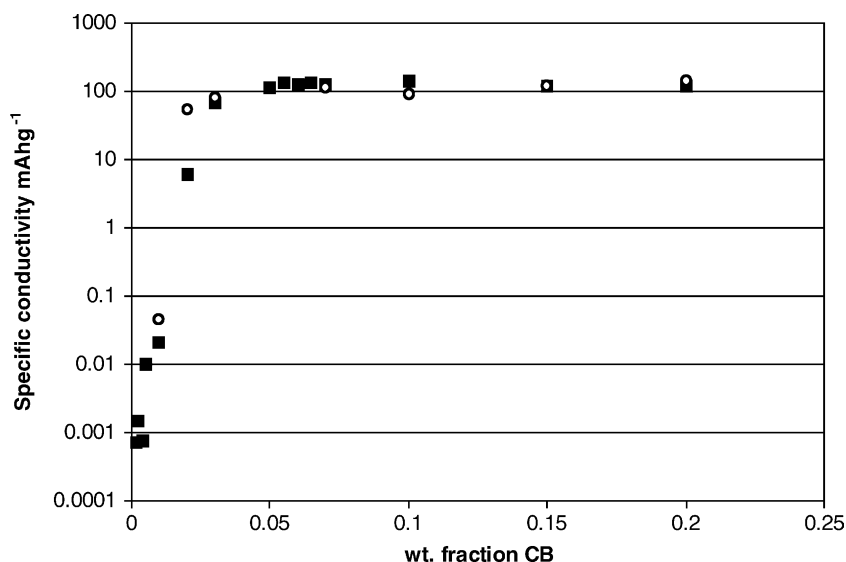


Fig. 7. Capacity vs. composition curves comparing results: for individual cells (circles), with results averaged from the array (open squares).

the objectives of reducing size and cost. The sample mass of just <1 mg is also convenient for post-deposition analysis as well as economically desirable for a program involving many thousands of samples per library. The duplication of experiments for nominally identical samples is a welcome and affordable confidence indicator, and will probably be retained.

The use of slow-scan cyclic voltammetry instead of galvanostatic cycling has proved successful in this instance, providing a meaningful result at a reduced cost compared with a multi-channel galvanostat.

#### 4. Conclusions

A combinatorial synthesis method combined with a parallel screening method has been demonstrated for battery electrodes. Sixty-four electrodes were prepared in an array by an automated mixing and deposition system, then cycled simultaneously with individual current monitoring. Results on the effect of the amount of carbon black in  $\text{LiMn}_2\text{O}_4|\text{PVdF}|\text{HFPE}|\text{acetylene black}$  composite electrodes closely matched results of conventional experiments in the same system, showing a sharp electronic percolation threshold at 3% by volume.

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#### References

- [1] A.W. Czarnik, S.H. DeWitt, *A Practical Guide to Combinatorial Chemistry*, American Chemical Society, Washington DC, 1997 (ISBN 084123485X).
- [2] *Combinatorial Chemistry*, Mol Divers, Biotechnology and Bioengineering, J. Comb. Chem.
- [3] <http://www.combichem.net>.
- [4] W.F. Maier, *Angew. Chem. Int. Ed.* 38 (1999) 1216–1218.
- [5] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, *Science* 280 (1998) 1735–1737.
- [6] K.C. Hewitt, A. Bankdarpour, D. MacNeil, Z. Chen, J.R. Dahn, *Electrochem. Soc., Abstracts vol. MA (2001–2)* (Abstract no. 145).
- [7] J.R. Dahn, IMLB 11, Monterey (2001).
- [8] K. Fujimoto, I. Yanase, T. Ohtaki, A. Kajiyama, K. Takada, T. Sasaki, M. Watanabe, IMLB 11, Monterey (2001) (Abstract no. 268).
- [9] Z. Liu, J.R. Dahn, *J. Electrochem. Soc.* 148 (2001) A237–A240.
- [10] L. Flandin, T. Prasse, R. Schueler, K. Schulte, W. Bauhofer, J.Y. Cavaille, *Phys. Rev. B* 59 (1999) 14349–14355.
- [11] S. Mandal, J.M. Amarilla, J. Ibanez, J.M. Rojo, *J. Electrochem. Soc.* 148 (2001) A24–A29.