Adsorption (2009) 15: 172–180
DOI 10.1007/s10450-009-9169-6

Quantitative assessment of hysteresis in voltammetric curves of electrochemical capacitors

Marek Kosmulski · Piotr Próchniak · Czesław Saneluta

Published online: 26 March 2009

Abstract A family of coefficients for quantitative assessment of hysteresis in cyclic voltammetric (CV) curves of electrochemical capacitors and of electrodes for electrochemical capacitors has been defined. Hysteresis index 1 (HI1) is based on the maximum in the difference in current measured at the same potential in ascending and descending branch of CV curve, and HI2 is based on the average difference in current measured at the same potential in ascending and descending branch of CV curve. The values of HI1 and HI2 range from 0 (no hysteresis) to 1 for an ideal capacitor. CV curves of two commercially available electrochemical capacitors over a potential range 0–1500 mV at scan rate of 5 mV/s showed HI1 of 0.94 and 0.97 and HI2 of 0.77 and 0.83, respectively. At the same experimental conditions, a series of 52 home made electrochemical capacitors showed HI1 up to 0.7 and HI2 up to 0.55. HI1 and HI2 measured at constant scan rate (5, 20 or 50 mV/s) in that series of capacitors showed a correlation coefficient >0.98 while HI1 and HI2 measured at different scan rates showed limited correlation. 98 CV curves of electrochemical capacitors and of electrodes for electrochemical capacitors from literature, obtained at various conditions show HI1 from 0.42 to 1, HI2 from 0.27 to 0.97, and a correlation coefficient of 0.90 between HI1 and HI2.

Keywords Cyclic voltammetry · Electrochemical capacitor · Electrode materials · Low temperature ionic liquids

M. Kosmulski (✉) · P. Próchniak · C. Saneluta
Department of Electrochemistry, Lublin University of Technology, Lublin, Poland
e-mail: mkosmuls@hektor.umcs.lublin.pl

1 Introduction

Cyclic voltammetry (CV) is used to assess the quality of electrochemical capacitors (built of two similar high-surface-area electrodes) (Arulepp et al. 2004; Fang and Binder 2006a, 2006b, 2007; Frackowiak and Beguin 2001; Frackowiak et al. 2002; Gryglewicz et al. 2005; Gu et al. 2000; Hahn et al. 2004; Janes et al. 2007; Jurewicz et al. 2004; Kierzek et al. 2004; C. Kim et al. 2004; Lewandowski et al. 2001, 2003; Lewandowski and Krzyzanowski 2003; Lewandowski and Olejniczak 2007; Lewandowski and Swiderska 2003; Lust et al. 2004a, 2004b; Michael and Prabaharan 2004; Ryu et al. 2007; Sun et al. 2006; Tripathi et al. 2006; Vix-Guterl et al. 2004, 2005) and of electrodes for electrochemical capacitors (high-surface-area electrode and low-surface-area counter electrode, usually Pt) (Balducci et al. 2004; Barbieri et al. 2005; Chang and Hu 2006; Conway 1991; Dong et al. 2006; Eliad et al. 2001; Fischer et al. 2007; Gupta and Miura 2006; Hu et al. 2007a, 2007b, 2007c; Huang et al. 2007; Hulicova et al. 2005, 2006; Jang et al. 2006; Jung et al. 2004; Karandikar et al. 2007; Kim and Mitani 2006; K.M. Kim et al. 2004; Kim et al. 2006; Lee and Pyun 2006; Lee et al. 2004; Lee et al. 2007; Leitner et al. 2006; Li et al. 2006; Li et al. 2007; Liu et al. 2006; Miller and Dunn 1999; Mitani et al. 2006; Morishita et al. 2007; Nam et al. 2007; Nanbu et al. 2006; Okajima et al. 2005a, 2005b; Pollak et al. 2007; Prasad et al. 2004; Sugimoto et al. 2005, 2006; Tashima et al. 2007; Toyoda et al. 2004; Wan et al. 2007; Wang and Xia 2005; Wang et al. 2006; Wen et al. 2006; Xing et al. 2006; Xu et al. 2007; Yamada et al. 2007; Yang et al. 2005; Zhou et al. 2007; Zhu et al. 2006; Zolfaghari et al. 2007). Figures 1a–1c presents voltammetric curves for ideal capacitor (a), for ideal resistor (b), and a typical curve for actual (nonideal) electrochemical capacitor (c). Usually

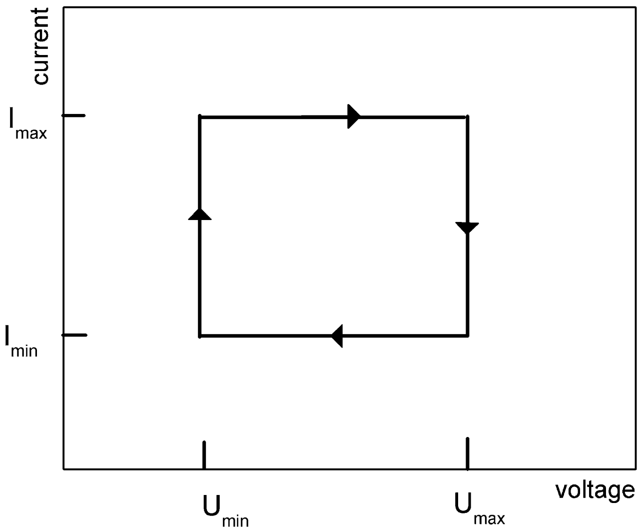

Fig. 1a CV curve of ideal capacitor

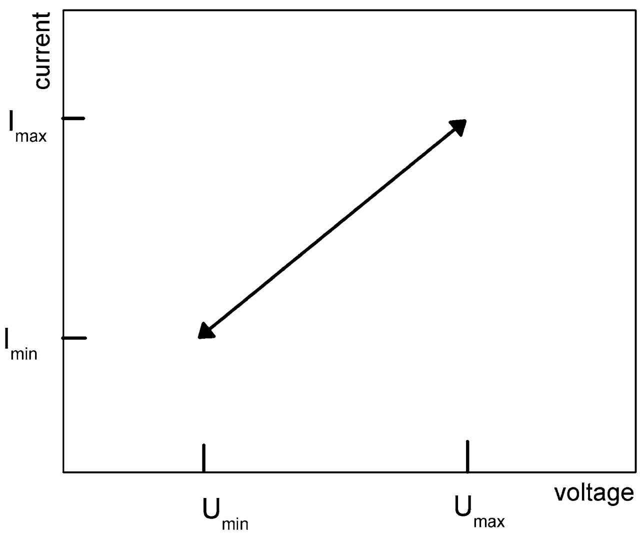

Fig. 1b CV curve of ideal resistor

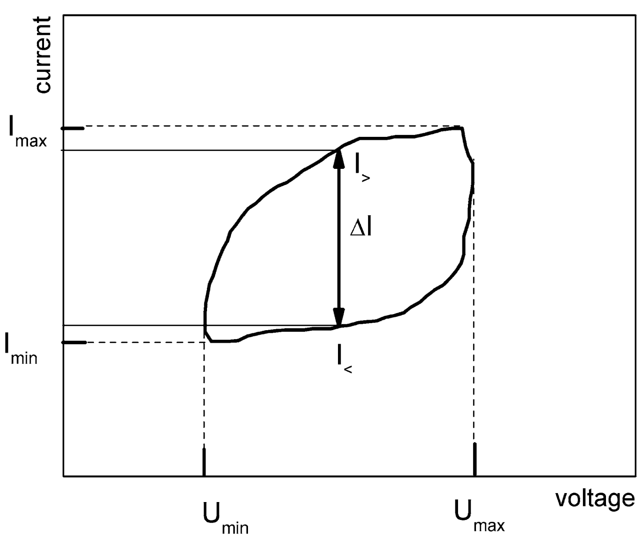

Fig. 1c CV curve of typical electrochemical capacitor

the current is plotted as a function of voltage. In several publications, the quantities other than current, e.g., current per unit of mass (Chang and Hu 2006; Fischer et al. 2007; Hu et al. 2007a, 2007b, 2007c; Huang et al. 2007; Kim and Mitani 2006; Kim et al. 2006; Lee et al. 2007; Li et al. 2006; Mitani et al. 2006; Nanbu et al. 2006; Okajima et al. 2005a, 2005b; Prasad et al. 2004; Sugimoto et al. 2005; Toyoda et al. 2004; Wen et al. 2006; Xing et al. 2006), current per unit of surface area (Chang and Hu 2006; Karandikar et al. 2007; Lee and Pyun 2006; Yang et al. 2005; Zhu et al. 2006; Nam et al. 2007) or capacitance per unit of mass (Barbieri et al. 2005; Frackowiak et al. 2002; Gryglewicz et al. 2005; Jurewicz et al. 2004; Lee et al. 2004; Leitner et al. 2006; Liu et al. 2006; Okajima et al. 2005a, 2005b; Pollak et al. 2007; Sugimoto et al. 2006) are plotted as a function of voltage. These quantities are obtained by multiplication of the current by a constant number, and as we show later, the method proposed in the present study applies for all these types of plots. We examined 77 recent papers from over 30 laboratories, in which electrochemical capacitors and electrodes for electrochemical capacitors were studied by CV. In those papers the assessment of CV curves was limited to qualitative statements. Several voltammograms were described as "box-like" (Gryglewicz et al. 2005; Jurewicz et al. 2004; Morishita et al. 2007; Xu et al. 2007), rectangular (Hu et al. 2007a, 2007b, 2007c; Lee and Pyun 2006; Lee et al. 2004; Lee et al. 2007; Li et al. 2007; Nam et al. 2007; Okajima et al. 2005a, 2005b; Sugimoto et al. 2006; Yang et al. 2005; Zolfaghari et al. 2007), "nearly rectangular" (Conway 1991; Fischer et al. 2007; Huang et al. 2007; C. Kim et al. 2004; Li et al. 2006; Liu et al. 2006; Prasad et al. 2004; Toyoda et al. 2004; Zhu et al. 2006; Xing et al. 2006), etc. (more examples are given in Table 4), while in several other voltammograms, deviations from rectangular shape were pointed (Lee and Pyun 2006; Mitani et al. 2006; Okajima et al. 2005a, 2005b; Pollak et al. 2007). Those subjective statements are of limited significance, and similar shape is assessed as nearly rectangular by one author and as substantially different from rectangular by another author. A few authors (Fang and Binder 2006a, 2006b, 2007) used terms like "more rectangular" or "most rectangular" to compare different CV curves presented in one publication. In the present paper we developed a versatile and objective method to quantify the deviations of CV curves of capacitors from ideal shape. Hysteresis indices have been widely used in different fields, e.g., in adsorption-desorption studies (Sander et al. 2005). To our best knowledge hysteresis indices have not been used in assessment of CV curves. It should be emphasized that the hysteresis in CV curves (or more generally in force-flow curves) does not represent deviations from equilibrium state as it is the case for the hysteresis in adsorption-desorption curves.

Hysteresis indices introduced in the present study are not aimed at explanation of the nature of physical and electrochemical phenomena responsible for deviations of CV curves from rectangular shape. Deviations of CV curves of actual capacitors from rectangular shape are chiefly due to their electric resistance and to redox processes (Frackowiak and Beguin 2001), and the shape of CV curves has been widely used as a source of information about these processes. The present study is focused on development of quantitative method of assessment of the deviations of shape of CV curves from rectangular, rather than on physical interpretation of these deviations.

2 Definition of hysteresis indices

Let us consider a CV curve shown schematically in Fig. 1c. The potential range is from $U_{\min}$ to $U_{\max}$ and the current ranges from $I_{\min}$ to $I_{\max}$. Often, but not always $I_{\min}$ corresponds to $U_{\min}$ and $I_{\max}$ corresponds to $U_{\max}$. The CV curve is presented as a continuous curve but in fact it consists of finite number of data points measured at discrete U values. For each discrete U value, ΔI is defined as $I_{>} - I_{<}$ where $I_{>}$ is the current on the increasing branch and $I_{<}$ is the current on the decreasing branch at the same U, and

$$\Delta I_{\mathrm{rel}} = \Delta I/(I_{\max} - I_{\min}) \tag{1}$$

ΔI_{rel} is a dimensionless number, and the same value of ΔI_{rel} is obtained when current in ΔI, $I_{\min}$ and $I_{\max}$ in (1) is replaced by current per unit of mass, current per unit of surface area, capacitance per unit of mass or by any other quantity obtained by multiplication of current by a constant number.

The hysteresis indices are defined as

$$\mathrm{HI1} = \text{maximum in } \Delta I_{\mathrm{rel}}(U_{\min} \cdots U_{\max}), \tag{2}$$

$$\mathrm{HI2} = \text{average of } \Delta I_{\mathrm{rel}}(U_{\min} \cdots U_{\max}) \tag{3}$$

If the data points in the increasing and decreasing branch were measured at the same values of U, ΔI can be obtained directly from data points. Otherwise interpolation can be used to obtain $I_{>}$ and $I_{<}$ for certain values of U. With a smooth CV curve without maximums and minimums (caused by redox processes), HI1 is rather insensitive to the number and distribution of data points taken into consideration. HI2 is more sensitive to the number and distribution of data points than HI1. For example with limited number of data points evenly distributed between $U_{\min}$ and $U_{\max}$, the narrow ends of the CV curve are overrepresented and HI2 is underestimated. Obviously HI1 and HI2 are both equal to 0 for an ideal resistor (Fig. 1b) and to 1 for an ideal capacitor (Fig. 1a), and HI1 $\geq$ HI2 for any capacitor. Since value of maximum difference between $I_{\min}$ and $I_{\max}$ is in denominator of indices, theirs values are never more than 1. Good electrodes and good capacitors have high HI1 and HI2 (close to 1), and poor electrodes and poor capacitors have low HI1 and HI2 (close to 0).

3 Experimental

The properties of HI1 and HI2 hysteresis indices have been tested against actual capacitors. PC5 and PC10 are commercial electrochemical capacitors from Maxwell. A series of 52 home made coin-type capacitors has been also studied. Namely, two co-axial, identical, coin-sized and coin-shaped, porous electrodes were separated by a thin layer of a porous insulating material, pressed together, and the pores were saturated with the electrolyte. The electrodes of these capacitors were made by deposition of carbon in pores of porous ceramic monoliths by different methods, from different carbon precursors. Ceramic monoliths were obtained from 3 types of alumina, silica, titania and Y-stabilized zirconia. Dichloromethane, cyclohexene and glucose were used as precursors of carbon deposits. Another series of composites was obtained by carbonization of 1-decanol and phenol-formaldehyde resin Nowolak-L. Impregnated ceramic matrix was heated at 500 °C for 2 hours for 1-decanol and 6 hours for Nowolak-L. Then samples was heated to 800 °C for 3 hours in hydrogen. Ceramic monolith was used as a separator, and low temperature ionic liquids (1-alkyl-3-methylimidazolium trifluoromethylsulfonates, tetrafluoroborates, and hexafluorophosphates) were used as electrolytes. Details of preparation of electrodes from dichloromethane, cyclohexane, glucose and of the experimental setup are reported elsewhere (Kosmulski et al. 2007). The series of 52 capacitors used to test the properties of HI includes many unsuccessful attempts to make an electrochemical capacitor. Such unsuccessful attempts are seldom published. M16 electrochemical analyzer (MTM-ANKO, Poland) was used. The CV curves in potentiodynamic conditions in two-electrode system were obtained over the potential range 0 to +1500 mV for all 52 capacitors and over the potential range −1500 mV to +1500 mV for 23 selected capacitors (with 1-ethyl-3-methylimidazolium trifluoromethylsulfonate as the electrolyte). The scan rates were 5, 20, 50 mV/s. Every CV curve consisted of about 560 data points (the exact number depended on the scan rate and range). In another home made capacitor the electrodes were made of similar ceramic-carbon composite, but 20% H_2SO_4 was used as an electrolyte. In view of a narrow electrochemical window of water, the potential range was limited to 0 to +1000 mV for that capacitor. The numerical values of HI and of correlation coefficients reported below were rounded to 2 decimal digits.

4 Results and discussion

The CV curve of PC5 (commercial capacitor) over a potential range 0–1500 mV at scan rate of 5 mV/s showed HI1 of 0.97 and HI2 of 0.83 and the CV curve of PC10, showed HI1 of 0.94 and HI2 of 0.77. The CV curves of home made capacitor with 20% H_2SO_4 over a potential range 0–1000 mV showed HI1(5) = 0.65, HI1(20) = 0.76, and HI1(50) = 0.78, and HI2(5) = 0.61, HI2(20) = 0.67, and HI2(50) = 0.63, where the number in brackets is the scan rate in mV/s. In spite of different scan ranges the results obtained for home made capacitor and for commercial capacitors can be compared, and the values of HI are clearly higher for the commercial capacitors. This result is not surprising, namely, coin-type geometry is not the optimal one for performance of capacitors. Moreover the ceramic-carbon composite in home-made capacitors showed a high electric resistance. The values of HI for home made capacitor with 20% H_2SO_4 were scan-rate-dependent, but there was no systematic trend, and the effect was not dramatic.

The results obtained for home made capacitors with low temperature ionic liquids as the electrolytes are summarized in Tables 1–3. The maximum, minimum, average and median values of HI1 and HI2 at different scan rates, and correlation coefficients between particular HI are reported. The highest HI reported in Tables 1–3 are comparable with corresponding HI for home made capacitor with 20% H_2SO_4, but on average the HI reported in Tables 1–3 are lower. The average and median HI in a series of capacitors decreased when the scan rate increased, but the effect was not very significant, and for individual capacitors different types of frequency dependence were observed. HI1 and HI2 at different scan rates showed some degree of linear correlation, that is, a capacitor which shows a high value of one HI is likely to show a high value of another HI and vice versa. The HI obtained at 20 and 50 mV/s showed a correlation coefficient >0.9, and the results obtained at 5 mV/s showed limited correlation with the results obtained at higher scan rates. HI1 and HI2 at the same scan rate showed a correlation coefficient >0.98. Then the assessment of deviations from rectangular shape in a series of CV curves based on HI1 and HI2 at the same scan rate favors the same capacitors, but it is not the case for HI at different scan rates. We also compared HI obtained for the same capacitor and different potential ranges. The HI for the potential range −1500 to 1500 mV were slightly higher than for the potential range 0 to 1500 mV (with a few exceptions), and the correlation coefficient of HI obtained for two potential ranges in a series of 23 capacitors was >0.95 at scan rates of 20 and 50 mV/s, and 0.78 (HI1) and 0.72 (HI2) at scan rate of 5 mV/s. Thus the choice of the scan range has limited effect on assessment of capacitors by means of HI.

We used an extensive set of experimental CV curves obtained at different conditions with different electrochemical

Table 1 Hysteresis indices HI1 and HI2 in a series of 52 home made capacitors, potential range 0 to 1500 mV. The numbers in brackets are scan rates in mV/s

	HI1(5)	HI1(20)	HI1(50)	HI2(5)	HI2(20)	HI2(50)
Maximum	0.7	0.76	0.74	0.55	0.6	0.54
Minimum	0.13	0.1	0.1	0.1	0.08	0.08
Average	0.41	0.39	0.33	0.32	0.3	0.25
Median	0.41	0.38	0.28	0.33	0.28	0.21
Correlation coefficients						
HI1(5)	1	0.74	0.57	0.99	0.7	0.54
HI1(20)		1	0.92	0.78	0.99	0.9
HI1(50)			1	0.64	0.95	1
HI2(5)				1	0.75	0.61
HI2(20)					1	0.94
HI2(50)						1

Table 2 Hysteresis indices HI1 and HI2 in a series of 23 home made capacitors, potential range 0 to 1500 mV. The numbers in brackets are scan rates in mV/s

	HI1(5)	HI1(20)	HI1(50)	HI2(5)	HI2(20)	HI2(50)
Maximum	0.7	0.75	0.74	0.55	0.6	0.54
Minimum	0.16	0.1	0.1	0.12	0.08	0.08
Average	0.45	0.42	0.37	0.34	0.32	0.27
Median	0.44	0.43	0.29	0.35	0.34	0.22
Correlation coefficients						
HI1(5)	1	0.7	0.44	0.99	0.64	0.41
HI1(20)		1	0.9	0.72	0.99	0.87
HI1(50)			1	0.51	0.94	1
HI2(5)				1	0.67	0.48
HI2(20)					1	0.92
HI2(50)						1

Table 3 Hysteresis indices HI1 and HI2 in a series of 23 home made capacitors, potential range −1500 to 1500 mV. The numbers in brackets are scan rates in mV/s

	HI1(5)	HI1(20)	HI1(50)	HI2(5)	HI2(20)	HI2(50)
Maximum	0.74	0.76	0.7	0.59	0.61	0.56
Minimum	0.15	0.11	0.1	0.11	0.08	0.07
Average	0.53	0.47	0.37	0.39	0.36	0.29
Median	0.56	0.49	0.37	0.41	0.36	0.27
Correlation coefficients						
HI1(5)	1	0.72	0.41	0.98	0.68	0.38
HI1(20)		1	0.9	0.69	1	0.88
HI1(50)			1	0.38	0.91	1
HI2(5)				1	0.65	0.33
HI2(20)					1	0.9
HI2(50)						1

Table 4 Hysteresis indices HI1 and HI2 calculated from CV curves taken from literature

Reference	Figure #	Scan range/V	Scan rate/mV/s	HI1	HI2	Author's assessment
Yamada et al. 2007	5	−0.1 to 0.7	5	1.00	0.97	rectangular
Yamada et al. 2007	5	−0.1 to 0.7	20	1.00	0.88	leaf-like
Janes et al. 2007	7b	0 to 3.2	1	1.00	0.85	ideal
Arulepp et al. 2004	3a	−2.25 to 0	5	1.00	0.90	
Arulepp et al. 2004	3a	−2.25 to 0	10	1.00	0.88	
Arulepp et al. 2004	3b	−2.25 to 0	5	1.00	0.84	
Gupta and Miura 2006	5b	0 to 0.7	10	1.00	0.77	close to rectangular
Hahn et al. 2004	2b	0 to 2	10	0.99	0.84	
Frackowiak and Beguin 2001	14	0 to 0.8	10	0.99	0.85	
Janes et al. 2007	7a	0 to 2.7	1	0.99	0.85	ideal
Jang et al. 2006	8	0 to 1	10	0.99	0.92	
Arulepp et al. 2004	3a	−2.25 to 0	50	0.98	0.88	
Janes et al. 2007	7a	0 to 3	1	0.97	0.84	ideal
Arulepp et al. 2004	3b	−2.25 to 0	10	0.96	0.88	
Janes et al. 2007	7b	0 to 3.2	1	0.95	0.82	ideal
Arulepp et al. 2004	3b	−2.25 to 0	50	0.95	0.83	
Hulicova et al. 2006	4	−1 to 0	1	0.95	0.73	non rectangular
Tripathi et al. 2006	2a	−0.85 to 0.85	20	0.95	0.87	almost square
Gupta and Miura 2006	5c	0 to 0.7	10	0.95	0.71	close to rectangular
Tripathi et al. 2006	2c	−0.85 to 0.85	20	0.95	0.87	almost square
Janes et al. 2007	7a	0 to 3.2	1	0.94	0.75	ideal
Hulicova et al. 2005	6a	0 to 0.5	0.1	0.94	0.82	almost square
Fang and Binder 2007	3a	0 to 3	100	0.93	0.93	
Hahn et al. 2004	2a	−1 to 1	10	0.93	0.67	butterfly
Fang and Binder 2006a	3b	−1 to 1	25	0.91	0.87	
Lewandowski and Olejniczak 2007	4	0 to 2	2	0.91	0.73	rectangular
Vix-Guterl et al. 2005	2a	0 to 2	10	0.91	0.85	near rectangular
Tripathi et al. 2006	2c	−0.85 to 0.85	50	0.91	0.75	almost square
Wang et al. 2006	4a	−1 to 0	5	0.91	0.69	rectangular
Fang and Binder 2007	3a	0 to 3	100	0.91	0.86	
Wang et al. 2006	4b	−1 to 0	30	0.91	0.61	quasirectangular
Tripathi et al. 2006	2b	−0.85 to 0.85	20	0.90	0.80	almost square
Fang and Binder 2007	1b	−1 to 1	25	0.90	0.89	
Lewandowski and Olejniczak 2007	4	0 to 1	2	0.90	0.80	rectangular
Vix-Guterl et al. 2005	2a	0 to 2	2	0.90	0.83	near rectangular
Hulicova et al. 2005	6b	0 to 0.5	0.1	0.90	0.70	not square
Fang and Binder 2006a	3b	−1 to 1	100	0.89	0.78	
Hulicova et al. 2006	4	−1 to 0	1	0.89	0.69	non rectangular
Tripathi et al. 2006	2a	−0.85 to 0.85	50	0.89	0.74	almost square
Fang and Binder 2007	1b	−1 to 1	100	0.89	0.80	
Hulicova et al. 2006	4	−1 to 0	1	0.89	0.68	non rectangular
C. Kim et al. 2004	5	−2 to 2	5	0.88	0.74	
Fang and Binder 2007	1a	−1 to 1	25	0.88	0.83	
Lewandowski and Olejniczak 2007	4	0 to 3	2	0.88	0.69	rectangular
Gupta and Miura 2006	5c	0 to 0.7	50	0.87	0.65	close to rectangular
Wang et al. 2006	4b	−1 to 0	50	0.86	0.67	quasirectangular
Zhu et al. 2006	3	0 to 0.8	10	0.86	0.82	nearly rectangular
Hulicova et al. 2006	4	−1 to 0	1	0.85	0.63	non rectangular
Lewandowski et al. 2003	5	0 to 2	5	0.85	0.77	rectangular

Table 4 (*Continued*)

Reference	Figure #	Scan range/V	Scan rate/mV/s	HI1	HI2	Author's assessment
Fang and Binder 2006a	3a	−1 to 1	100	0.84	0.71	
Kierzek et al. 2004	6	0 to 0.8	1	0.84	0.70	
Tripathi et al. 2006	2b	−0.85 to 0.85	50	0.83	0.65	almost square
Lewandowski et al. 2003	6	−1 to 1	5	0.83	0.81	less rectangular
Lewandowski et al. 2003	6	−1 to 1	10	0.83	0.81	less rectangular
Fang and Binder 2007	3a	0 to 3	100	0.83	0.73	
Zhu et al. 2006	3	0 to 0.8	10	0.83	0.73	nearly rectangular
Fang and Binder 2007	1a	−1 to 1	100	0.83	0.72	
K.M. Kim et al. 2004	5	−2 to 2	5	0.82	0.62	
Frackowiak and Beguin 2001	4	−0.28 to 0.65	2	0.82	0.72	
Wang et al. 2006	4b	−1 to 0	5	0.81	0.57	rectangular
Lewandowski et al. 2003	6	−1 to 1	50	0.81	0.71	less rectangular
Fang and Binder 2006a	3a	−1 to 1	25	0.80	0.76	
C. Kim et al. 2004	5	−2 to 2	5	0.80	0.62	
Frackowiak and Beguin 2001	4	0.22 to 0.75	2	0.79	0.63	
C. Kim et al. 2004	5	−2 to 2	5	0.78	0.66	
Kierzek et al. 2004	6	0 to 0.8	20	0.78	0.75	
Tripathi et al. 2006	2c	−0.85 to 0.85	100	0.78	0.60	
Lewandowski and Olejniczak 2007	4	0 to 4	2	0.78	0.63	rectangular
Lewandowski et al. 2003	6	−1 to 1	100	0.78	0.64	less rectangular
Tripathi et al. 2006	2a	−0.85 to 0.85	100	0.77	0.62	
Gupta and Miura 2006	5a	0 to 0.7	10	0.77	0.62	close to rectangular
Lewandowski et al. 2001	1	0 to 1	2	0.75	0.70	ill-defined box-like
Jang et al. 2006	8	0 to 1	10	0.74	0.69	
Wang et al. 2006	4a	−1 to 0	30	0.74	0.58	quasirectangular
Gupta and Miura 2006	5b	0 to 0.7	50	0.73	0.56	close to rectangular
Kierzek et al. 2004	6	0 to 0.8	5	0.73	0.68	
Fang and Binder 2007	1b	−1 to 1	500	0.72	0.53	
Hulicova et al. 2006	4	−1 to 0	1	0.70	0.50	non rectangular
Dong et al. 2006	5	0 to 1	5	0.70	0.57	not nearly rectangles
Hulicova et al. 2006	4	−1 to 0	1	0.69	0.50	non rectangular
Lewandowski and Krzyzanowski 2003	5	0 to 2.5	5	0.67	0.63	box-like shape
Gupta and Miura 2006	5a	0 to 0.7	50	0.67	0.55	close to rectangular
Yamada et al. 2007	5	−0.1 to 0.7	100	0.67	0.49	leaf-like
Sun et al. 2006	12	−1 to 1.5		0.66	0.62	
Dong et al. 2006	5	0 to 1	5	0.66	0.43	not nearly rectangles
Tripathi et al. 2006	2b	−0.85 to 0.85	100	0.66	0.50	
Fang and Binder 2007	1a	−1 to 1	500	0.65	0.49	
Fang and Binder 2006a	3b	−1 to 1	500	0.65	0.45	
Wang et al. 2006	4a	−1 to 0	50	0.65	0.52	quasirectangular, triangular
Sun et al. 2006	12	−1 to 1.5		0.63	0.60	
Frackowiak and Beguin 2001	4	−0.25 to 0.65	2	0.63	0.54	
Lewandowski et al. 2001	2	0 to 0.8	5	0.63	0.61	close to rectangular
Gu et al. 2000	1	−3.5 to 3.5	20	0.62	0.52	
Fang and Binder 2006a	3a	−1 to 1	500	0.59	0.42	
Gu et al. 2000	1	−3.5 to 3.5	20	0.53	0.42	
Dong et al. 2006	5	0 to 1	5	0.46	0.37	not nearly rectangles
Michael and Prabaharan 2004	4	0 to 4.5	10	0.43	0.27	non rectangular
Dong et al. 2006	5	0 to 1	5	0.42	0.32	not nearly rectangles

capacitors. Our best capacitors showed HI1 of about 0.7 and HI2 of about 0.6, and our worst capacitors showed HI1 and HI2 of about 0.1. Comparison of the performances of two capacitors based on HI obtained at the same experimental conditions is preferred, but we demonstrated that HI1 and HI2 are not very sensitive to the scan rate and scan range. Therefore, HI1 and HI2 can be also used to compare the shapes of CV curves taken from literature, which have been obtained at different scan rates and scan ranges.

5 Application for literature data

98 CV curves of electrochemical capacitors and of electrodes for electrochemical capacitors from literature were analyzed by means of HI1 and HI2. These CV curves were obtained by means of different instruments, for various electrode materials and electrolytes, at different scan rates and scan ranges. The scan rates and scan ranges are reported in Table 4, and more detailed experimental information can be found in the original publications (references and figure numbers provided). Each CV curve was manually digitized, and the scanned potential range was divided into 10 equal parts. The $I_>$ and $I_<$ obtained for U_i $i = 0, 1, \ldots, 10$ were used to calculate HI1 and HI2. The start and end point were rejected in the calculation of HI2 to avoid overrepresentation of the narrow ends of the CV curves. The results (rounded to 2 decimal digits) are summarized in Table 4 and plotted in Fig. 2.

The highest HI reported in Table 4 are higher than the HI obtained in this study for commercial capacitors, and the lowest HI reported in Table 4 are similar to average HI obtained in this study for home made materials and reported in Tables 1–3. The CV curves in Table 4 are arranged from the highest to the lowest HI1, and the last column in Table 4 reports authors' assessment of the shape of CV curves, which was found in original papers. Usually the authors' assessment is in line with HI1, that is, the curves with a high HI are assessed as rectangular, and the curves with a low HI are assessed as non-rectangular, but many exceptions from this rule indicate the subjective character and limited significance of the authors' assessment. A CV curve with HI1 as high as 1, and HI2 as high as 0.88 was described as "leaf like", that is, not-rectangular. On the other hand, a CV curve with HI1 as low as 0.63, and HI2 as low as 0.6 was described as "close to ideal rectangular" in the original paper. The correlation coefficient between HI1 and HI2 in Table 4 is 0.9, and it is lower than in a set of HI obtained at the same scan rate for home made capacitors (Tables 1–3). Yet, the results presented in Table 4 were obtained at very different experimental conditions, e.g., the lowest and the highest scan rate differ by a factor of 5000. The HI obtained at different scan rates are indicated by different symbols in Fig. 2, but no clear correlation between HI1 or HI2 or HI1/HI2 on the one hand and the scan rate on the other is apparent. Thus HI reflect the properties of capacitor/electrode, and the choice of the scan rate is not crucial. In most studied CV curves HI1/HI2 ratio ranges from 1.1 to 1.3, and very high or very low HI1/HI2 ratio is an indication of peculiar shape of CV curves.

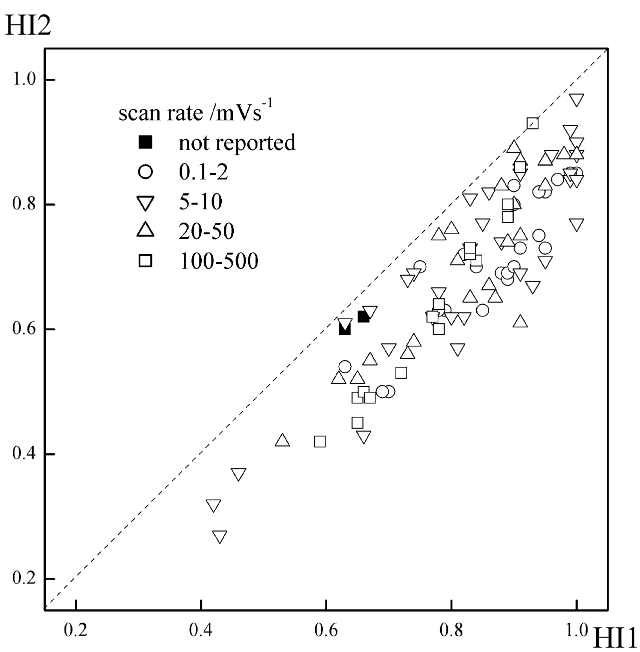

Fig. 2 Correlation between HI1 and HI2. The line represents HI1 = HI2

6 Conclusion

We argue that HI defined in the present study are superior to subjective methods in assessment of the deviations of CV curves of electrochemical capacitors from ideal rectangular shape.

References

Arulepp, M., Permann, L., Leis, J., Perkson, A., Rumma, K., Jänes, A., Lust, E.: Influence of the solvent properties on the characteristics of a double layer capacitor. J. Power Sources **133**, 320–328 (2004)

Balducci, A., Bardi, U., Caporali, S., Mastragostino, M., Soavi, F.: Ionic liquids for hybrid supercapacitors. Electrochem. Commun. **6**, 566–570 (2004)

Barbieri, O., Hahn, M., Herzog, A., Kötz, R.: Capacitance limits of high surface area activated carbons for double layer capacitors. Carbon **43**, 1303–1310 (2005)

Chang, K.-H., Hu, C.-C.: Hydrothermal synthesis of binary Ru–Ti oxides with excellent performances for supercapacitors. Electrochim. Acta **52**, 1749–1757 (2006)

Conway, B.E.: Transition from "supercapacitor" to "battery" behavior in electrochemical energy storage. J. Electrochem. Soc. **138**, 1539–1548 (1991)

Dong, X., Shen, W., Gu, J., Xiong, L., Zhu, Y., Li, H., Shi, J.: MnO_2-embedded-in-mesoporous-carbon-wall structure for use as electrochemical capacitors. J. Phys. Chem. B **110**, 6015–6019 (2006)

Eliad, L., Salitra, G., Soffer, A., Aurbach, D.: Ion sieving effects in the electrical double layer of porous carbon electrodes: estimating effective ion size in electrolytic solutions. J. Phys. Chem. B **105**, 6880–6887 (2001)

Fang, B.Z., Binder, L.: A modified activated carbon aerogel for high-energy storage in electric double layer capacitors. J. Power Sources **163**, 616–622 (2006a)

Fang, B.Z., Binder, L.: A novel carbon electrode material for highly improved EDLC performance. J. Phys. Chem. B **110**, 7877–7882 (2006b)

Fang, B.Z., Binder, L.: Enhanced surface hydrophobisation for improved performance of carbon aerogel electrochemical capacitor. Electrochim. Acta **52**, 6916–6921 (2007)

Fischer, A.E., Pettigrew, K.A., Rolison, D.R., Stroud, M.R., Long, J.W.: Incorporation of homogeneous, nanoscale MnO_2 within ultraporous carbon structures via self-limiting electroless deposition: implications for electrochemical capacitors. Nano Lett. **7**, 281–286 (2007)

Frackowiak, E., Beguin, F.: Carbon materials for the electrochemical storage of energy in capacitors. Carbon **39**, 937–950 (2001)

Frackowiak, E., Delpeux, S., Jurewicz, K., Szostak, K., Cazorla-Amoros, D., Beguin, F.: Enhanced capacitance of carbon nanotubes through chemical activation. Chem. Phys. Lett. **361**, 35 (2002)

Gryglewicz, G., Machnikowski, J., Lorenc-Grabowska, E., Lota, G., Frackowiak, E.: Effect of pore size distribution of coal-based activated carbons on double layer capacitance. Electrochim. Acta **50**, 1197–1206 (2005)

Gu, H.B., Kim, J.U., Song, H.W., Park, G.C., Park, B.K.: Electrochemical properties of carbon composite electrode with polymer electrolyte for electric double-layer capacitor. Electrochim. Acta **45**, 1533 (2000)

Gupta, V., Miura, N.: Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors. Electrochim. Acta **52**, 1721–1726 (2006)

Hahn, M., Baertschi, M., Barbieri, O., Sauter, J.-C., Kotz, R., Gallay, R.: Interfacial capacitance and electronic conductance of activated carbon double-layer electrodes. Electrochem. Solid-State Lett. **7**, A33–A36 (2004)

Hu, C.-C., Chang, K.-H., Wang, C.-C.: Two-step hydrothermal synthesis of Ru-Sn oxide composites for electrochemical supercapacitors. Electrochim. Acta **52**, 4411–4418 (2007a)

Hu, C.-C., Liu, M.-J., Chang, K.-H.: Anodic deposition of hydrous ruthenium oxide for supercapacitors. J. Power Sources **163**, 1126–1131 (2007b)

Hu, C.-C., Wang, C.-C., Wu, F.-C., Tseng, R.-L.: Characterization of pistachio shell-derived carbons activated by a combination of KOH and CO_2 for electric double-layer capacitors. Electrochim. Acta **52**, 2498–2505 (2007c)

Huang, Q., Wang, X., Li, J., Dai, C., Gamboa, S., Sebastian, P.J.: Nickel hydroxide/activated carbon composite electrodes for electrochemical capacitors. J. Power Sources **164**, 425–429 (2007)

Hulicova, D., Yamashita, J., Soneda, Y., Hatori, H., Kodama, M.: Supercapacitors prepared from melamine-based carbon. Chem. Mater. **17**, 1241–1247 (2005)

Hulicova, D., Kodam, M., Hatori, H.: Electrochemical performance of nitrogen-enriched carbons in aqueous and non-aqueous supercapacitors. Chem. Mater. **18**, 2318–2326 (2006)

Janes, A., Kurig, H., Lust, E.: Characterisation of activated nanoporous carbon for supercapacitor electrode materials. Carbon **45**, 1226–1233 (2007)

Jang, J.H., Machida, K., Kim, Y., Naoi, K.: Electrophoretic deposition (EPD) of hydrous ruthenium oxides with PTFE and their supercapacitor performances. Electrochim. Acta **52**, 1733–1741 (2006)

Jung, M., Kim, H.-G., Lee, J.-K., Joo, O.-S., Mho, S.-I.: EDLC characteristics of CNTs grown on nanoporous alumina templates. Electrochim. Acta **50**, 857–862 (2004)

Jurewicz, K., Vix-Guterl, C., Frackowiak, E., Saadallah, S., Reda, M., Parmentier, J., Patarin, J., Beguin, F.: Capacitance properties of ordered porous carbon materials prepared by a templating procedure. J. Phys. Chem. Solids **65**, 287–293 (2004)

Karandikar, P., Patil, K.R., Mitra, A., Kakade, B., Chandwadkar, A.J.: Synthesis and characterization of mesoporous carbon through inexpensive mesoporous silica as template. Microporous Mesoporous Mater. **98**, 189–199 (2007)

Kierzek, K., Frackowiak, E., Lota, G., Machnikowski, J.: Electrochemical capacitors based on highly porous carbons prepared by KOH activation. Electrochim. Acta **49**, 515 (2004)

Kim, C., Choi, Y.-O., Lee, W.-J., Yang, K.-S.: Supercapacitor performances of activated carbon fiber webs prepared by electrospinning of PMDA-ODA poly(amic acid) solutions. Electrochim. Acta **50**, 883–887 (2004)

Kim, J.-H., Lee, Y.-S., Sharma, A.K., Liu, C.G.: Polypyrrole/carbon composite electrode for high-power electrochemical capacitors. Electrochim. Acta **52**, 1727–1732 (2006)

Kim, K.M., Hur, J.W., Jung, S.I., Kang, A.S.: Electrochemical characteristics of activated carbon/PPY electrode combined with PVDF-co-HFP/PVD for EDLC. Electrochim. Acta **50**, 863 (2004)

Kim, Y.-T., Mitani, T.: Competitive effect of carbon nanotubes oxidation on aqueous EDLC performance: Balancing hydrophilicity and conductivity. J. Power Sources **158**, 1517–1522 (2006)

Kosmulski, M., Skubiszewska-Zieba, J., Leboda, R., Marczewska-Boczkowska, K., Prochniak, P.: New ceramic–carbon composites for electrodes for electrochemical capacitors. J. Colloid Interface Sci. **309**, 160–168 (2007)

Lee, B.J., Sivakkumar, S.R., Ko, J.M., Kim, J.H., Jo, S.M., Kim, D.Y.: Carbon nanofibre/hydrous RuO_2 nanocomposite electrodes for supercapacitors. J. Power Sources **168**, 546–552 (2007)

Lee, G.-J., Pyun, S.I.: Effect of microcrystallite structures on electrochemical characteristics of mesoporous carbon electrodes for electric double-layer capacitors. Electrochim. Acta **51**, 3029–3038 (2006)

Lee, J., Kim, J., Lee, Y., Yoon, S., Oh, S.M., Hyeon, T.: Simple synthesis of uniform mesoporous carbons with diverse structures from mesostructured polymer/silica nanocomposites. Chem. Mater. **16**, 3323–3330 (2004)

Leitner, K., Lerf, A., Winter, M., Besenhard, J.O., Villar-Rodil, S., Suárez-García, F., Martinez-Alonso, A., Tascon, J.M.D.: Effect of microcrystallite structures on electrochemical characteristics of mesoporous carbon electrodes for electric double-layer capacitors. J. Power Sources **153**, 419–423 (2006)

Lewandowski, A., Krzyzanowski, M.: A new polymer electrolyte poly(acrylonitrile)–dimethylsulphoxide–salt for electrochemical capacitors. Electrochim. Acta **48**, 1325–1329 (2003)

Lewandowski, A., Olejniczak, A.: N-methyl-N-propylpiperidinium bis(trifluoromethanesulphonyl)imide as an electrolyte for carbon-based double-layer capacitors. J. Power Sources **172**, 487–492 (2007)

Lewandowski, A., Swiderska, A.: Electrochemical capacitors with polymer electrolytes based on ionic liquids. Solid State Ion. **161**, 243–249 (2003)

Lewandowski, A., Zajder, M., Frackowiak, E., Béguin, F.: Supercapacitor based on activated carbon and polyethylene oxide–KOH–H_2O polymer electrolyte. Electrochim. Acta **46**, 2777–2780 (2001)

Lewandowski, A., Galinski, M., Krzyzanowski, M.: New polymer electrolyte poly(acrylonitrile)–sulpholane–$(C_2H_5)_4NBF_4$ for chemical capacitors. Solid State Ion. **158**, 367–373 (2003)

Li, H., Xi, H., Zhu, S., Wen, Z., Wang, R.: Preparation, structural characterization, and electrochemical properties of chemically modified mesoporous carbon. Microporous Mesoporous Mater. **96**, 357–362 (2006)

Li, W., Chen, D., Li, Z., Shi, Y., Wan, Y., Wang, G., Jiang, Z., Zhao, D.: Nitrogen-containing carbon spheres with very large uniform mesopores: the superior electrode materials for EDLC in organic electrolyte. Carbon **45**, 1757–1763 (2007)

Liu, G., Kang, F., Li, B., Huang, Z., Chuan, X.: Characterization of the porous carbon prepared by using halloysite as template and its application to EDLC. J. Phys. Chem. Solids **67**, 5487–5493 (2006)

Lust, E., Janes, A., Arulepp, M.: Influence of electrolyte characteristics on the electrochemical parameters of Electric Double Layer Capacitors. J. Solid State Electrochem. **8**, 488 (2004a)

Lust, E., Janes, A., Arulepp, M.: Influence of solvent nature on the electrochemical parameters of Electric Double Layer Capacitors. J. Electroanal. Chem. **562**, 33 (2004b)

Michael, M.S., Prabaharan, S.R.S.: High voltage electrochemical double layer capacitors using conductive carbons as additives. J. Power Sources **136**, 250 (2004)

Miller, J.M., Dunn, B.: Morphology and electrochemistry of ruthenium/carbon aerogel nanostructures. Langmuir **15**, 799–806 (1999)

Mitani, S., Lee, S.-I., Saito, K., Korai, Y., Mochida, I.: Contrast structure and EDLC performances of activated spherical carbons with medium and large surface areas. Electrochim. Acta **51**, 5487–5493 (2006)

Morishita, T., Soneda, Y., Hatori, H., Inagaki, M.: Carbon-coated tungsten and molybdenum carbides for electrode of electrochemical capacitor. Electrochim. Acta **52**, 2478–2484 (2007)

Nam, K.-W., Kim, M.G., Kim, K.-B.: In situ Mn K-edge X-ray Absorption Spectroscopy studies of electrodeposited manganese oxide films for Electrochemical Capacitors. J. Phys. Chem. C **111**, 749–758 (2007)

Nanbu, N., Ebina, T., Uno, H., Ishizawa, S., Sasaki, Y.: Physical and electrochemical properties of quaternary ammonium bis(oxalato)borates and their application to electric double-layer capacitors. Electrochim. Acta **52**, 1763–1770 (2006)

Okajima, K., Ohta, K., Sudoh, M.: Capacitance behavior of activated carbon fibers with oxygen-plasma treatment. Electrochim. Acta **50**, 2227–2231 (2005a)

Okajima, K., Ikeda, A., Kamoshita, K., Sudoh, M.: High rate performance of highly dispersed C_{60} on activated carbon capacitor. Electrochim. Acta **51**, 972–977 (2005b)

Pollak, E., Anderson, A., Salitra, G., Soffer, A., Aurbach, D.: The anomaly in the dependence of the electronic conductivity of activated carbon electrodes at different charging states. J. Electroanal. Chem. **601**, 47–52 (2007)

Prasad, K.R., Koga, K., Miura, N.: Electrochemical deposition of nanostructured indium oxide: high-performance electrode material for redox supercapacitors. Chem. Mater. **16**, 1845–1847 (2004)

Ryu, K.S., Jeong, S.K., Joo, J., Kim, K.M.: Polyaniline doped with dimethyl sulfate as a nucleophilic dopant and its electrochemical properties as an electrode in a lithium secondary battery and a redox supercapacitor. J. Phys. Chem. B **111**, 731–739 (2007)

Sander, M., Lu, Y.F., Pignatello, J.J.: A thermodynamically based method to quantify true sorption hysteresis. J. Environ. Qual. **34**, 1063–1072 (2005)

Sugimoto, W., Iwata, H., Yokoshima, K., Murakami, Y., Takasu, Y.: Proton and electron conductivity in hydrous ruthenium oxides evaluated by electrochemical impedance spectroscopy: the origin of large capacitance. J. Phys. Chem. B **109**, 7330–7338 (2005)

Sugimoto, W., Yokoshima, K., Murakami, Y., Takasu, Y.: Charge storage mechanism of nanostructured anhydrous and hydrous ruthenium-based oxides. Electrochim. Acta **52**, 1742–1748 (2006)

Sun, G.-H., Li, K-X., Sun, C.-G.: Application of 1-ethyl-3-methylimidazolium thiocyanate to the electrolyte of electrochemical double layer capacitors. J. Power Sources **162**, 1444–1450 (2006)

Tashima, D., Kurosawatsu, K., Uota, M., Karashima, T., Sung, Y.M., Otsubo, M., Honda, C.: Space charge behaviors of electric double layer capacitors with nanocomposite electrode. Surf. Coat. Technol. **201**, 5392–5395 (2007)

Toyoda, M., Tani, Y., Soneda, Y.: Exfoliated carbon fibers as an electrode for electric double layer capacitors in a 1 mol/dm^3 H_2SO_4 electrolyte. Carbon **42**, 2833–2837 (2004)

Tripathi, S.K., Kumar, A., Hashmi, S.A.: Electrochemical redox supercapacitors using PVdF-HFP based gel electrolytes and polypyrrole as conducting polymer electrode. Solid State Ion. **177**, 2979–2985 (2006)

Vix-Guterl, C., Saadallah, S., Jurewicz, K., Frackowiak, E., Reda, M., Parmentier, J., Patarin, J., Beguin, F.: Supercapacitor electrodes from new ordered porous carbon materials obtained by a templating procedure. Mater. Sci. Eng. B **108**, 148–155 (2004)

Vix-Guterl, C., Frackowiak, E., Jurewicz, K., Friebe, M., Parmentier, J., Beguin, F.: Electrochemical energy storage in ordered porous carbon materials. Carbon **43**, 1293–1302 (2005)

Wan, C., Azumi, K., Konno, H.: Hydrated Mn(IV) oxide-exfoliated graphite composites for electrochemical capacitor. Electrochim. Acta **52**, 3061–3066 (2007)

Wang, D.-W., Li, F., Fang, H.-T., Liu, M., Lu, G.-Q., Cheng, H.-M.: Effect of pore packing defects in 2-d ordered mesoporous carbons on ionic transport. J. Phys. Chem. B **110**, 8570–8575 (2006)

Wang, Y.G., Xia, Y.Y.: A new concept hybrid electrochemical supercapacitor: carbon/$LiMn_2O_4$ aqueous system. Electrochem. Commun. **7**, 1138–1142 (2005)

Wen, S., Jung, M., Joo, O.-S., Mho, S.-I.: EDLC characteristics with high specific capacitance of the CNT electrodes grown on nanoporous alumina templates. Current Appl. Phys. **6**, 1012–1015 (2006)

Xing, W., Qiao, S.Z., Ding, R.G., Li, F., Lu, G.Q., Yan, Z.F., Cheng, H.M.: Superior electric double layer capacitors using ordered mesoporous carbons. Carbon **44**, 216–224 (2006)

Xu, B., Wu, F., Chen, S., Zhang, C., Cao, G., Yang, Y.: Activated carbon fiber cloths as electrodes for high performance electric double layer capacitors. Electrochim. Acta **52**, 4595–4598 (2007)

Yamada, H., Nakamura, H., Nakahara, F., Moriguchi, I., Kudo, T.: Electrochemical study of high Electrochemical Double Layer Capacitance of ordered porous carbons with both meso/macropores and micropores. J. Phys. Chem. C **111**, 227–233 (2007)

Yang, C.-C., Hsu, S.-T., Chien, W.-C.: All solid-state electric double-layer capacitors based on alkaline polyvinyl alcohol polymer electrolytes. J. Power Sources **152**, 303–310 (2005)

Zhou, J., Booker, C., Li, R., Zhou, X., Sham, T.-K., Sun, X., Ding, Z.: An electrochemical avenue to blue luminescent nanocrystals from multiwalled carbon nanotubes (MWCNTs). J. Am. Chem. Soc. **129**, 744–745 (2007)

Zhu, Y., Hu, H., Li, W.C., Zhang, X.: Cresol–formaldehyde based carbon aerogel as electrode material for electrochemical capacitor. J. Power Sources **162**, 738–742 (2006)

Zolfaghari, A., Ataherian, F., Ghaemi, M., Gholami, A.: Capacitive behavior of nanostructured MnO_2 prepared by sonochemistry method. Electrochim. Acta **52**, 2806–2814 (2007)